2ND EDITION

Reverse Osmosis

Design, Processes, and Applications for Engineers

JANE KUCERA

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For my dad; he'll always be O.K.

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Preface

The use of reverse osmosis (RO) technology has grown rapidly through the 1990's and early 2000's. The ability of RO to replace or augment conventional ion exchange saves end users the need to store, handle, and dispose of large amounts of acid and caustic, making RO a "greener" technology. Additionally, costs for membranes have declined significantly since the introduction of interfacial composite membranes in the 1980's, adding to the attractiveness of RO. Membrane productivity and salt rejection have both increased, reducing the size of RO systems and minimizing the amount of post treatment necessary to achieve desired product quality.

Unfortunately, knowledge about RO has not kept pace with the growth in technology and use. Operators and others familiar with ion exchange technology are often faced with an RO system with little or no training. This has resulted in poor performance of RO systems and perpetuation of misconceptions about RO.

Much of the current literature about RO includes lengthy discussions or focuses on a niche application that makes it difficult to find an answer to a practical question or problems associated with more common applications. Hence, my objective in writing this book is to bring clear, concise, and practical information about RO to end users, applications engineers, and consultants. In essence, the book is a reference bringing together knowledge from other references as well as that gained through personal experience.

The book focuses on brackish water industrial RO, but many principles apply to seawater RO and process water as well.

Acknowledgements for the First Edition

My enthusiasm for reverse osmosis (RO) began while working with my thesis advisor at UCLA, Professor Julius "Bud" Glater, a pioneer who worked at UCLA with Sidney Loeb in the early days of commercializing RO. Professor Glater was kind enough to extend a Research Assistantship to me, when my first choice was not available. That was fortunate for me, as membrane technology is a growing field with great future potential. Professor Glater's guidance and support were invaluable to me as a graduate student and has continued to be throughout my career.

My knowledge grew at Bend Research, Inc. under Harry Lonsdale, another membrane pioneer who was involved in the theoretical and practical side of membranes since the early 1960's at Gulf General Atomic (predecessor of Fluid Systems, now Koch Membrane Systems), Alza, and later Bend Research, which he co-founded with Richard Baker. At Bend Research, I had the opportunity to develop novel membranes and membrane-based separation processes, including leading several membrane-based projects for water recovery and reuse aboard the International Space Station.

My desire to write this book was fostered by Loraine Huchler, president of Mar-Tech Systems, which she founded in the mid 1990's, and author of the book series, Operating Practices for Industrial Water Management. Loraine has provided both technical and moral support.

Thanks also go to Nalco Company, Naperville, IL, for supporting me in this endeavor. Individuals at Nalco who have provided technical and administrative support include: Ching Liang, Anne Arza, Anders Hallsby, Beth Meyers, Carl Rossow, Alice Korneffel, and Kevin O'Leary. Nalco-Crossbow LLC personnel who have provided support include Mark Sadus (contributor to Chapter 6), Scott Watkins, Mike Antenore, Jason Fues, and Dave Weygandt.

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I would like to thank my graphic artist, Diana Szustowski, for her excellent and tireless efforts.

Finally, I would like to thank Paul Szustowski and Irma Kucera for their support.

Acknowledgements for the Second Edition

As I continue to work with membrane systems, I continue to learn. This second edition is a further communication of what I have learned. I hope the reader will find the updated and supplemental material as useful as I have.

I would like to thank my editor, Phil Carmical, for keeping me on track and for his guidance and encouragement. Also, contributions from my colleagues for this second edition include Anne Arza for her direct contributions, and Bruce Tait and Brendan Kranzmann for helping me understand some of the subtleties of membrane technology. Thanks also go to Wayne Bates of Hydranautics, Madalyn Epple and John Buonassisi of Toray Membrane USA, Henia Yacobowitz of KOCH, and Paul Olson and Leaelaf Hailemariam of Dow Water and Process Solutions, for their support regarding upgrades to their respective RO design projection programs.

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1

FUNDAMENTALS

1

Introduction and History of Development

1.1 Introduction

Reverse Osmosis (RO) is a membrane-based demineralization technique used to separate dissolved solids (i.e., ions) from solution (most applications involve water-based solutions, which is the focus of this work). Membranes in general act as perm-selective barriers, barriers that allow some species (such as water) to selectively permeate through them while selectively retaining other dissolved species (such as ions). Figure 1.1 shows how RO perm-selectivity compares to many other membrane-based and conventional filtration techniques. As shown in the figure, RO offers the finest filtration currently available, rejecting most dissolved solids as well as suspended solids. (Note that although RO membranes will remove suspended solids, these solids, if present in RO feed water, will collect on the membrane surface and foul the membrane. See Chapters 3.7 and 7 for more discussion on membrane fouling).

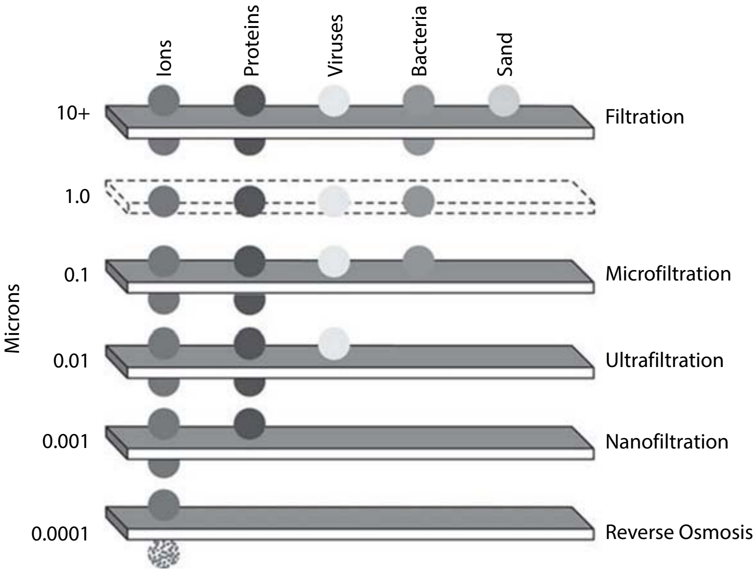


Figure 1.1 "Filtration Spectrum" comparing the rejection capabilities of reverse osmosis with other membrane technologies and with the separation afforded by conventional, multimedia filtration.

1.1.1 Uses of Reverse Osmosis

Reverse osmosis can be used to either purify water or to concentrate and recover dissolved solids in the feed water (known as "dewatering"). The most common application of RO is to replace ion exchange, including sodium softening, to purify water for use as boiler make-up to low- and medium-pressure boilers, as the product quality from an RO can directly meet the boiler make-up requirements for these pressures. For higher-pressure boilers and steam generators, RO is used in conjunction with ion exchange, usually as a pretreatment to a two-bed or mixed-bed ion exchange system. The use of RO prior to ion exchange can significantly reduce the frequency of resin regenerations, and hence, drastically reduce the amount of acid, caustic, and regeneration waste that must be handled and stored. In some cases, a secondary RO unit can be used in place of ion exchange to further purify product water from an RO unit (see Chapter 5.3). Effluent from the second RO may be used directly or is sometimes polished with mixed-bed ion exchange or continuous electrodeionization to achieve even higher product water purity (see Chapter 16.4).

Other common applications of RO include:

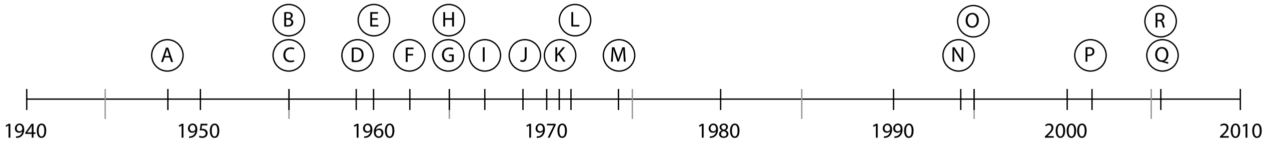
1. Desalination of seawater and brackish water for potable use. This is very common in coastal areas and the Middle East where supply of fresh water is scarce.
2. Generation of ultrapure water for the microelectronics industry.
3. Generation of high-purity water for pharmaceuticals.
4. Generation of process water for beverages (fruit juices, bottled water, beer).
5. Processing of dairy products.
6. Concentration of corn sweeteners.
7. Waste treatment for the recovery of process materials such as metals for the metal finishing industries, and dyes used in the manufacture of textiles.
8. Water reclamation of municipal and industrial waste-waters.

1.1.2 History of Reverse Osmosis Development

One of the earliest recorded documentation of semipermeable membranes was in 1748, when Abbe Nollet observed the phenomenon of osmosis.[1] Others, including Pfeffer and Traube, studied osmotic phenomena using ceramic membranes in the 1850's. However, current technology dates back to the 1940's when Dr. Gerald Hassler at the Unitversity of California at Los Angeles (UCLA) began investigation of osmotic properties of cellophane in 1948.[2] In 1948, he proposed an "air film" bounded by two cellophane membranes.[3] Hassler assumed that osmosis takes place via evaporation at one membrane surface followed by passage through the air gap as a vapor, with condensation on the opposing membrane surface. Today, we know that osmosis does not involve evaporation, but most likely involves solution and diffusion of the solute in the membrane (see Chapter 4).

Figure 1.2 shows a time line with important events in the development of RO technology. Highlights are discussed below.

In 1959, C.E. Reid and E.J. Breton at University of Florida, demonstrated the desalination capabilities of cellulose acetate film.[4] They evaluated candidate semipermeable membranes in a trial-and-error approach, focusing on polymer films containing hydrophilic groups. Materials tested included cellophane, rubber hydrochloride, polystyrene, and cellulose acetate. Many of these materials exhibited no permeate flow, under pressures as high at 800 psi, and had chloride rejections of less than 35%. Cellulose



A. 1948 – Hassler studies osmotic properties of cellophane membranes at USA
B. 1955 – First reported use of them "reverse osmosis"
C. 1955 – Reid begins study of membranes of demineralization at University of Florida
D. 1959 – Breton and Reid demonstrate desalination capability of cellulose acetate film
E. 1960 – Loeb and Sourirajan develop asymmetric cellulose acetate membrane at UCLA
F. 1963 – First practical spiral wound module developed by General Atomics (see Chapter 4.3.3)
G. 1965 – First commercial brackish water RO facility at Coalinga, CA
H. 1965 – Solution-Diffusion transport model described by Lonsdale, et. al (See Chapter 4.1.1)
I. 1967 – First commercially successful hollow fiber module developed by DuPont (see Chapter 4.3.4)
J. 1968 – First multi-leaf spiral wound module developed by Gulf General Atomics later Fluid Systems (See Chapter 4.3.3)
K. 1971 – Richer-Hoehn at DuPont patents aromatic polyamide membrane (see Chapter 4.2.2.1.)
L. 1972 – Cadotte develops interfacial composite membrane (See Chapter 4.2.2.2)
M. 1974 – Frst commercial seawater RO facility at Bermuda
N. 1994 - TriSep introduces first "low fouling" membrane (see Chapter 4.4.2.3)
O. 1995 - Hydranautics introduces first "energy saving" polymide membrane (see Chapter 4.4.2.1)
P. 2002 – Koch Membrane Systems introduces first 18-inch diameter "MegaMagnum" module
Q. 2006 – Thin-film nanocomposite membrane developed at UCLA
R. 2006 – Lab-Scale carbon nanotube membrane developed at Lawrance Livermore National Laboratory.

Figure 1.2 Historical time line in the development of reverse osmosis.

acetate (specifically the DuPont 88 CA-43), however, exhibited chloride rejections of greater than 96%, even at pressures as low as 400 psi. Fluxes ranged from about 2 gallons per square foot-day (gfd) for a 22-micron thick cellulose acetate film to greater than 14 gfd for a 3.7-micron thick film when tested at 600 psi on a 0.1M sodium chloride solution. Reid and Breton's conclusions were that cellulose acetate showed requisite semipermeability properties for practical application, but that improvements in flux and durability were required for commercial viability.

A decade after Dr. Hassler's efforts, Sidney Loeb and Srinivasa Sourirajan at UCLA attempted an approach to osmosis and reverse osmosis that differed from that of Dr. Hassler. Their approach consisted of pressurizing a solution directly against a flat, plastic film.[3] Their work led to the development of the first asymmetric cellulose acetate membrane in 1960 (see Chapter 4.2.1).[2] This membrane made RO a commercial viability due to the significantly improved flux, which was 10 times that of other known membrane materials at the time (such as Reid and Breton's membranes).[5] These membranes were first cast by hand as flat sheets. Continued development in this area led to casting of tubular membranes. Figure 1.3 is a schematic of the tubular casting equipment used by Loeb and Sourirajan. Figure 1.4 shows the capped, in-floor immersion well that was used by Loeb and students and is still located in Boelter Hall at UCLA.

Following the lead of Loeb and Sourirajan, researchers in the 1960's and early 1970's made rapid progress in the development of commercially-viable RO membranes. Harry Lonsdale, U. Merten, and Robert Riley formulated the "solution-diffusion" model of mass transport through RO membranes (see Chapter 4.1.1).[6] Although most membranes at the time were cellulose acetate, this model represented empirical data very well, even with respect to present-day polyamide membranes.[7] Understanding transport mechanisms was important to the development of membranes that exhibit improved performance (flux and rejection).

In 1971, E. I. Du Pont De Nemours & Company, Inc. (DuPont) patented a linear aromatic polyamide with pendant sulfonic acid groups, which they commercialized as the Permasep™ B-9 and B-10 membranes (Permasep is a registered trademark of DuPont Company, Inc. Wilmington, DE). These membranes exhibited higher water flux at slightly lower operating pressures than cellulose acetate membranes. The membranes were spun as unique hollow fine fibers rather than in flat sheets or a tubes (see Chapter 4.3.4).

Cellulose acetate and linear aromatic polyamide membranes were the industry standard until 1972, when John Cadotte, then at North Star

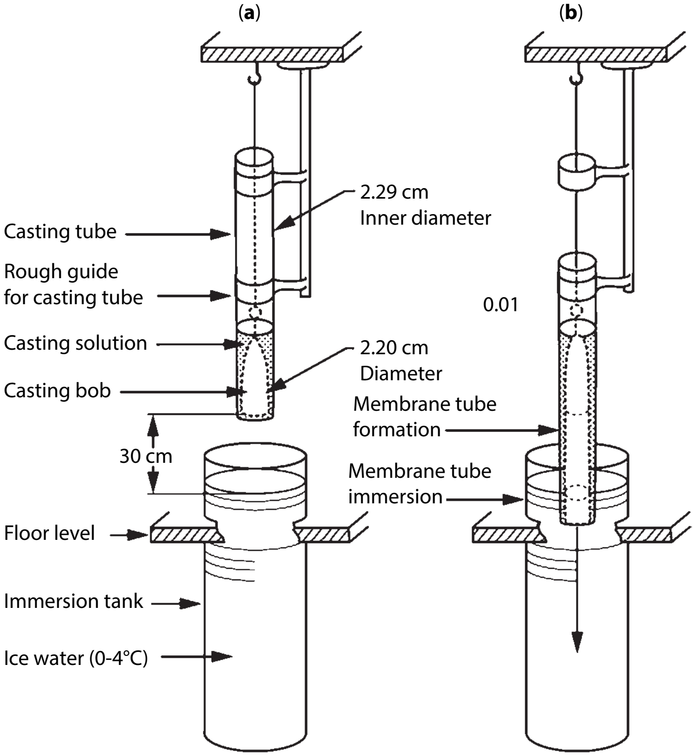


Figure 1.3 Schematic on tubular casting equipment used by Loeb. *Courtesy of Julius Glater, UCLA.*

Figure 1.4 Capped, in-floor immersion tank located at Boelter Hall that was used by Loeb and Sourirajan to cast tubular cellulose acetate membranes at UCLA, as viewed in 2008.

Research, prepared the first interfacial composite polyamide membrane.[8] This new membrane exhibited both higher through-put and rejection of solutes at lower operating pressure than the here-to-date cellulose acetate and linear aromatic polyamide membranes. Later, Cadotte developed a fully aromatic interfacial composite membrane based on the reaction of phenylene diamine and trimesoyl chloride. This membrane became the new industry standard and is known today as FT30, and it is the basis for the majority of Dow Water and Process Solutions' FilmTec™ membranes (e.g., BW30, which means "Brackish Water membrane," FT30 chemistry"; TW30, which means "Tap Water membrane," FT30 chemistry; and so on) as well as many commercially available membranes from other producers (FilmTec is a trademark of Dow Chemical Company, Midland, Michigan). See Chapter 4.2 for more information about interfacial composite membranes.

Other noteworthy developments in membrane technology include the following:

- 1963: First practical spiral wound module developed at Gulf General Atomics (later known as Fluid Systems®, now owned by Koch Membrane Systems, Wilmington, MA.) This increased the packing density of membrane in a module to reduce the size of the RO system (see Chapter 4.3.3).
- 1965: The first commercial brackish water RO (BWRO) was on line at the Raintree facility in Coalinga, California. Tubular cellulose acetate membranes developed and prepared at UCLA were used in the facility. Additionally, the hardware for the system was fabricated at UCLA and transported piecemeal to the facility.[9]
- 1967: First commercial hollow-fiber membrane module developed by DuPont. This module configuration further increased the packing density of membrane modules.
- 1968: First multi-leaf spiral wound membrane module developed by Don Bray and others at Gulf General Atomic, under US Patent no. 3,417,870, "Reverse Osmosis Purification Apparatus," December, 1968. A multi-leaf spiral configuration improves the flow characteristics of the RO module by minimizing the pressure drop encountered by permeate as it spirals into the central collection tube.
- 1978: FT-30 membrane patented and assigned to FilmTec (now owned by Dow Chemical Company, Midland, MI).

1.1.3 Recent Advances in RO Membrane Technology

Since the 1970's, the membrane industry has focused on developing membranes that exhibit ever greater rejection of solutes while at the same time exhibiting higher throughput (flux) at lower operating pressure. Table 1.1 shows the growth in RO membrane development with respect to rejection, flux, and operating pressure.[10] Along with advances in membrane performance, membrane costs have also improved. Table 1.2 lists costs of membranes relative to 1980.[5]

In addition to the progress shown in Table 1.1, some membranes now exhibit up to 99.85% rejection (a drop of 50% in salt passage over membranes exhibiting 99.7% rejection). Other advancements in membrane technology include "low pressure" RO membranes that allow for operation

Table 1.1 Development of RO membranes for brackish water desalination.

Year	Pressure (psi)	Relative Flux	Rejection (%)	Membrane Material
1970's	435	1	97	Cellulose acetate
1980's	290	1.9	99.0	Cross-linked polyamide composite
1987	220	3.0	99.7	Cross-linked aromatic polyamide composite
1988	145	4.2	99.7	Cross-linked aromatic polyamide composite
1996	110	5.6	99.7	Cross-linked aromatic polyamide composite
1999	75	8.0	99.7	Cross-linked aromatic polyamide composite

Table 1.2 Membrane cost decline relative to 1980.[5]

Year	Relative Cost
1980	1.00
1985	0.65
1990	0.34
1995	0.19
2000	0.14

at lower water temperatures (< 50°F (10°C)) with reasonably low operating pressure (see Chapter 4.4.2.1). And, "fouling resistant" membranes have been developed that purport to minimize fouling by suspended solids, organics, and microbes (see Chapter 4.4.2.3).

Since the late 1970's, researchers in the US, Japan, Korea, and other locations have been making an effort to develop chlorine-tolerant RO membranes that exhibit high flux and high rejection. Most work, such as that by Riley and Ridgway et. al., focuses on modifications in the preparation of polyamide composite membranes.[11] Other work by Freeman (University of Texas at Austin) and others involves the development of chlorine-tolerant membrane materials other than polyamide. To date, no chlorine-resistant polyamide composite membranes are commercially available for large-scale application.

Nanotechnology came to RO membranes on a research and development scale in the mid 2000's, with the creation of thin-film nanocomposite membranes.[2,12,13] The novel membranes created at UCLA in 2006 by Dr. Eric M.V. Hoek and team include a type of zeolite nanoparticle dispersed within the polyamide thin film. The nanoparticles have pores that are very hydrophilic such that water permeates through the nanoparticle pores with very little applied pressure as compared to the polyamide film, which requires relatively high pressure for water to permeate. Hence, the water permeability through the nanocomposite membranes at the highest nanoparticle loading investigated, is twice that of a conventional polyamide membrane.[12] The rejection exhibited by the nanocomposite membrane was equivalent to that of the conventional polyamide membrane.[12] The controlled structure of the nanocomposite membrane purports to improve key performance characteristics of reverse osmosis membranes by controlling membrane roughness, hydrophilicity, surface charge, and adhesion of bacteria cells.[14] The thin-film nanocomposite membrane (TFN) technology was licensed from UCLA in 2007 by NanoH_2O, Inc. (el segundo, CA acquired by LG Chem (COREA) in 2014) for further research and development toward commercialization.[15]

Along similar lines, other researchers have been looking into nanocomposite membranes.[16] Researchers at the University of Colorado at Boulder have been developing lyotropic liquid crystals (LLCs) to form what they call nanostructured polymer membranes.[16] The LLCs can form liquid crystalline phases with regular geometries which act as conduits for water transport while rejection ions based on size exclusion. In bench-scale tests, nanostructuered polymer membranes exhibited a rejections of 95% and 99.3% of sodium chloride and calcium chloride, respectively.[13] These membranes also exhibited greater resistance to chlorine degradation than commercially-available polyamide composite membranes. The nanostructured polymer membranes are not yet in commercial production.

1.1.4 Future Advancements

Improvements will be necessary as RO is used to treat the ever greater expanding candidate feed waters, including municipal and industrial wastewater effluents, and other source waters that are less than optimal for conventional RO membranes (e.g., wastewaters containing high concentrations of biological chemical demand (BOD), chemical oxygen demand (COD), TOC, silica, and suspended solids, such as food-processing condensates and cooling tower blowdown). Membranes will need to be developed that are tolerant of chlorine for microbial growth control, and resist to fouling with suspended solids and organics. Other membrane technologies, such as microfiltration and ultrafiltration, are finding fresh application in pre-treating RO systems operating on these challenging water sources.

There is also continuing research into higher-performance (high flux and high rejection) membranes to further reduce the size and cost of RO systems. Nanotechnology shows promise for having a role in the development of these high-performance membranes.

Improvements will be required in the chemistries used to treat RO. These chemistries include antiscalants, which will be needed to address higher concentrations of scale formers such as silica, and membrane cleaners, which will have to address microbes, biofilms, and organics.

1.1.5 Advances Since First Edition of this Book

The history of RO membranes up through the 1980's was sprinkled with great technological leaps in development; the last two decades have seen relatively incremental, but continuous, improvements in RO technology that, nevertheless, has led to significant cost reductions. These improvements included advances in process design, feed water pretreatment, and energy reduction/recovery, but the greatest improvements have come through modifications to the RO membrane and membrane modules.[17] Improvements over the years in membrane functionality, stability, permeability, and selectivity, have resulted in decreases in salt passage and increases in permeability (as measured by energy consumption) (see Figure 1.5).[17] Module improvements have included increasing the membrane area per module, the module-to-module connection within

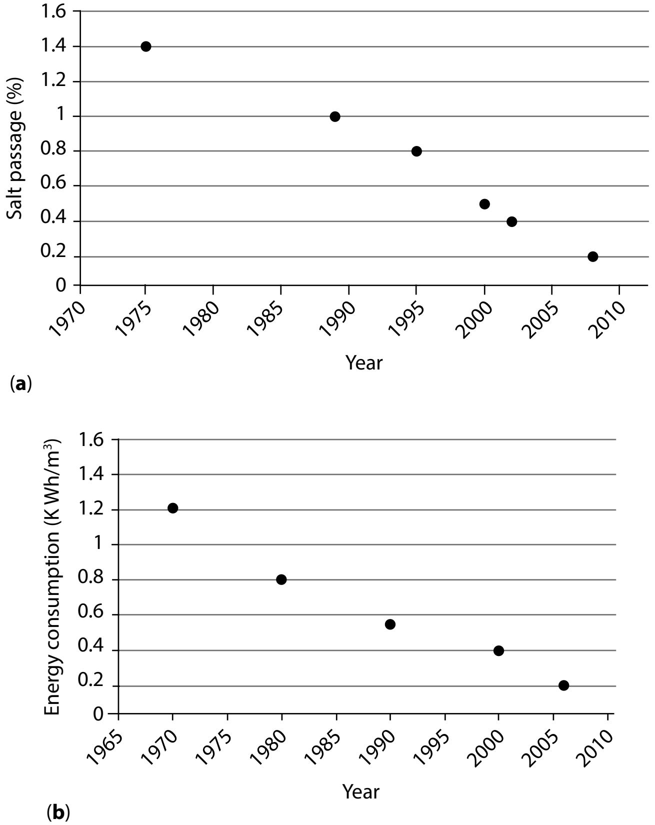


Figure 1.5 Improvement in membrane performance since the 1970s: (a) salt passage, (b) permeability, as measured by energy requirements.

a pressure vessel (e.g., Dow *iLec*® interconnection system), and, perhaps most significantly, modifications to the feed spacer thickness, materials of construction, and design. Spacer modifications have focused on trying to minimize concentration polarization (see Chapter 3.5) via spacer geometry changes; minimizing biofouling by impregnating or coating the spacer with biocidal chemicals; and minimizing fouling with particulates and improving cleaning efficiency by increasing the spacer thickness while keeping the membrane area per module high.

The search for membrane materials with high permeability and high rejection at an affordable price still is the primary goal of current research efforts.[17] At the same time, RO is tasked with treating evermore challenging feed water sources, as availability of "good" brackish water sources are dwindling. Therefore, work continues on basic membrane and application research, addressing specific challenges that include:

- Characterizing the feed water to the RO: Having a good understanding of what is in the feed water is critical to developing a pretreatment system and the actual design of the RO unit itself to minimize detrimental effects (i.e., fouling, scaling, degradation) of the components in the feed water, thereby reducing the frequency of membrane cleaning and replacement.
- Materials development: Constructing membranes that have resistance to fouling, scaling, and degradation while offering high permeability and solute rejection is key. As the feed water sources become more complicated, the membranes need to not only reject the solutes present in the feed water, but also not foul with the various species present.
- Reducing the energy requirements of RO: Updates to module construction and modifications to membrane materials to reduce pressure losses are required. Note that the operating pressure of current RO membranes is near the thermodynamic limit[18] such that any membrane improvements would have minor impacts on performance. However, changes in module design could improve pressure losses and reduce energy requirements of the system.
- Product water quality standards: As water quality standards become more stringent and limits on contaminants keep decreasing in specific value, membranes need to improve their rejection capabilities of all species (e.g., boron, which has become important for potable water considerations).[19]
- Tolerance to chlorine: The destruction of current polyamide membranes upon exposure to oxidizers is a significant handicap when trying to treat water sources such as surface water (lakes and rivers) and wastewater. These feed sources contain biological materials and nutrients to propagate microbes that severely foul RO membranes. Development of halogen-resistant membranes is vitally important as more challenging feed waters are treated by RO.

This list is by no means an exhaustive account of the challenges facing RO today, but it presents examples of the numerous issues that researchers confront.

One of the more interesting fronts of development includes the search for improved membrane materials. While no new polymeric RO membranes have been introduced commercially over the last 20 to 30 years, there have been developments in performance (see Figure 1.5). These improvements in performance were achieved via modifications to the membrane itself (surface modifications made possible due to more advanced membrane characterization techniques) and closer tolerances in the interfacial polymerization reaction to make the membrane,[17] and enhancements of the module design.[17] Membranes with these improvements are commercially available today. While work is continuing with modifications to the current thin-film composite polyamide membranes, researchers are looking toward additional materials that might be suitable for use as RO membranes.

Non-polymeric RO membranes, including inorganic, combination inorganic/polymer, and biomimetric membranes,[20] are under various phases of development. Nanoparticle/polymeric combination membranes using titanium oxide coatings of polyamide thin-film composite membranes have been prepared.[21] These membranes exhibited excellent antibiofouling properties while operating at the same flux and salt rejection as the original polyamide membrane.[21] NanoH$_2$O has commercialized its TFN membrane, under the *Quantum*Flux family of TFN membranes, for seawater desalination. These membranes incorporate a metal zeolite into the thin-film polyamide, rather than a coating of the thin film. The *Quantum*Flux membrane family compares favorably with common polyamide seawater composite membranes, as shown in Table 1.3. Other membranes under development also include carbon nanotubes/polymeric membranes.[22] These membranes show significantly higher transport flow of water through them, but salt rejection is too low at this stage to make them suitable for desalination applications.[17] The high water transport properties of biological membranes has researchers looking to incorporate biological materials into tri-block co-polymers. Biomimetric RO membranes involve incorporating proteins (aquaporins), which function as water-selective channels in biological cell membranes, into the walls of the tri-block co-polymer, poly(2-methyl-2-oxazoline)-block-poly(dimethylsiloxane)-block-poly(2-methyl-2-oxazoine).[23] These biomimetric membranes have shown better permeability than polyamide composite membranes,[23] with salt rejection results yet to be reported (but salt rejection is expected to be high because the biological performance of the aquaporin proteins allows only water to pass).[17]

Research work is progressing on several fronts to try to achieve membranes and modules with characteristics that will improve system

Table 1.3 :Performance comparison of thin-film nanoparticle membrane, *Quantum*Flux, with conventional thin-film composite membranes.

Make	**NanoH$_2$O**	**Hydranautics**	**Dow Filmtec**	**Toray**
Model	**Qfx SW 400R**	**SWC5-LD**	**SW30XLE-400i**	**TM820R-400**
Membrane Area, ft^2(m^2)	400 (37)	400 (37)	400 (37)	400 (37)
Permeate, GPD(m^3/d)	9000 (34)	9000 (34)	9000 (34)	8500 (32.2)
Stabilized Salt Rejection, %	99.85	99.8	99.8	99.8
Stabilized Boron Rejection, %	93	92	91.5	95
Feed Spacer Thickness, mil	28	34	28	28
NanoH$_2$O advantage	-	25% lower salt passage	25% lower salt passage	25% lower salt passage 6% higher productivity

performance. Technical factors regarding some membrane types need further development and issues of mass production of novel membranes at a reasonable cost are two major challenges that must be overcome to make these membranes more commercially viable.

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2

Reverse Osmosis Principles

Reverse osmosis is a demineralization process that relies on a semipermeable membrane to effect the separation of dissolved solids from a liquid. The semipermeable membrane allows liquid and some ions to pass, but retains the bulk of the dissolved solids (ions). Although many liquids (solvents) may be used, the primary application of RO is water-based systems. Hence, all subsequent discussion and examples will be based on the use of water as the liquid solvent.

To understand how RO works, it is first necessary to understand the natural process of osmosis. This chapter covers the fundamentals of osmosis and reverse osmosis.

2.1 Osmosis

Osmosis is a natural process where water flows through a semipermeable membrane from a solution with a low concentration of dissolved solids to a solution with a high concentration of dissolved solids.

Picture a cell divided into 2 compartments by a semipermeable membrane, as shown in Figure 2.1. This membrane allows water and some ions to pass through it, but is impermeable to most dissolved solids. One compartment in the cell has a solution with a high concentration of dissolved solids while the other compartment has a solution with a low concentration of dissolved solids. Osmosis is the natural process where water will flow from the compartment with the low concentration of dissolved solids to the compartment with the high concentration of dissolved solids. Water will continue to flow through the membrane in that one direction until the concentration is equalized on both sides of the membrane.

At equilibrium, the concentration of dissolved solids is the same in both compartments (Figure 2.2); there is no more net flow from one

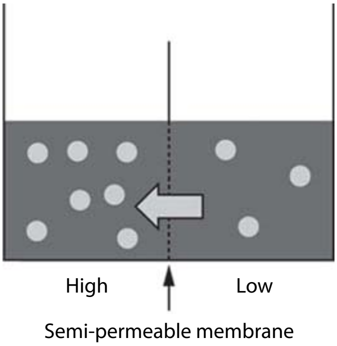

Figure 2.1 Cell divided into 2 compartments separated by a semipermeable membrane. Water moves by osmosis from the low-concentration solution in one compartment through the semipermeable membrane into the high-concentration solution in the other compartment.

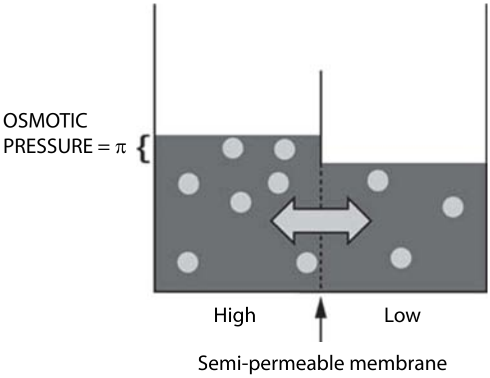

Figure 2.2 Concentration equilibrium. Difference in height corresponds to osmotic pressure of the solution.

compartment to the other. However, the compartment that once contained the higher concentration solution now has a higher water level than the other compartment.

The difference in height between the 2 compartments corresponds to the osmotic pressure of the solution that is now at equilibrium. Osmotic pressure (typically represented by π (pi)) is a function of the concentration of dissolved solids. It ranges from 0.6 to 1.1 psi for every 100 ppm total dissolved solids (TDS). For example, brackish water at 1,500 ppm TDS would have an osmotic pressure of about 15 psi. Seawater, at 35,000 ppm TDS, would have an osmotic pressure of about 350 psi.

2.2 Reverse Osmosis

Reverse osmosis is the process by which an applied pressure, greater than the osmotic pressure, is exerted on the compartment that once contained the high-concentration solution (Figure 2.3). This pressure forces water to pass through the membrane in the direction reverse to that of osmosis. Water now moves from the compartment with the high-concentration solution to that with the low concentration solution. In this manner, relatively pure water passes through membrane into the one compartment while dissolved solids are retained in the other compartment. Hence, the water in the one compartment is purified or "demineralized," and the solids in the other compartment are concentrated or dewatered.

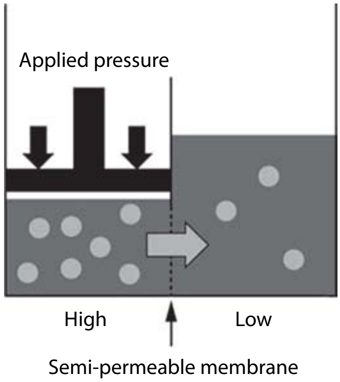

Figure 2.3 Reverse osmosis is the process by which an applied pressure, greater than the osmotic pressure, is exerted on the compartment that once contained the high-concentration solution, forcing water to move through the semipermeable membrane in the reverse direction of osmosis.

Due to the added resistance of the membrane, the applied pressures required to achieve reverse osmosis are significantly higher than the osmotic pressure. For example, for 1,500 ppm TDS brackish water, RO operating pressures can range from about 150 psi to 400 psi. For seawater at 35,000 ppm TDS, RO operating pressures as high as 1,500 psi may be required.

2.3 Dead-End Filtration

The type of filtration illustrated in Figures 2.1, 2.2, and 2.3 is called "dead end" ("end flow" or "direct flow") filtration. Dead end filtration involves all of the feed water passing through the membrane, leaving the solids behind on the membrane.

Consider a common coffee filter as shown in Figure 2.4. Feed water mixes with the coffee grounds on one side of the filter. The water then passes through the filter to become coffee that is largely free of coffee grounds. Virtually all of the feed water passes through the filter to become coffee. One influent stream, in this case water, produces, only one effluent stream, in this case coffee. This is dead end filtration.

Dead end filtration is a batch process. That means that the filter will accumulate and eventually blind off with particulates such that water can no longer pass through. The filtration system will need to be taken off line and the filter will need to be either cleaned or replaced.

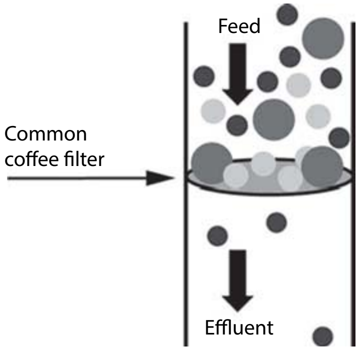

Figure 2.4 Dead-end filtration is a batch process that produces one effluent stream given one influent stream.

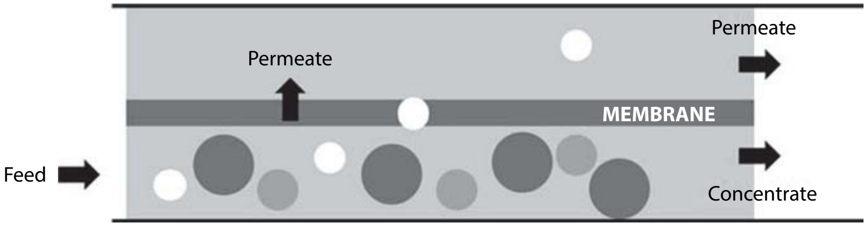

Figure 2.5 Cross-flow filtration is a continuous process that produces two effluent streams given one influent stream.

2.4 Cross-Flow Filtration

In cross-flow filtration, feed water passes tangentially over the membrane surface rather than perpendicularly to it. Water and some dissolved solids pass through the membrane while the majority of dissolved solids and some water do not pass through the membrane. Hence, cross-flow filtration has one influent stream but yields two effluent streams. This is shown is Figure 2.5.

Cross-flow helps to minimize fouling or scaling of the RO membrane. In an effort to keep the membrane surface free of solids that may accumulate and foul or scale the membrane, tangential flow across the membrane surface provides shear forces that scoure the surface to keep it clean; minimum flow rates across the membrane surface are required to effectively scour the surface. See Chapter 9.5 for more details about cross-flow filtration and RO system flow rates.

In theory, cross-flow is a continuous operation, as the scouring process keeps the membrane surface free of foulants. In practice, however, the scouring action of cross flow is not always enough to prevent all fouling and scaling. Periodically, the membranes will need to be taken off line and cleaned free of material that has accumulated at the surface.

Figure 2.6 is a simplified block diagram showing how cross-flow RO actually works. The diagonal line inside the rectangle represents the membrane. This diagram shows how the influent stream, with an applied pressure greater than the osmotic pressure of the solution, is separated into two effluent streams. The solution that passes through the membrane is called the permeate or product, and the solution retained by the membrane is called the concentrate, reject, waste, brine, or retentate. The flow control valve on the concentrate stream provides the back-pressure

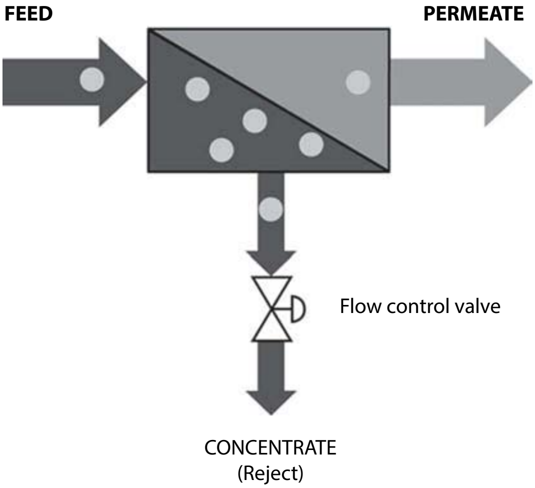

Figure 2.6 Cross-flow filtration showing concentrate flow control valve.

needed to cause reverse osmosis to occur. Closing down on the valve will result in an overall increase in pressure driving force, and a corresponding increase of influent water that passes through the membrane to become permeate.

3

Basic Terms and Definitions

This chapter defines basic terms used in conjunction with RO systems. Also see Chapter 9 for additional information as to how these parameters affect the performance of an RO system.

3.1 Reverse Osmosis System Flow Rating

An RO system is rated based on product flow rate. An 800-gpm RO would yield 800 gpm of permeate. The influent and reject flows are typically not indicated except in the design details (they are usually calculated knowing the product flow rate and the percent recovery).

In some cases, the actual design permeate flow rate of the RO system may differ from the "name plate" flow rating. In most of these situations, the RO system is de-rated by design due to a poor feed water source or as a natural result of low feed water temperature.

3.2 Recovery

Recovery (sometime referred to as "conversion") is a term used to describe what volume percentage of influent water is "recovered" as permeate. Generally, RO *system* recoveries range from about 50% to 85%, with the majority of systems designed for 75% recovery. (Individual spiral wound membrane module recoveries vary from about 10% to 15%—see Chapter 4.3). A system recovery of 75% means that for every 100 gpm influent, 75 gpm will become permeate and 25 gpm will be retained as concentrate.

Recovery is calculated using the following equation:

$$\% \text{ Recovery} = (\text{permeate flow} / \text{feed flow}) * 100 \qquad (3.1)$$

At 75% recovery, the concentrate volume is one-fourth that of the influent volume. If it were assumed that the membrane retains all the dissolved solids, they would be contained in one-fourth of the volume of influent water. Hence, the concentration of retained dissolved solids would be four times that of the influent stream (since not all dissolved solids are retained by the membrane, this becomes only an approximation). This is called the "concentration factor." At 50% recovery, the concentrate volume would be one-half that of the influent water. In this case, the dissolved solids would be concentrated by a factor of two, so the concentration factor would be 2. Table 3.1 shows the concentration factor as a function of recovery. Understanding the reject concentration is important as the concentrate side of the membrane is the area where fouling and scaling occur (see Chapters 3.6 and 3.7 respectively).

Table 3.1 Concentration factor as a function of recovery.

Recovery (%)	Concentration Factor
50	2
66	~ 3
75	4
80	5
83	6
87.5	8

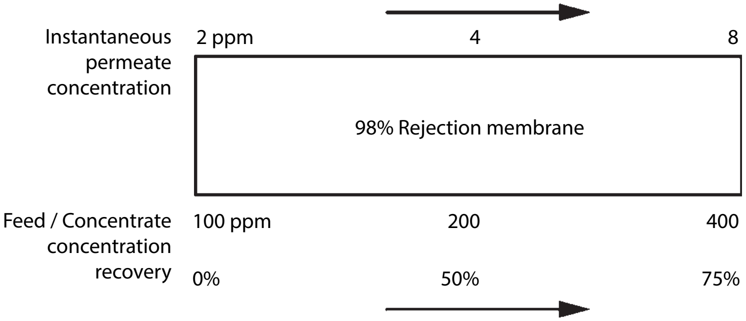

Figure 3.1 Concentrate and instantaneous permeate concentration as functions of recovery.

Higher recovery results in the need to dispose of less reject water. However, higher recovery also results in lower-purity permeate. Consider the example shown in Figure 3.1. At the influent end of the membrane, the influent concentration is 100 ppm, while the recovery is 0%, and the membrane passes 2% total dissolved solids (TDS) (see Chapter 3.3). The permeate right at this spot would be about 2 ppm. As the influent water passes across more and more membrane area, more water is recovered. At 50% recovery, the concentration factor is 2, so the influent water now has a concentration of about 200 ppm. The permeate water at this point would now have a concentration of 4 ppm. At 75% recovery, the concentration factor is 4, so the influent water now has a concentration of about 400 ppm. The permeate water at this point would have a concentration of 8 ppm. Hence, higher recovery results in lower product purity.

The designer of the RO system selects the recovery for the system; it is not a property of the membrane. The designer must consider the trade off between higher recovery resulting in less concentrate water to dispose of but also lower permeate purity.

In practice, the recovery of the RO system is adjusted using the flow control valve located on the RO concentrate stream (see Figure 2.6). Throttling the valve will result in higher operating pressure, which forces more water through the membrane as opposed to down along the feed/concentrate side of the membrane, and results in higher recovery.

The recovery of an RO system is fixed by the designer. Exceeding the design recovery can result in accelerated fouling and scaling of the membranes, because less water is available to scour the membrane on the concentrate side. Falling below the design recovery will not adversely impact membrane fouling or scaling, but will result in higher volumes of wastewater from the RO system.

3.3 Rejection

Rejection is a term used to describe what percentage of an influent species a membrane retains. For example, 98% rejection of silica means that the membrane will retain 98% of the influent silica. It also means that 2% of influent silica will pass through the membrane into the permeate (known as "salt passage").

Rejection of a given species is calculated using the following equation:

$$\% \text{ Rejection} = [(C_f - C_p)/ C_f] * 100 \tag{3.2}$$

where:

C_f = influent concentration of a specific component

C_p = permeate concentration of a specific component

Note that for exact calculation, the average feed concentration that takes in account both the feed and concentrate concentration rather than just the feed concentration at a single point in time should be used.

Salt passage is essentially the opposite of rejection:

$$\% \text{ Salt Passage} = 100 - \% \text{ Rejection} \tag{3.3}$$

$$\% \text{ Salt Passage} = (C_p / C_f) * 100 \tag{3.4}$$

Sometimes, it is easier to consider membrane performance in terms of what passes through the membrane than what is retained by the membrane.

Rejection is a property of the specific feed water component and the membrane of interest. Table 3.2 lists the general rejection ability of the most common polyamide composite RO membranes. Note that ionic charge of the component of interest plays a key role its rejection by an RO membrane; the rejection of multivalent ions is generally greater than for mono-valent ions.

In addition to the ionic charge, rejection of a particular species is also based on the following characteristics:[1]

- Degree of dissociation: in general, the greater the dissociation, the greater the rejection, for example, weak acids are rejected better at higher pH.
- Molecular weight: in general, the greater the molecular weight, the greater the rejection, for example, the rejection of calcium is marginally better than the rejection of magnesium.
- Polarity: in general, the greater the polarity, the lower the rejection, for example, organics are rejected better than water.

- Degree of hydration: in general, the greater the degree of hydration, the greater the rejection, for example, chloride is rejecter better than nitrate.
- Degree of molecular branching: in general, the more branching, the greater the rejection, for example, isopropanol is rejected better than normal propanol.

Table 3.2 General rejection capabilities of most polyamide composite membranes at room temperature.

Species	**Rejection (%)**
Sodium	92–98
Calcium	93 – 99+
Magnesium	93–98
Potassium	92–96
Iron	96–98
Manganese	96–98
Aluminum	96–98
Ammonium*	80–90
Copper	96–99
Nickel	96–99
Zinc	96–98
Silver	93–96
Mercury	94–97
Hardness	93–99
Chloride	92–98
Bicarbonate	96–99
Sulfate	96–99+
Fluoride	92–95
Silicate	92–95
Phosphate	96–98
Bromide	90–95
Borate	30–50
Chromate	85–95
Cyanide	90–99+

* below pH 7.5. Above this pH, a greater percentange of the ammonia exists as a gas which is not rejected by RO membranes.

The rejection of gases is 0%, meaning that the concentration in the permeate stream will be the same as it is in the influent and concentrate streams. Gases that are not rejected include free chlorine that may used to disinfect RO feed water through the pretreatment system (see Chapter 8.2) and carbon dioxide. RO systems operating at near neutral pH will have some carbon dioxide in the feed water. Since gases are not rejected by RO membranes, the permeate and concentrate streams will also contain carbon dioxide. If the permeate is sent to ion exchange demineralization or electrodeionization after the RO, the carbon dioxide will use sites on the anion resin so that other anions are not well removed. In these cases, caustic soda (NaOH) is sometimes added to the RO feed water. This raises the pH and converts the carbon dioxide, which is not rejected by the RO membrane, to bicarbonate, which is rejected by the RO membrane. Caustic addition is recommended after sodium softening, which removes hardness (calcium, magnesium, barium, and strontium). Without softening, hardness in the feed water would saturate at the higher pH following caustic addition and scale the membranes. Caustic is also sometimes added between passes in a two-pass RO system (see Chapter 5.3); the first-pass RO removes the hardness while the effluent from the second pass is relatively free of carbon dioxide following caustic addition to the second pass feed.

Because carbon dioxide passes through RO membranes, the pH of the permeate is lower than the pH of the feed stream for feed water with a pH lower than about 9. Any carbon dioxide in the feed will pass through the membrane while any bicarbonate will not. This changes the ratio of carbon dioxide to bicarbonate in both the permeate and the concentrate, with the permeate having a higher ratio of carbon dioxide to bicarbonate than the feed and the concentrate having a higher ratio of bicarbonate to carbon dioxide than the feed. Hence, the pH of the permeate will be lower than the feed, while the pH of the concentrate will be higher than the feed.

Another gas that is not rejected by RO membranes is ammonia. Ammonia is a consideration when treating wastewaters as well as feed water that has been treated with chloramine. Figure 3.2 shows the relative concentrations of ammonia gas and ammonium ion as a function of pH. At a pH of approximately 9.3, half of the ammonia species is present as ammonia gas and half as ammonium ion. The gas is not rejected, while the ion has a rejection of upwards of 80% (see Table 3.1), making the overall rejection of ammonia typically less than 50%. To achieve a relatively high rejection of ammonia, the pH of the water to the RO membranes should be less than 7–7.5, as shown in Figure 3.2. Note that ammonia gas is known to swell polyamide membranes, which causes the rejection of salts to be

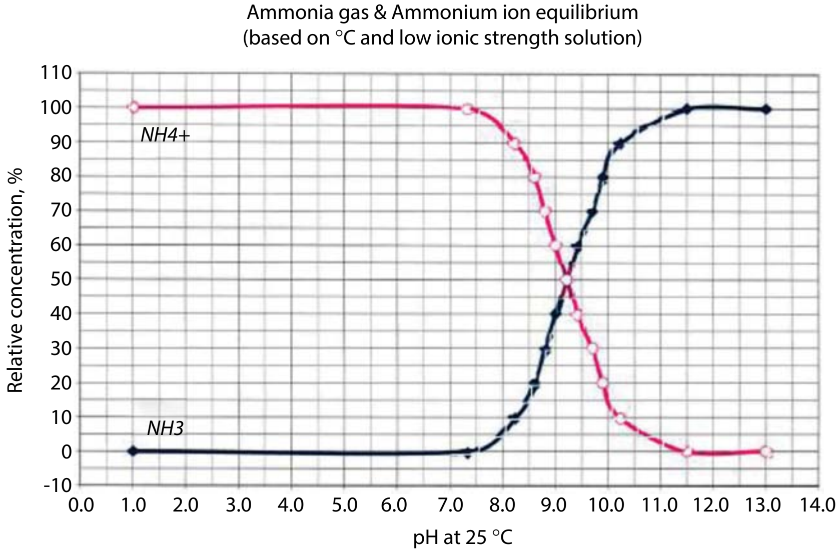

Figure 3.2 Concentration of ammonia gas and ammonium ion as functions of pH.

reduced. Salt passage can double when the membranes are exposed to free ammonia. However, this is a reversible condition, and once the free ammonia is removed, typically by reducing the pH of the water, the rejection of the RO membranes will return to normal. Membrane systems operating on city water treated with chloramine, particularly when breakpoint chloramination is occurring, can expect to see an increase in salt passage, should the pH be greater than about 8 (which is common for municipal water sources). Thus, when a system operating on city water experiences a sudden decrease in permeate quality, city workers should be consulted to determine if they are currently using chloramine.

3.4 Flux

Flux is defined as the volumetric flow rate of a fluid through a given area. In the case of RO, the fluid is water and the area is that of the membrane. In the language of RO, flux is expressed as gallons of water per square foot of membrane area per day, (gfd). The flux of water through an RO membrane is proportional to the net pressure driving force applied to the water (see Chapter 4.1 for a discussion on transport models):

$$J = K\,(\Delta P - \Delta \Pi) \tag{3.5}$$

where:

J = water flux
K = water transport coefficient = permeability / thickness of the membrane active layer
ΔP = pressure difference across the membrane
$\Delta \Pi$ = osmotic pressure difference across the membrane

Note that the water transport coefficient is unique to a given membrane and is not a constant; it varies directly with temperature. The coefficient for some newer polyamide membranes also varies with pH.

The designer of the RO system chooses the flux rate; it is not a property of the membrane. In general, the flux that an RO system is designed for should be a function of the influent water quality. This is because higher flux results in more rapid fouling of the membranes. So, the lower the influent water quality, the lower the operating flux of the RO system should be. Table 3.3 shows the recommended flux as a function of influent water source (which is an indirect measure of the water quality) and silt density index (SDI), which is a measure of the tendency of water to foul a membrane (See Chapter 3.9). When in doubt, a default flux of 14 gfd is usually recommended.

Specific flux is sometimes discussed in comparing the performance of one type of membrane with another. Since not all membranes are tested at the same pressure. Specific flux is approximated by taking the overall system flux and dividing by the applied driving pressure:

$$\text{Specific Flux} = \text{Flux / Applied Pressure} \tag{3.6}$$

Table 3.3 Recommended flux as a function of influent water source.

Feed Water Source	SDI	Recommended Flux, gfd *
RO Permeate	<1	21–25
Well Water	<3	14–16
Surface Supply	<3	12–14
Surface Supply	<5	10–12
Secondary Municipal Effluent—Microfiltration Pretreatment**	<3	10–14
Secondary Municipal Effluent—Conventional Pretreatment	<5	8–12

* for 8-inch diameter, brackish water membrane modules

** Microfiltration pore size < 0.5 microns.

In comparing membranes, the higher the specific flux the lower the driving pressure required to operate the RO system. Specific flux is also defined as the "permeability" of the membrane.

3.5 Concentration Polarization

In simplest terms, the flow of water past an RO membrane is similar to that of the flow of water through a pipe, Figure 3.3. The flow in the bulk solution is convective, while the flow in the boundary layer is diffusive and is perpendicular to the convective flow of the bulk solution. There is no convective flow in the boundary layer. The slower the velocity of water through the pipe, the thicker the boundary layer becomes.

Now, consider flow along the surface of a membrane. The same boundary layer forms as with flow through a pipe. However, with a membrane system, because there is a net flow out through the membrane, there is convective flow to the membrane, but only diffusional flow away from the membrane. Since diffusion is slower than convection, solutes rejected by the membrane tend to build up on the surface and in the boundary layer. Thus, the concentration of solutes at the membrane surface is higher than in the bulk solution. This boundary layer is called "concentration polarization."[2] The phenomenon is shown in Figure 3.4.

Concentration polarization has a negative effect on the performance of an RO membrane. It acts to reduce the throughput of the membrane in three important ways. First, it acts as a hydraulic resistance to water flow through the membrane. Second, the build up of solutes increases the osmotic pressure within the boundary layer, effectively reducing the driving force for water through the membrane. Third, the higher concentration of solutes on the membrane surface than in the bulk solution, leads to higher passage of solutes than would be predicted by the feed water

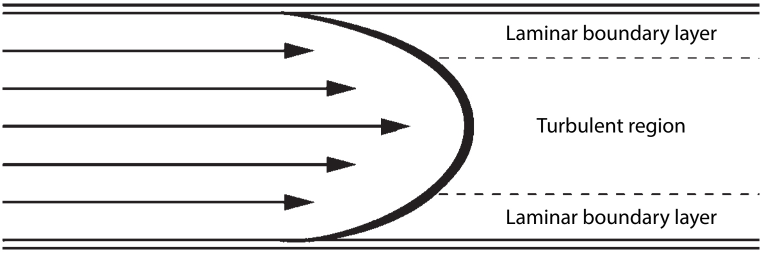

Figure 3.3 Hydraulic boundary layer formed with fluid flow in a pipe.

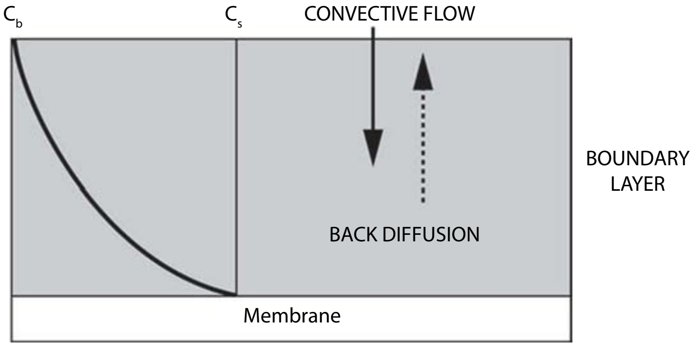

Figure 3.4 Concentration polarization, where C_b is the bulk concentration and C_s is the concentration at the membrane surface.

concentration. This is because an RO membrane rejects solutes based on the concentration of the salt that it "sees." If the concentration of a species is higher at the membrane surface, as is the case with concentration polarization, the amount of solute passing into the permeate will be higher than the expected amount of solute based on the bulk concentration of that solute. The actual rejection and salt passage exhibited by the membrane does not change. However, the apparent rejection/passage does. For example, assume that the bulk concentration of silica is 10 ppm, while the concentration at the membrane surface is 11.5 ppm. If the rejection is 98%, the silica concentration that would be expected to be in the permeate based on the bulk concentration is 0.20 ppm. However, the membrane "sees" 11.5 ppm, so the actual salt passage is 2% of 11.5 ppm, or 0.23 ppm. Actual rejection is still 98%. Apparent rejection is 97.7%.

See reference 1 for a more complete discussion about concentration polarization.

3.6 Beta

Beta, sometimes called the "concentration polarization factor," is the ratio of the concentration of a species at the membrane surface to that in the bulk solution. Hence, Beta is a way of quantifying concentration polarization.

The higher the Beta number, the more likely the membranes are to foul or scale. Again, since Beta measures the ratio of concentration at the surface to that in the bulk solution, the higher the beta number, the higher the relative concentration at the surface. If the concentration at the surface gets high enough, saturation may be reached and scale will begin to form.

Maximum acceptable Beta typically ranges from about 1.0 to 1.2 to minimize formation of scale. (see Chapter 9.6).

Beta is not a property of the membrane; it is an artifact of the system design that is selected. Specifically, Beta is a function of how quickly the influent stream is dewatered through the RO system. If water is removed too quickly from the influent stream, Beta will increase, as a relatively high volume of dissolved solids is left behind on the membrane because of the high volume of water that permeates out through the membrane. Concentration polarization further exacerbates the problem because of the diffusional-only flow away from the membrane surface. See Chapter 9.6 for more information about Beta and its relationship with water flux and salt passage.

3.7 Fouling

Membrane fouling is a result of deposition of suspended solids, organics, or microbes on the surface of the membrane, typically on the feed/concentrate side. Fouling species include:

- colloids, such as alumina- and iron-silicates. Silica can precipitate at concentration below saturation in the presence of metals including calcium, aluminum, or iron, forming colloidal materials.[1]
- organics, which also provide nutrients for microbes,
- microbes,
- color, which irreversibly adsorbs onto the membrane polymer, resulting in permanent flus loss
- metals, such as iron and manganese that precipitate when oxidized; aluminum, typically from alum, which is commonly overfed, particularly into municipal/surface sources; and hydrogen sulfide, which releases elemental sulfur/iron compounds upon oxidation, sticky materials very difficult if not impossible to remove from a membrane.

Table 3.4 lists generally-accepted water quality guidelines to minimize fouling of RO membranes.[3]

Fouling is exacerbated by high membrane flux and low cross-flow velocity, both conditions that increase concentration polarization. Higher flux translates into water being removed through the membrane at a faster rate, leaving behind solids that now accumulate more rapidly in the concentration polarization boundary layer. If the residence time is sufficient in the

Table 3.4 Generally-accepted water quality guidelines to minimize RO membrane fouling.

Species	Measure	Value
Suspended Solids	Turbidity	<1 NTU
Colloids	SDI	<5
Microbes	Dip Slides*	<1,000 CFU/ml**
Organics	TOC Concentration	<3 ppm
Color	Color units	<3 APHA
Metals: iron, manganese, aluminum	Concentration	<0.05 ppm
Hydrogen Sulfide	Concentration	<0.1 ppm

* Other methods see Chapter 7.3

** In RO reject stream

boundary layer, these solids will deposit on the membrane surface, sometimes permanently. Cross-flow velocity affects the thickness of the boundary layer. Lower cross-flow velocity corresponds to a thicker boundary layer. A thicker boundary layer allows for greater accumulation of solids in the layer, and the solids spend more time in the layer due to the increased thickness of the boundary layer, setting up the potential for accelerated fouling of the membrane.

A fouled membrane exhibits two major performance issues: higher than normal operating pressure (to compensate for lower membrane flux at constant pressure) and higher than normal pressure drop. As foulants collect on the surface of the membrane, they form an additional barrier layer to transport through the membrane (see Figure 3.5). This additional barrier requires a greater net driving force, which translates into higher operating pressure. Higher pressure drop is a result of the increased resistance to cross-flow caused by the layer of foulants typically on the feed spacer in the membrane module. Pressure drop translates into axial pressure on the membrane module (see Chapter 11.3.1.3). If the pressure drop gets high enough, the axial pressure on the membrane module can become great enough to cause the membrane and module to fail (see Figures 11.5 and 11.6). Failure can manifest as cracks in the outer module casing and telescoped membranes and spacers (Figure 3.6A and B respectively).

Fouling of a membrane is primarily a physical filtration event, although in some cases, charge of a species can determine its potential to foul an

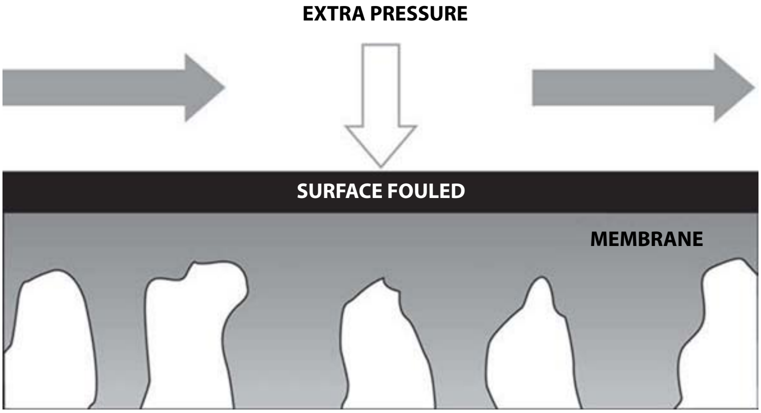

Figure 3.5 Fouling on membrane surface creates an additional barrier to permeate transport that requires additional pressure to force permeate through the fouling layer.

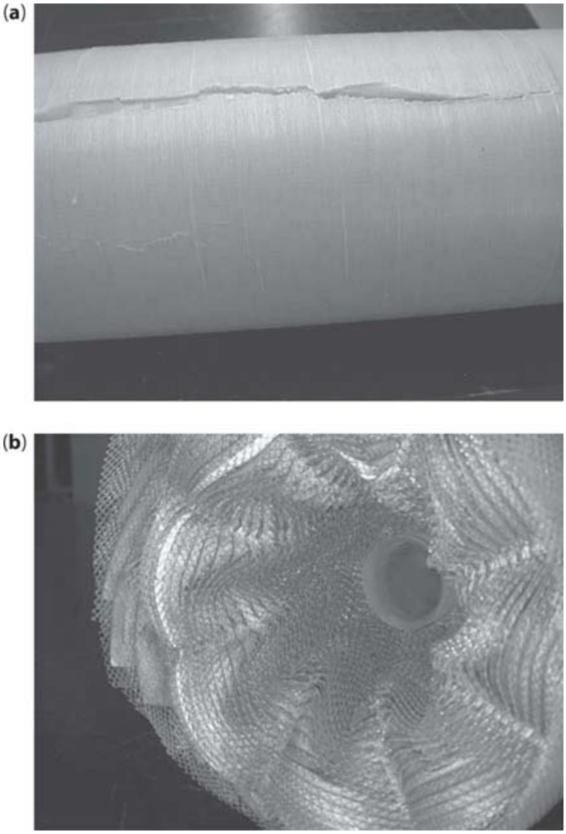

Figure 3.6 Cracked outer module casing (a) and telescoped membranes and spacers (b) due to excessive pressure drop.

RO membrane (as is the case with cationic coagulants on the negatively-charged polyamide RO membrane—see Chapter 8.1.1.1). The lead membrane modules in an RO system are generally most affected by fouling ("lead" membrane module is the end module in a pressure vessel that feed water contacts first). One exception is microbial fouling. Microbes can establish colonies anywhere in the membrane system where conditions favor growth. Satellite colonies can break off and further distribute themselves throughout the system. Note that even short term exposure to potential foulants can result in long-term and even permanent fouling issues for a membrane.[4]

3.8 Scaling

Scaling of RO membranes is a result of precipitation of saturated salts onto the surface of the membrane. Table 3.5 lists generally- accepted water guidelines for minimizing scaling of RO membranes.[3] The table includes the following species:

- calcium scales, including carbonate, sulfate, fluoride, and phosphate,
- reactive silica, which is measured in the RO reject and is a function of temperature and pH, and
- sulfate-based scales of trace metals, such as barium and strontium.

Scaling is exacerbated by high membrane flux and low cross-flow velocity, in the same manner as membrane fouling is increased. Higher flux brings more solutes into the concentration polarization boundary layer quicker. If the concentration of the solutes in the boundary layer reaches saturation,

Table 3.5 Generally-accepted water quality guidelines to minimize RO membrane scaling.

Species	Measure	Value
Silica (Soluble)	ppm	140–200*
Barium, Strontium	ppm	<0.05
Calcium	LSI	<0**

* In RO reject stream

** Can go up to 2.0–2.5 with appropriate antiscalant these solutes will scale the membrane. Lower cross-flow velocity corresponds to a thicker boundary layer. This increases the residence time for solute within the boundary layer, increasing the chance that saturation will be achieved and scale will form.

A scaled membrane exhibits three major performance issues: higher than normal operating pressure (to compensate for lower flux at constant pressure), higher pressure drop, and lower than expected salt rejection. As with fouled membranes, scale forms an additional barrier layer through which water has to travel. Additional driving force is required to push water through this barrier layer if the same productivity is to be maintained. Higher pressure drop is due to resistance of the scale to cross flow. Lower salt rejection is a function of concentration polarization, in that the concentration of the scaled mineral is higher at the membrane surface than in the bulk solution. Thus, the membrane "sees" a higher concentration, and, although the intrinsic rejection by the membrane remains constant, the actual amount of a solute that passes through the membrane is greater (see Equation 4.2, which predicts that the flux of a solute through an RO membrane is a function of the concentration difference between the solute in the boundary layer and in the permeate). Hence, the apparent rejection is lower and product purity is lower.

Since scaling is a concentration phenomenon, it goes to reason that scale would be most likely found in the last stage(s) of an RO system where the concentration of salts is the highest. To determine the potential for a salt to form scale, the ion product of the salt in question (taken in the reject stream) is compared with the solubility product for the salt under the conditions in the reject.

Equation 3.7 defines the ion product at any *degree of saturation:*

$$\mathrm{IP} = [\mathrm{cation}]^{a}[\mathrm{anion}]^{b} \tag{3.7}$$

Where:

IP = ion product
[cation] = cation concentration
[anion] = anion concentration
Superscripts:
  a = the quantity of cation present within the salt
  b = the quantity of anion present within the salt.

Equation 3.8 defines the solubility product at *saturation*:

$$K_{sp} = [\mathrm{cation}]^{a}[\mathrm{anion}]^{b} \tag{3.8}$$

where:

K_{sp} = solubility product
[cation] = cation concentration
[anion] = anion concentration
Superscripts:
a = the quantity of cation present within the salt
b = the quantity of anion present within the salt.

In general, scale will form when the ion product is greater than the solubility product. For sulfate-based scales, scaling can occur when the ion product is greater than 80% of the solubility product.[1]

Scaling indexes are used to aid in the determination of whether a salt will scale an RO membrane. The Langelier Saturation Index (LSI) and the Stiff–Davis Saturation Index are commonly used to predict calcium carbonate scale (see Chapter 3.11). Design programs developed by membrane manufacturers typically report scaling indexes for other forms of scale as a percent of saturation (see Chapter 10). A scaling index is 100% when the ion product equals the solubility constant for most salts. For sulfate-based scales, the saturation index is 100% when the ion product is equal to 80% of the solubility constant. Feed water softening or the use of antiscalants is required when the saturation index is 100% or greater.

3.9 Silt Density Index

Silt density index (SDI) is a test that measures the potential of an influent water to foul an RO membrane with suspended solids and colloids. The test involves timing flow of the influent water through a 0.45-micron filter pad.[5] Consult ASTM DC1189-7 "standard test method for silt density index (SDI) of water" for more details.

Figure 3.7 shows the basic materials required to run an SDI test. The apparatus shown in Figure 3.7 should be connected as close to the inlet of the RO as possible (preferably between the cartridge filters and the RO, if possible).

Procedures to run an SDI test call for a 0.45-micron filter pad to be placed with the shiny side up in the filter holder. According to the ASTM procedure referenced above, the filter used should be hydrophilic and composed of mixed cellulose nitrate (50–75%) and cellulose acetate. Thickness should be 115–180 microns, with a pure water flow of 25–50 seconds per 500 ml of samples collected. Experience has shown that the Millipore filter, model number HAWP04700, has the desired characteristics as defined by

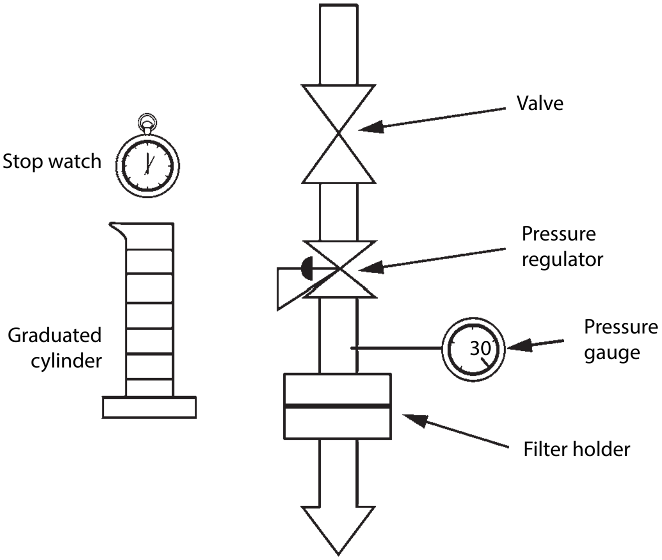

Figure 3.7 Silt density index test apparatus and ancillary equipment.

the ASTM procedure, and is preferred for the test. A small squirt of water from a water bottle is used to wet and completely seat the filter pad. (If the pad shows signs of air bubbles or erratic coverage of foulant of the pad upon removal from the filter holder, the filter was not seated properly and the SDI test is invalid). The isolation valve is opened and the pressure regulator is set to 30 psi. The time it takes to collect 500 ml of water through the 0.45-micron filter pad is then recorded. This initial time should be greater than 25 seconds on the ASTM procedure. If this initial time is less than 25 seconds, the filter being used is not appropriate. After this initial 500ml volume of water has been collected, water is allowed to run through the filter continuously for a total time of 15 minutes. If necessary, the pressure should be adjusted to remain at 30 psi. At the end of 15 minutes, the time it takes to collect another 500 ml of water is recorded. Both recorded times are then entered into Equation 3.9 to calculate the SDI (note that SDI is unit-less):

$$\mathrm{SDI}_n = \frac{1 - t_0 / t_n}{n} \times 100 \tag{3.9}$$

where:

n = total run time, 15 minutes
t_0 = time to collect 500 ml of influent water at time = 0, in seconds

t_n = time to collect 500 ml of influent water at time = n (15 min), in seconds

The test must be run at 30 psi. As mentioned above, if the pressure drops during the test, it should be adjusted back to 30 psi.

(Note that the SDI test can also be run for 5 minutes and 10 minutes. However, most literature references to SDI discuss the 15 minute-run, unless otherwise stated.)

The maximum SDI_{15} that can possibly be calculated from equation 3.9 occurs when the time to collect the final 500-ml of water, t_n, is infinite. The maximum SDI_{15} then becomes $(1/15) \times 100$ or 6.7.

An SDI test must be conducted on line using a representative sample of feed water; shipping samples off to a laboratory for testing is not recommended, as solids may settle or adhere to the shipping container, invalidating the test. Silt Density Index is preferable run as close as possible to the influent of the RO membranes, which means after the cartridge filter. If testing after the cartridge filter is not possible, then just before the cartridge filter is the next best location. Water should be run through the sample port or tap for at least an hour and preferably overnight before running an SDI test. This is necessary to realize a representative sample of feed water that is free of solids that may have accumulated over time in the sample port or tap.

Although there are no truly automated SDI devices, there are semi-automatic devices in addition to the manual device shown in Figure 3.7. These semi-automatic units run the SDI test, including the timing and collection of water through the SDI filter. Human intervention is required to replace the SDI filter pad and to record the test results. Note that the automatic units should be flushed with high-quality water after each use, as there are "dead" spots in the lines where contaminants and bacteria can collect and foul the tubing. Without flushing, these contaminants will affect subsequent SDI tests.

The lower the SDI, the lower the potential for fouling a membrane with suspended solids. Membrane manufacturers require that the SDI_{15} be less than 5 to meet their warranty conditions (Hydranautics warranty states an SDI of less than 4 is required). However, even though the SDI may be less than 5, the water may still be capable of fouling the membranes. In practice, an SDI_{15} of less than 3 is usually necessary to reduce the potential for fouling to an acceptable level.

Note that SDI and turbidity are only loosely related. In general, the higher the turbidity, the higher the SDI will be. However, low turbidity (<1 NTU) does not, in turn, imply low (<5) SDI.

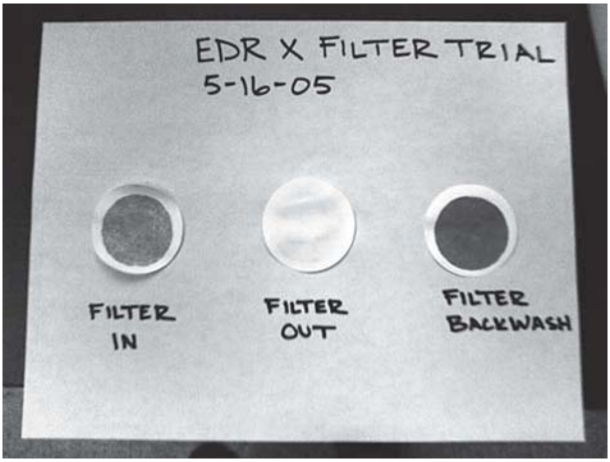

Figure 3.8 Silt density index pads taken before and after a filter treating RO influent water.

Figure 3.8 shows SDI filter pads taken before and after a multimedia filter treating RO influent water. The pads in this figure illustrate 2 important issues. First, the filter pads provide a visual confirmation about the efficacy of the multimedia filter to reduce the concentration of suspended solids in the RO influent water. Second, the filters pads can be analyzed to determine the nature of the deposit on them. Visually, the following colors are indicative of specific potential foulants:

- Yellow: possibly iron or organics
- Red to reddish brown: iron
- Black: manganese (if the color dissolves when the pad is treated with acid)

The SDI filter pads can also be sent into a lab for analysis of the deposit. The results of the deposit analysis will aid in the development of an appropriate pretreatment scheme, as specific species contributing to the suspended solids loading can be targeted for treatment to reduce their concentration in the feed water to the RO.

3.10 Modified Fouling Index

Fifty years ago, the SDI test was developed to predict the fouling tendency for the DuPont Permasep Permeators (hollow fine fiber RO elements).[6] The SDI test is still the standard method for fouling prediction on spiral wound RO and NF membranes in the United States (ASTM). The test, which relies on a 0.45 micron microfiltration (MF) filter paper to run, is a good measure of the particulate fouling of spacers in spiral wound elements, but it is not sufficient for predicting the direct fouling of the membrane surface itself. Surface fouling of RO and NF membranes is generally considered to be a cake filtration mechanism, while MF membrane fouling is both cake filtration and blocking mechanisms.[7] Thus, measurement of the SDI using an MF filter would yield not only the cake-based fouling but also the pore blocking fouling, which typically occurs first with an MF membrane.

A test method called the modified fouling index (MFI or MFI-0.45) is gaining popularity and has been used in Europe for 25 years.[8] The test was developed based on Darcy's Law that relates flux (dV/dt) to the thickness of the cake layer, which is the sum of the filter resistance (R_m) and the cake resistance (R_c)[9]:

$$dV/dt = \Delta P/\mu * A_m/(R_m + R_c) \tag{3.10}$$

$$t = \mu V R_m/\Delta P A_m + \mu V^2 \alpha C_b/2\Delta P A_m{}^2 \tag{3.11}$$

$$t/V = \mu R_m/\Delta P A_m + \mu V \alpha C_b/2\Delta P A_m{}^2 \tag{3.12}$$

$$1/Q = a + MFI * V \tag{3.13}$$

Where:

V = total volume produced
ΔP = transmembrane pressure
μ = dynamic viscosity of water
A_m = membrane area
α = specific cake resistance
Cb = concentration of particles
Q = average flow
a = a constant

These equations predict a linear relationship between t/V and V during cake formation.

The MFI test uses the same apparatus as the SDI test; however, the total volume collected is recorded every 30 seconds and the data is plotted as t/V vs V (where t = time in seconds, V = volume in liters). The test covers the initial pore blocking fouling mechanism, the cake filtration mechanism, and the longer term cake blocking/cake compression mechanism (See Figure 3.9).[6] The minimum slope (or linear part) of the curve in Figure 3.9, which corresponds to the cake filtration portion of the curve, is the MFI expressed in seconds per square liter (s/L^2).

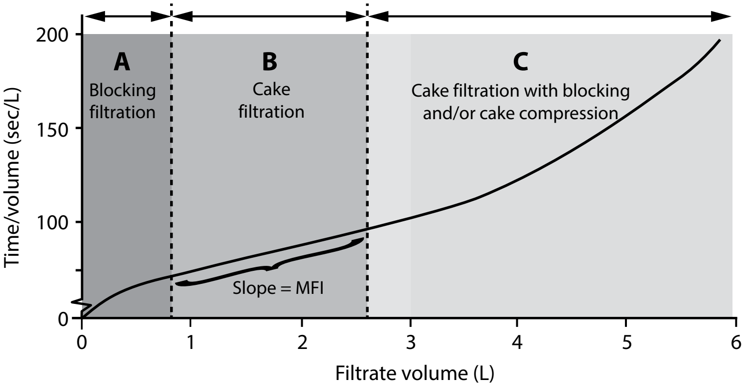

Figure 3.9 Ratio of filtration time to volume as a function of total volume of filtered water, showing the three dominant filtration mechanisms of A: blocking filtering; B: cake filtration; C: cake blocking/compaction. The MFI is represented as the slope of the linear curve during cake filtration.

One difficulty with the MFI is that it uses a 0.45 MF membrane, which allows smaller colloidal particles to pass that foul RO or NF membranes. Thus, researchers have proposed an MFI-UF test that uses ultrafiltration (UF) membranes rather than the MF membranes.[7] The UF membranes have an order of magnitude smaller pore side and can capture more of the smaller colloids.

The ASTM is currently working on WK45948, "New Test Method for Modified Fouling Index (MFI-0.45) of Water," to develop a companion procedure to the SDI for more accurate prediction of membrane fouling.[6,8] Although there are devices on the market that automatically or semi-automatically measure both SDI and MFI-0.45, the MFI still has the following issues that need to be resolved[6]:

- Test membranes with smaller pores approaching 0.5 kDa. These are not commercially available in flat sheet form.
- A database of MFI values to determine what a "safe" MFI value is.
- Overcoming full-scale plant issues, such as the enhanced osmotic pressure effect due to fouling, which is difficult to capture in the MFI test.

Numerous other fouling indexes are noted in the literature, including the ROFix (reverse osmosis fouling index)[10] PI (permeation index)[11] (Nakamura), and CFI (combined fouling index).[12] None of these indexes have been as widely accepted as the SDI and, to a lesser extent, the MFI.[6]

3.11 Langelier Saturation Index

The Langelier Saturation Index (LSI) is a method for quantifying the scaling or corrosion tendency of water. It was originally applied to cooling water. The LSI is based on the pH and temperature of the water in question as well as the concentrations of TDS, calcium hardness, and alkalinity.

Langelier Saturation Index is calculated using equation 3.10:

$$LSI = pH - pH_a \tag{3.14}$$

where:

$$pH_a = (9.30 + A + B) - (C + D) \tag{3.15}$$

and:

$A = (\text{Log}_{10}[\text{TDS}] - 1)/10$, where [TDS] is in ppm
$B = -13.12 \times \text{Log}_{10}\,(°\text{C} + 273) + 34.55$
$C = \text{Log}_{10}[\text{Ca}^{2+}] - 0.4$, where $[\text{Ca}^{2+}]$ is in ppm $CaCO_3$
$D = \text{Log}_{10}[\text{alkalinity}]$, where [alkalinity] is in ppm $CaCO_3$

If LSI is greater than 0, the water has the tendency to form calcium carbonate scale. If the LSI is equal to 0, the water is in chemical balance. If the LSI is less than 0, the water is corrosive (refer to Table 3.6).

Langelier Saturation Index is valid up to about 4,000 ppm TDS. At higher TDS concentrations, the Stiff–Davis Saturation Index (SDSI) is used, Equation 3.12:

$$SDSI = pH - pCa - p_{ALK} - K \tag{3.16}$$

Table 3.6 Langelier Saturation Index.

LSI	Condition
+3.0	Extremely severe scaling
+2.0	Very severe scaling
+1.0	Severe scaling
+0.5	Moderate scaling
+0.2	Slight scaling
0.0	Stable water (no scale)
−0.2	No scale, very slight tendency to dissolve scale

where:

pCa = $-\text{Log}_{10}[\text{Ca}^{2+}]$, where $[\text{Ca}^{2+}]$ is in ppm
pAlk = $-\text{Log}_{10}$[total alkalinity], where alkalinity is in ppm
K = a constant based on the total ionic strength and temperature

For RO applications, a positive LSI or SDSI indicates that the influent water has a tendency to form calcium carbonate scale. In these cases, pretreatment in the form of softening (either with lime or ion exchange), or via the use of antiscalants and/or acid is required. Note that most membrane manufactures recommend an LSI of +1.8 or lower in the concentrate with antiscalant feed to control scaling.

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4

Membranes

Membranes

Pertinent to the understanding of the operation of an RO system is the fundamental knowledge of various theoretical models describing movement of solutes and water through an RO membrane. By understanding how solutes and water are transported through membranes, appropriate modifications can be made to the membrane polymers to improve performance (flux and rejection). See the book by Richard Baker, Membrane Technology and Applications, 2nd edition (John Wiley & Sons, 2004) for more detail about the history and development of membrane and transport models.

This chapter briefly covers the development of transport models. Discussed in detail are basic membrane polymers and modules, and how they are made.

4.1 Transport Models

The purpose of a transport model is to mathematically relate performance (typically flux (see Chapter 3.4) of both solvent and solute) to operating conditions (typically pressure and concentration driving forces).[1] The objective is to predict membrane behavior under certain conditions.

There are several models that describe the transport of mass through RO membranes. These are based on different assumptions and have varying degrees of complexity. The solution–diffusion model best describes the performance of "perfect," defect-free membranes and is considered the leading theory on membrane transport.[2] Three other theories are presented here for completeness.

Transport models fall into three basic classifications: models based on solution/diffusion of solvents (nonporous transport models), models based on irreversible thermodynamics, and models based on porous membranes. Highlights of some of these models are discussed below.

4.1.1 Solution–Diffusion Model (non-porous model)

The solution-diffusion transport model was originally described by Lonsdale et al.[3] This model assumes that the membrane is nonporous (without imperfections). The theory is that transport through the membrane occurs as the molecule of interest dissolves in the membrane and then diffuses through the membrane. This holds true for both the solvent and solute in solution.

In the solution–diffusion model, the transport of solvent and solute are independent of each other, as seen in Equations 4.1 and 4.2. The flux of solvent through the membrane is linearly proportional to the effective pressure difference across the membrane (Equation 4.1):

$$J_w = A(\Delta P - \Delta \Pi) \tag{4.1}$$

where:

J_w = flux of solvent

A = water permeability coefficient (a function of the diffusivity of water through the membrane)

ΔP = applied pressure driving force (a function of the feed, concentrate, and permeate pressures)

$\Delta \Pi$ = osmotic pressure of the solution (a function of the feed, concentrate, and permeate concentrations)

The flux of solute through the membrane is proportional to the effective solute concentration difference across the membrane (Equation 4.1):

$$J_s = K(C_{A2} - C_{A3}) \tag{4.2}$$

where:

J_s = flux of solute

K = salt permeability coefficient (a function of the salt diffusivity through the membrane)

C_A = molar concentration of solute

Subscripts:

2 = at the boundary layer

3 = in the permeate

Equations 4.1 and 4.2 are most commonly used to describe transport of water and solutes through membranes due to their simplicity and their

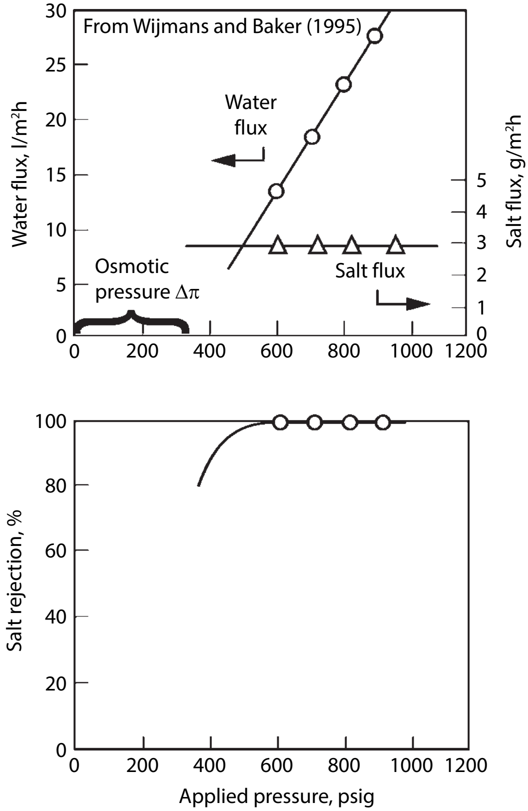

Figure 4.1 Flux and rejection data for a seawater FilmTec FT-30 membranes operating on 35,000 ppm (350 psi osmotic pressure) sodium chloride solution.[2]

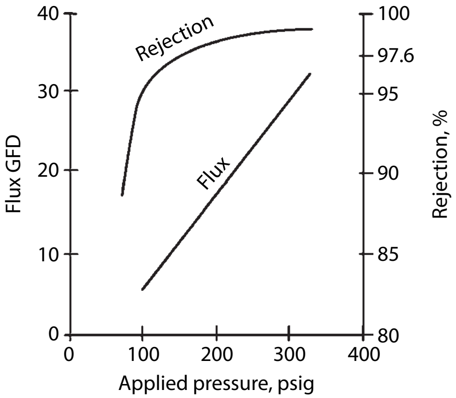

Figure 4.2 Polyamide membrane flux and rejection as a function of applied pressure. Test conditions: 5,000 ppm NaCl solution at 25°C.[4]

close approximation to empirical data. Consider Figure 4.1, which shows the flux of both water and salt and the rejection of salt exhibited by a seawater membrane as a function of applied pressure[2]. Specifically, a seawater FilmTec FT-30 membrane was operated on a 35,000 ppm sodium chloride solution with an osmotic pressure of 350 psi (2.5 MPa). As the figure shows, there is virtually no water flux until the applied pressure exceeds the osmotic pressure of the solution. Upon commencement of water flux, it increased linearly with increasing pressure, as is predicted by Equation 4.1. The salt flux, on the other hand, remained fairly constant over the range of applied pressure, as predicted by equation 4.2. Hence, as applied pressure is increased, progressively more water passes through the membrane relative to salt. This leads to the conclusion that the concentration of salt in the permeate should decrease with increasing applied pressure. Referring back to Equation 3.2, as the concentration in the permeate goes down, the percent salt rejection should approach 100% as applied pressure increases. Indeed, that is what is shown in Figure 4.1. These results are confirmed in Figure 4.2 for a low-pressure membrane operated on a 5,000 ppm sodium chloride solution at 25°C.

4.1.2 Solution–Diffusion Imperfection Model (porous model)

The solution–diffusion theory models the performance of the perfect membrane. In reality, industrial membranes are plagued with imperfections that some argue must be considered when developing a complete theory that models performance. The basis of the Diffusion Imperfection Model is the assumption that slight imperfections in the membrane occur during manufacturing that allow for leakage of solution through the membrane.[5] This model helps explain why lower-than-projected separation of solutes from water were observed for industrial membranes than was predicted by the non-porous, solution – diffusion model.

Water flux through the membrane is represented by Equation 4.3. This flux is based on the solutions – diffusion model with the added term to reflect transport due to the imperfections.

$$N_w = J_w + K_3\, \Delta P C_w = A(\Delta P - \Delta \Pi) + K_3\, \Delta P C_w \tag{4.3}$$

where:

N_w = total water flux
K_3 = coupling coefficient
C_w = concentration of water on the feed side of the membrane

The solute flux is given in Equation 4.4:

$$N_s = J_s + K_3\, \Delta P C_R = K(C_{A2} - C_{A3}) + K_3\, \Delta P C_R \tag{4.4}$$

where:

N_s = total solute flux
C_R = solute concentration on the feed side of the membrane.

Again, the solute flux is equivalent to that for the solution – diffusion model (Equations 4.1 and 4.2) with the added term to represent the flow through the imperfections.

Experiments have shown that the solution – diffusion imperfection model fits data better than the solution – diffusion model alone and better than all other porous flow models.[6] However, the solution- diffusion model is most often cited due to its simplicity, the fact that it accurately models the performance of the perfect RO membrane and because it is difficult to quantify the degree of defects in a membrane.

4.1.3 Finely-Porous Model (porous model)

The finely-porous model is based on a balance of applied and frictional forces in a 1-dimentional pore.[7] The model considers friction between the solute and solvent, and between the solute and the membrane material. The model also includes the membrane thickness and the fractional pore area of the membrane surface.

Due to the complexity of the model, it is not represented mathematically here, but the reader is advised to consider references[1,8] for further details.

4.1.4 Preferential Sorption – Capillary Flow Model (porous model)

This model is based on a generalized capillary flow model that includes viscous flow for water and solute transport, and for pore diffusion.[9] It further relies on film theory for transport through the boundary layers. The model states that by applying pressure, both the solvent *and* solute permeate through the micropores of the membrane, with water preferentially adsorbed onto the pore walls. Salt is rejected at the membrane surface for physiochemical reasons. Transport through the membrane is only through pores.

Solvent flux is given by Equation 4.1, where transport is proportional to the pressure driving force. The total solute flux depends on diffusion and is given by Equation 4.5:

$$N_s = (D_{AM}\, K / T)\, (C_{A2} - C_{A3}) \qquad 4.5$$

where:

D_{AM} = diffusivity of solute in membrane
T = effective thickness of the membrane
C_{A2} = molar concentration of solute in boundary layer
C_{A3} = molar concentration of solute in permeate

4.1.5 Phenomenological Transport Relationship (Irreversible thermodynamics)

Phenomenological transport relationships can be developed even in the absence of any knowledge of the mechanisms of transport through the membrane or any information about the membrane structure.[10] The basis of irreversible thermodynamics assumes that if the system is divided into small enough subsystems in which local equilibrium exists, thermodynamic equations can be written for the subsystems.

As with the finely-porous model, (Chapter 4.1.3), the mathematical representation of solvent and solute fluxes for the irreversible thermodynamic model is quite complex and beyond the scope of this work. However, it is recommended that readers consider references Dickson or Soltanieh[1,8] for details on this transport model.

4.2 Membrane Materials

The performance of reverse osmosis is directly dependent on the properties of the membrane material.[11] More specifically, the chemical nature of the membrane polymer and the structure of the membrane are what determines the rejection and flux properties of the RO system. Ideally, RO membranes should offer high flux and high rejection, in addition to high strength and durability. In practice, however, high rejection and high flux have been two mutually-exclusive goals that have eluded researches for decades of membrane development. Although the last few years has seen an increase in flux rates with no decrease in rejection (and in some cases, a slight increase in rejection), most membranes today represent a compromise between high rejection and high flux.[1,11]

Two most common families of RO membranes, based on the type of polymer backbone, are cellulose acetate and polyamide.[12] Membranes made from these polymers differ in many respects, including performance, physical properties, structure and the manner in which they are created. These aspects are discussed below.

4.2.1 Cellulose Acetate Membranes—Asymmetric Membranes

Cellulose acetate (CA) membranes were the first commercially-viable RO membranes developed.[13,14] These membranes were commercially viable because of their relatively high flux due to the extreme thinness of the membrane.[15] High flux was important to reduce the size and cost of an RO system.

Early cellulose acetate membranes were created by Loeb and Sourirajan using the non-solvent phase separation or "phase inversion" method.[16] In short, this method involves dissolving a non-water soluble polymer (cellulose acetate) in an organic solvent (such as acetone) along with a casting-solution modifier (initially magnesium perchlorate but later a swelling agent, formamide) and then casting a film on a sturdy surface such as a sheet of glass using a thin blade.[2,17] The film is left to stand for 10–100 seconds to partially evaporate the solvent. As the solvent evaporates, there is an increase in concentration of polymer at the solution/air interface, since the solvent evaporates more rapidly from the surface. This results in two phases within the film: a polymer-rich phase and a polymer-poor phase. Before the solvent completely evaporates, the membrane is immersed in water to completely form a thin "skin" as the remaining polymer diffuses out. The membrane is then "annealed" (heated to 70–90°C) in a hot water bath, which forms the small voids in the polymer-poor phase behind the skin. This porous region becomes the support structure. The thickness of the skin is typically about 0.2 microns, while the thickness of the entire membrane is about 100 microns.[19] It is the extreme thinness of the skin and the relatively high void volume of the supporting structure that gave these

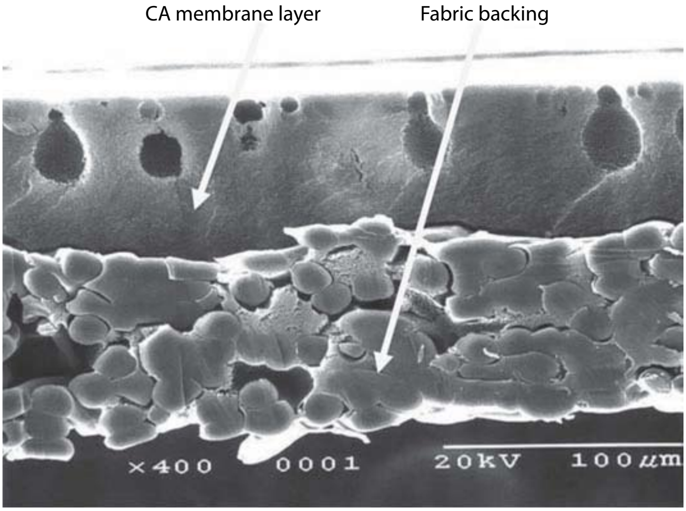

Figure 4.3 Cross section of a cellulose acetate RO membrane. Courtesy of Mark Wilf.

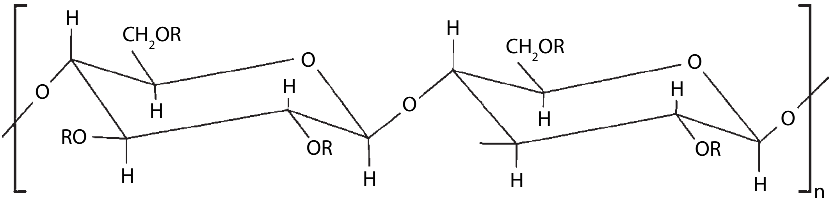

Figure 4.4 Chemical structure of cellulose acetate RO membranes.

early cellulose acetate membranes the high rejection and high flux needed for commercial viability. Subsequent development allowed for preparing the membrane from a blend of cellulose diacetate and triacetate and casting the membrane on a fabric backing.

Figure 4.3 shows a cross section of a CA membrane. The structure is asymmetric or "anisotropic," with a solute-rejecting layer on top of a microporous support, all made of the one polymeric material.

Figure 4.4 shows the chemical structure of CA membranes. Because the functional groups at the ends of the polymer chains are not highly charged, the membrane itself is considered uncharged.[12] This is an important characteristic, especially if charged (cationic) polymers are used ahead of the membrane to pretreat the influent water. The neutrality of charge will serve to minimize the potential for fouling with any polymer that carries over from the pretreatment system.

Table 4.1 lists the predominant characteristics of a CA membrane. Some of these characteristics are advantageous while others present quite severe limitations in using this type of membrane.

- The relatively smooth surface morphology of the membrane offers some protection from fouling, in that there are no obvious dead spaces on the membrane where foulants can become trapped. See Figure 4.5.
- Neutral surface charge minimizes the potential for fouling with cationic polymer that might carry over from the pretreatment system.
- Being able to tolerate up to 1 ppm free chlorine on continuous basis offers some protection from biological growth on the membrane. This is particularly important because the CA polymer itself supplies nutrients for microbial populations, which then metabolize the polymer and degrade the membrane.
- Temperature is limited to 35°C. Higher temperatures will further anneal the membrane, resulting is a much denser material that is difficult to force water through. Hydrolysis of the membrane may also occur, also leading to degradation of the membrane.[19]
- Operating pH of a CA membrane is limited to 4-6. This implies that acid is required to drop the influent pH to about 5 to 5.5 during nominal operations such that the reject pH remains less than 6. pH extremes will cause hydrolysis of the membrane polymer. Figure 4.6 shows lifetime of a CA membrane as a function of pH.
- Operating pressure for a CA membrane ranges from about 200–400 psig. The comparatively high pressure for brackish water applications is necessary because of the relatively dense nature of the CA membrane. Note that pressures above 400 psig (2.8MPa) will result in compaction of the membrane. Compaction occurs when the pressure essentially "crushes" the membrane, making it even denser.
- Salt rejection varies depending on whether "standard" or "high rejection" CA membranes are used. Rejection of silica, however, is only about 80%-85%.
- U.S. Domestic manufactures of CA membranes include Toray and TriSep.

Table 4.1 Characteristics of cellulose acetate RO membranes.

Property	**Value for CA Membranes**
Membrane Type	Homogenous asymmetric
Salt Rejection (%)	~95
Silica Rejection (%)	~85
pH Range	4–6
Feed Pressure (brackish membrane)	200–400 psi
Temperature Tolerence	Up to 35°C
Surface Charge	Neutral
Chlorine Tolerance	Up to 1 ppm continuously
Biological growth	Metabolizes membrane
Fouling Tolerance	Good
Surface Roughness	Smooth

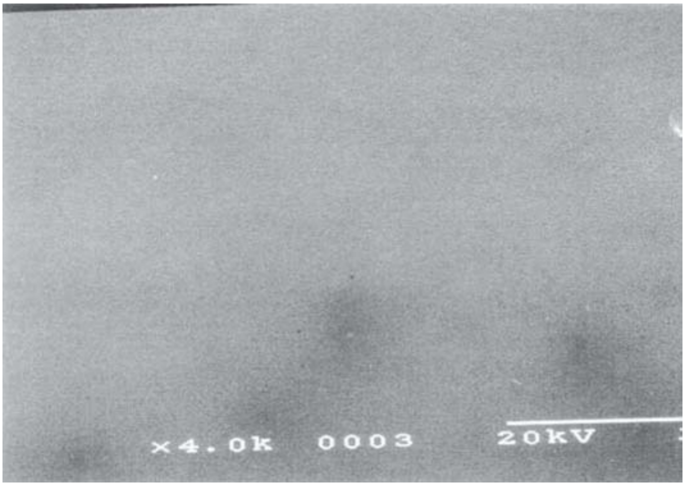

Figure 4.5 Smooth surface morphology of cellulose acetate membranes. Courtesy of Mark Wilf.

Cellulose acetate membranes were originally cast in tubular form (refer to Figure 1.3). These tubular membranes were used in the first commercial RO system at Coalinga, California in 1965. The membranes were developed and prepared at UCLA (see Chapter 1). The break for commercial viability came when as an appropriate swelling agent, formamide, was found for the cellulose acetate membrane during preparation.[17]

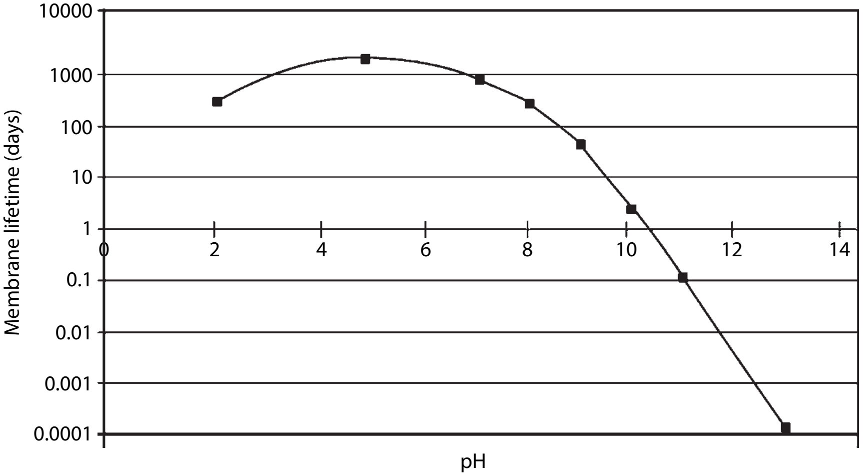

Figure 4.6 Lifetime of a CA membrane as a function of pH.

4.2.2 Polyamide and Composite Membranes

Polyamide membranes were developed in an effort to improve upon the performance of CA membranes. In particular, the higher operating pressure and relatively low salt rejection of CA membranes were holding back RO technology from becoming more commercially acceptable.

4.2.2.1 Linear Aromatic Polyamide Membranes

Aromatic polyamide membranes were developed by a few companies, including Toray, Monsanto and DuPont. DuPont developed a linear aromatic polyamide (nylon) membrane with pendant sulfonic acid groups, which they commercialized as the Permasep™ B-9 and B-10 membranes and as shown in Figure 4.7 (Permasep is a registered trademark of E. I. Du Pont De Nemours & Company, Inc. Wilmington, DE). Just as CA membranes were created out of a single polymer, Permasep membranes were also created out of single polymer rather than a composite (see below). These membranes exhibited higher rejection capabilities at higher flux and somewhat lower operating pressures than CA membranes. They were originally fabricated into hollow fine fiber membranes and used primarily for seawater and brackish water desalination and some specialty applications such a recovery of electric deposition paints (see Chapter 4.3.4 for more information about hollow fine fiber membranes). Dupont also developed a flat-sheet form of the basic, linear aramid polymer used to make the B-9 hollow fine fiber membranes. This asymmetric membrane was called the

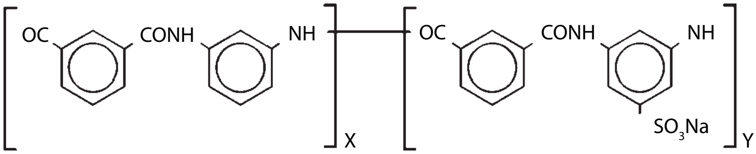

Figure 4.7 Aromatic polyamide membrane developed by DuPont.

B-15, and competed directly with CA membranes. DuPont withdrew their polyamide membranes from the market in 1991. DuPont sold their B15, A15, and X20 membranes under development to TriSep Corporation, who kept them for a few years before they licensed the FT30 chemistry from FilmTec.

4.2.2.2 Composite Polyamide Membranes

Composite membranes, sometimes called "thin film composite" or TFC® membranes are essentially a composite of two polymers cast upon a fabric support (TFC is a registered trademark of Koch Membrane Systems, Wilmington, MA). Today, cross-lined, fully aromatic polyamide membranes are the most popular RO membranes in use.[11] These membranes are generally formed using interfacial polymerization as shown in Figure 4.8 as developed by Cadotte. [2,19] A finely microporous substrate (typically polysulfone) is prepared using the Loeb-Sourirajan method described in Section 4.2.1.1, but without the annealing step such that the surface of the membrane does not "skin" over. The substrate is then exposed to monomers that are known to have high permeability to water but low permeability to salts, such as a polyamine. The amine in then immersed in a water-immiscible solvent containing a reactant, such as diacid chloride in hexane. The reactant and amine react at the interface of the water and organic solvent to form a highly-crosslinked thin film. This thin film formed on top of the substrate layer can be as thin as 400 to 1,000 Angstroms (0.04 to 0.1 microns). The substrate layer is typically 40–80 microns thick, while the overall thickness of the membrane, including the fabric backing, is about 1,500 to 2,000 microns thick.[18] By comparison, a sheet of paper varies from about 1,000 to 2,750 microns, depending on the weight. Figure 4.9 shows a cross section of a polyamide, composite membrane.

Figure 4.10 shows the chemical structure of a polyamide membrane, namely the Dow Water and Process Solutions-FilmTec™ FT30 (FilmTec is a trademark of Dow Chemical Company, Midland, MI). This membrane is created using poly(phenylenediamine trimesamide) and trimesoyl chloride (U.S. patent 4277344, July 7, 1981). This chemistry is used

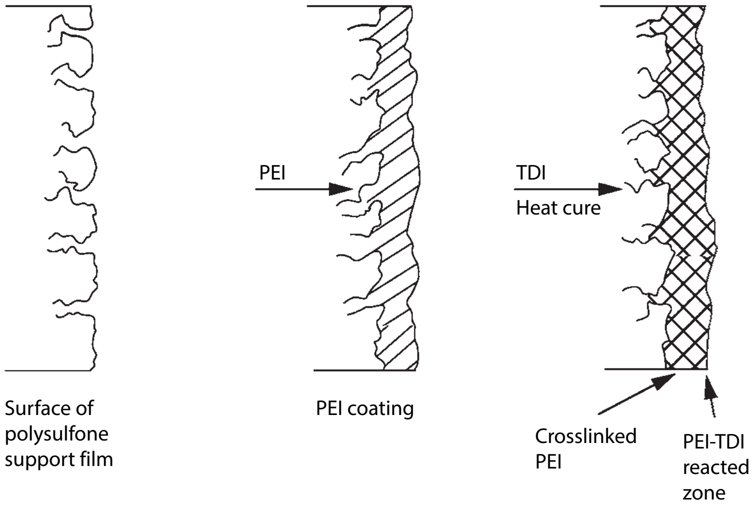

Figure 4.8 Interfacial polymerization, using polyethyleneimine (PEI) crosslinked with toluene diisocyanate (TDI) to from the NS-100 membrane as patented by Cadotte (U.S. Patent 4039440, August 2, 1977).

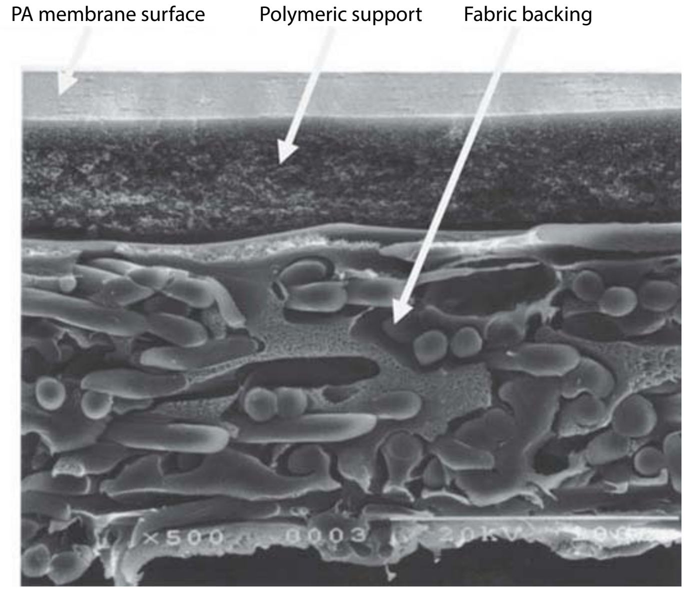

Figure 4.9 Cross-section of a polyamide composite RO membrane. Courtesy of Mark Wilf.

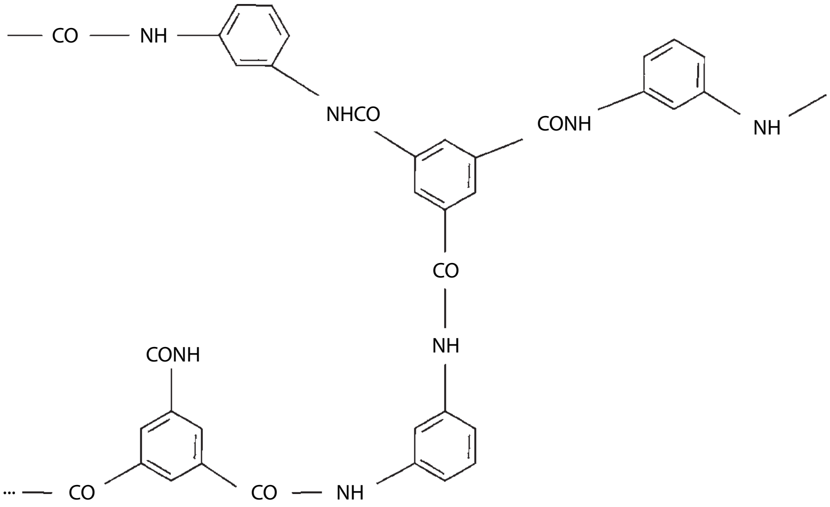

Figure 4.10 Chemical structure of the Dow Water Solutions FT30 polyamide composite RO membrane.

in some form by virtually all major RO membrane producers.[2] Unlike the CA membrane, the polyamide membrane has negatively-charged functional groups. This serves to attract cationic polymers, and other cationic species, which can permanently foul the membrane. Unlike the linear polyamide produced by DuPont, the FT-30 membrane is highly cross-linked, as shown in Figure 4.10.

Table 4.2 lists the predominant characteristics of polyamide, composite membranes.

- The surface morphology of a polyamide membrane is rough, allowing for many areas where foulants can be captured and held by the membrane. See Figure 4.11.
- As discussed above, the charge on the polyamide membrane is negative, thereby attracting cationic polymer should it break through the pretreatment equipment.
- Unlike CA membranes, polyamide membranes cannot tolerate free chlorine or any other oxidizers. Some manufacturers quote 200–1,000 ppm-hrs of exposure until the membrane rejection is lost.[21] This means after 200–1,000 hours of exposure to 1 ppm free chlorine, the membrane rejection will have approximately double the salt passage. Chlorine attack is faster at alkaline pH than at neutral or acidic pH.
- Polyamide membranes can tolerate higher operating temperatures than CA membranes can. Polyamide membranes

Table 4.2 Characteristics of polyamide composite RO membranes.

Property	Value for PA Membranes
Membrane Type	Homogenous asymmetric, thin-film composite
Salt Rejection (%)	~98+
Silica Rejection (%)	~96+
pH Range	2–12*
Feed Pressure (brackish membrane)	145–400 psi
Temperature Tolerence	Up to 45°C**
Surface Charge	Negative (anionic)
Chlorine Tolerance	<0.02 ppm
Biological growth	Causes membrane fouling
Fouling Tolerance	Fair
Surface Roughness	Rough

* Broader range possible for cleaning. Check with membrane manufacturer.

** Higher temperature possible for "heat sanitisable" membranes. Check with manufacturer.

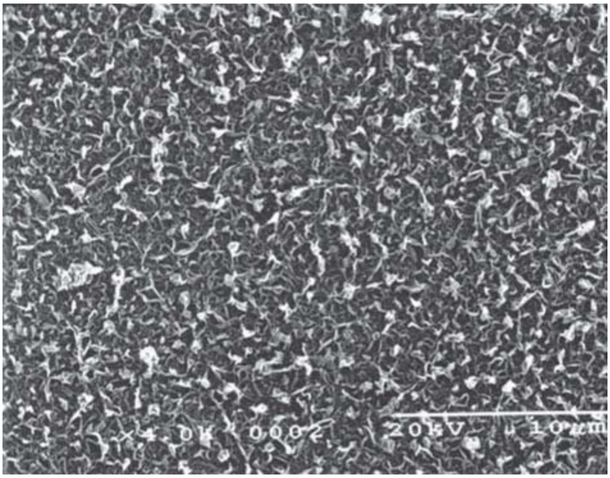

Figure 4.11 Rough surface morphology of polyamide composite RO membranes. Courtesy of Mark Wilf.

can be operated up to 45°F. However, the maximum temperature allowable is a function of pH. Table 4.3 lists maximum temperature as a function of pH. At temperatures greater than 45°C and pH greater than 11.5, the polyester support and polyamide layer themselves can be damaged.

Table 4.3: General temperature and pH relationship.

Temperature (°C)	pH
25	1 – 13
35	1 – 12
45	1 – 10.5

- Polyamide membranes have a much broader pH range over which the membranes can be operated compared to CA membranes. Operational pH can range from 2 to 11, but may vary slightly for different membranes and different manufacturers.
- Operating pressure for polyamide membranes is generally lower than for CA membranes, ranging from about 150 to 400 psig (1 – 2.8 MPa). This is because the polyamide membrane has a thinner rejecting layer and its microporous support layer is extremely porous offering minimal resistance to permeate flow.
- Passage of salts and silica is much lower for polyamide membranes than for CA membranes. Some membranes can achieve 99.7+% rejection on a standard test solution (2,000 ppm NaCl solution at 225 psi (1.6 MPa), 77°F (25°C), pH = 8, and 15% recovery). The salt passage at this rejection is only 0.3%, while the salt passage for high-rejection CA membranes at 98% rejection is 2%. So, the salt passage is nearly 7-fold lower for polyamide membranes than for CA membranes. See Chapter 3, Table 3.2 for complete rejection capabilities for polyamide membranes.
- The quintessential example of a polyamide membrane is the Dow FilmTec FT-30 membrane.

4.2.3 Improvements to Polyamide, Composite Membranes

There have been several improvements made to polyamide, composite membranes that have enhanced their performance. Perhaps the most important improvement has come through advanced manufacturing techniques, which have allowed for thinner membranes with few imperfections. Thinner membranes exhibit higher flux rates at the same operating pressure than their thicker counterparts.

Some membrane manufacturers now offer "low fouling" membranes (see Chapter 4.4.2.3). These membranes exhibit better resistance to fouling with suspended solids. This is accomplished in several ways. Greater crosslinking of the polymer chain eliminates "hanging" (non crossed-linked) function groups that can attract foulants.[12] Post-treatment of the membrane polymer, in a process sometimes called "sizing" is also used to minimize fouling of the membrane. Some manufacturers have created membranes with a lower surface charge and a smoother surface, both of which lead to minimal organic fouling.

Low-pressure membranes have also been developed. These membranes offer high flux at low temperatures and pressure albeit with some reduction in rejection (the permeability of polyamide membranes is a function of temperature, with lower water temperatures generally requiring higher operating pressures to maintain productivity—see Chapter 9.2). These low-pressure membranes allow for operation at low temperature at lower pressure than non low-pressure membranes.

4.2.4 Other Membrane Materials

Polyether urea (PEU) is another type of thin-film membrane. This membrane differs from polyamide membranes in the surface charge and morphology. Polyether urea membranes have a slightly positive charge to them. Further, the surface of a PEU membrane is smooth, similar to a CA membrane, thereby minimizing the potential for fouling. Hydranautics CPA membrane is an example of a polyamide/polyurea blend composite membrane.

4.3 Membrane Modules

Reverse osmosis membranes for industrial applications are typically modularized using configurations that pack a large amount of membrane area into a relatively small volume. This makes the RO system more economical to use in that the system requires a smaller footprint, and membranes can be replaced in smaller modules rather than system wide.

There are four basic forms for RO membrane modules: Plate and frame, tubular, spiral wound, and hollow fine fiber. These four configurations are summarized in Table 4.4 and discussed below. Additionally, some manufacturers have developed other module configurations that are briefly discussed in Chapter 4.3.5.

Table 4.4 Brief comparison of four basic RO membrane module configurations.[22]

Property	**Plate-and-Frame**	**Tubular**	**Spiral Wound**	**Hollow Fine Fiber**
Packing Density, ft^2/ft^3 (m^2/m^3)	45–150 (148–492)	6–120 (20–374)	150–380 (492–1247)	150–1,500 (492–4924)
Potential for Fouling	Moderate	Low	High	Very High
Ease of Cleaning	Good	Excellent	Poor	Poor
Relative Manufacturing Cost	High	High	Moderate	Low

4.3.1 Plate and Frame Modules

Plate and frame RO modules are typically used for specialty, high suspended solids applications and are not generally found in water purification facilities. These modules consist of flat sheets of membrane that are modularized into plates, typically two membranes placed back-to-back per plate. The plates are then stacked within a framework for support. There are patterned spacers materials that are used to keep the membranes from sticking to each other and providing open channels for the feed and permeate water to flow through. Figure 4.12 shows a typical plant-and-frame membrane module.

Characteristics of plate and frame modules are discussed below.

- These membrane modules are expensive per unit membrane area. This is because of a lot of hardware is used for relatively little membrane area.
- They are relatively easy to clean, hence their use in high suspended solids applications. Cleaning in-situ is possible but does not offer the best removal of foulants and scale. The best membrane cleaning involves removing the plates from the frame and hand-cleaning each individual flat sheet of membrane.
- These modules tend to foul because of the "dead" areas within the modules where cross-flow is not high enough to scour the surface free of debris.

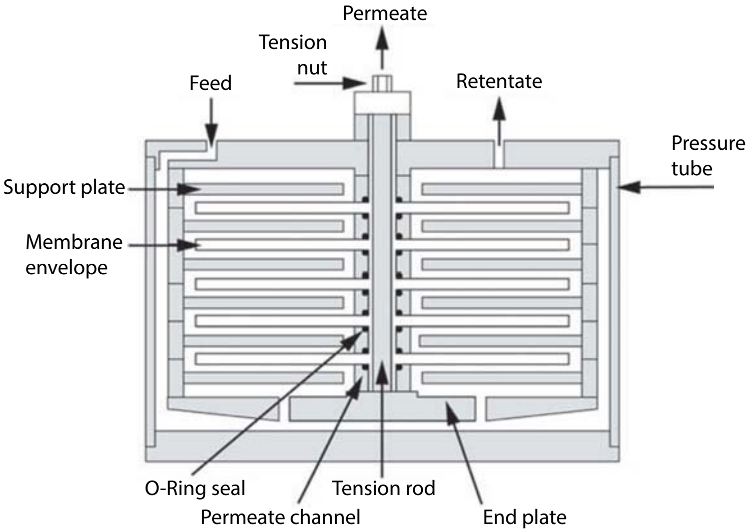

Figure 4.12 Plate-and-frame membrane module. *Courtesy of Elsevier.*

- These and tubular modules offer the low packing density (membrane area per unit volume). Typical packing density is less than about 45 – 150 ft^2/ft^3 for plate-and-frame modules.[22]

4.3.2 Tubular Modules

Tubular modules are also used for specialty, high-solids applications typically found in the food and biological processing industries. Tubular modules range from ½- to 1-inch (1.3–2.6 cm) in diameter with the membrane feed side on the inside of the tube. Packing densities run about 6–120 ft^2/ft^3.[22]

Figure 4.13 shows how a tubular module is assembled.[23] These modules essentially resemble a shell-and-tube heat exchanger, with the RO feed water on the tube side and RO permeate on the shell side. The membrane tubes are supported by perforated stainless steel tubes through which the permeate exits.

Characteristics of tubular membranes are described below.

- These modules are relatively expensive per unit membrane area. Again, the amount of hardware used per membrane unit area is significant.

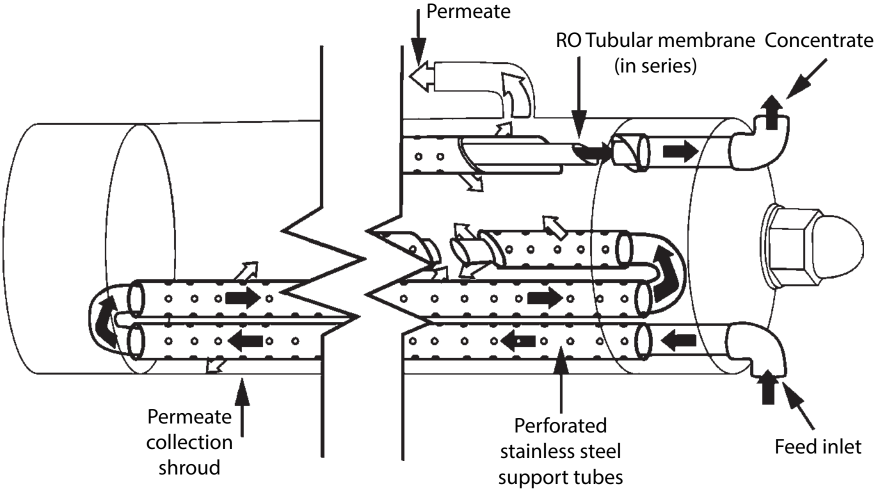

Figure 4.13 Tubular RO membrane module. Membrane tubes are placed in series in the housing.

- These modules are easy to clean. Typically, a sponge ball is shot down through the feed channel or tube to physically remove debris from the surface of the membrane. In most tubular applications, the membranes need to be cleaned on a daily basis. This is because the nature of the solution being treated by the membranes generally contains high concentrations of suspended solids and organics, which collect on the membrane. High feed flow rates, up to 20 gpm per tube, are necessary to achieve high cross-flow velocity and minimize rapid fouling.[11]

While some RO applications use tabular membrane modules, most tubular membrane modules are used for specialty microfiltration (MF) and ultrafiltration (UF) applications rather than RO due to the lower packing density of this type of module and because MF and UF typically treat higher-solids feed water (see Chapter 16.1).

4.3.3 Spiral Wound Modules

Spiral wound membrane modules are the most common type of module used for RO today. The major advantage of a spiral wound module is that the packing density is fairly high, about 150–380 ft^2/ft^3, higher then for

Figure 4.14 Eight-inch diameter spiral wound membrane module. *Courtesy of Dow Water and Process Solutions.*

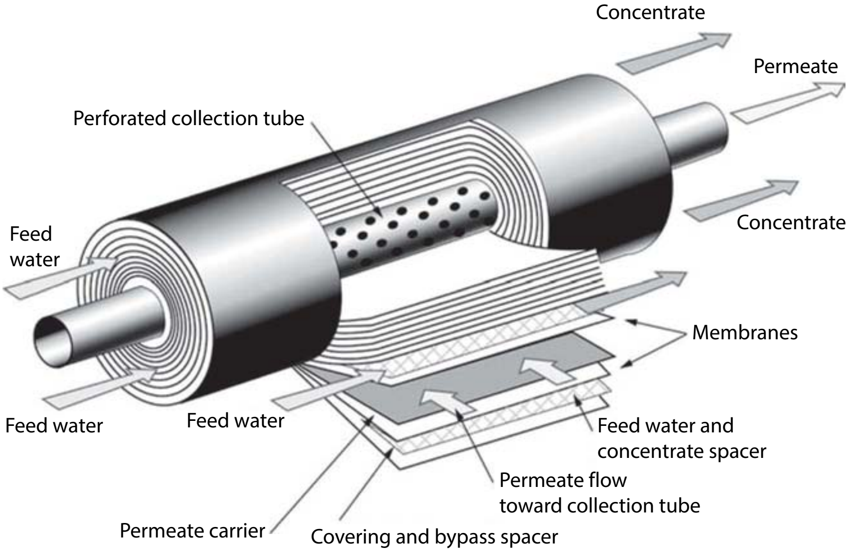

Figure 4.15 Deconstructed spiral-wound RO membrane module.

plate and frame or tubular modules.[21] Figure 4.14 shows an 8-inch diameter spiral wound membrane module.

Figure 4.15 shows deconstructed spiral wound module.[24] The spiral construction starts with two sheets of membrane placed back to back with a nylon tricot mesh spacer material in between. This tricot spacer provides the permeate channel for the membranes. These sheets of membrane and spacer are glued on 3 sides so that the permeate can only exit the spacer on one side. This set of membranes and spacer is called a "leaf." Leaves are then placed together with a low density polypropelene mesh spacer to provide the feed/reject channel for the membranes. The thickness of the mesh feed spacer can be adjusted from 28 mils to 34 mils to accommodate higher solids influent water (thicker feed spacers are more forgiving with respect to fouling with suspended solids than thinner spacers—see Chapter 4.4.2.3). The entire collection of leaves and mesh feed spacers are then wrapped around a perforated permeate collection tube so that the open side of the leaf is toward the perforated permeate tube (see Figure 4.16). Note that an 8-inch diameter membrane module has about 16 leaves, and each leaf is about 50 inches in length.

Influent that enters the spiral wound module does so tangentially to the membrane surface and the reject exits the module at the end opposite of the influent. Water that permeates the membrane does so perpendicularly to the surface of the membrane and is collected in the permeate spacer and then spirals into the perforated permeate tube. Permeate usually exits the module through only 1 end of the permeate tube (this simplifies piping).

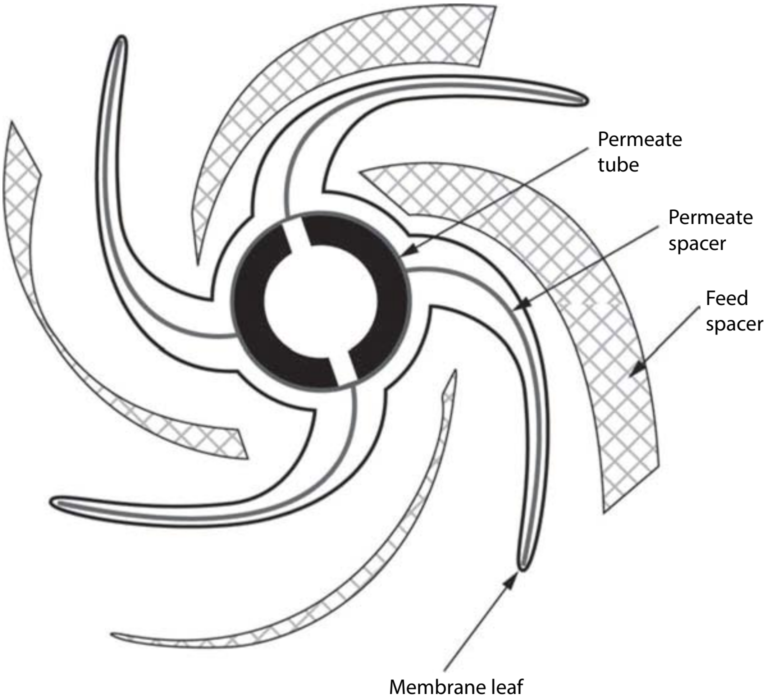

Figure 4.16 Spiral-wound RO membrane module showing leaves before winding.

Not shown in Figure 4.15 are the end caps to the membrane modules. End caps are placed on each end of a membrane module. There are various forms of end caps, also called anti-telescoping devices or ATDs. The purpose of the end caps or ATDs is to prevent the membranes and spacers from telescoping under high differential pressure drop (see Chapters 11.3.1.3 and 12.3). Telescoping occurs when the membranes and spacer

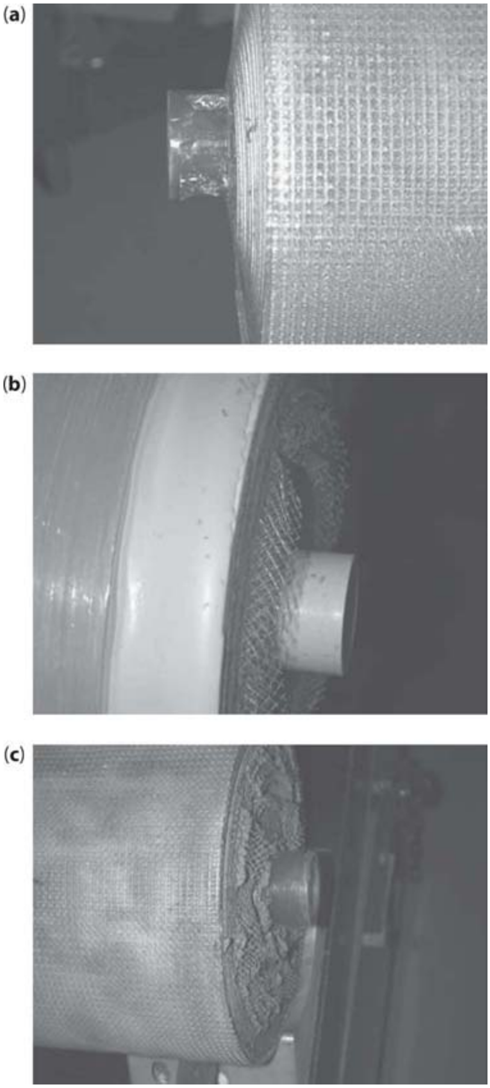

Figure 4.17 Uniform telescoping (a), protruding feed spacers (b), and protruding spacers and membranes (c).

devices slide past each other and form a cone-shaped end rather than a flush end (see Chapter 11.3.1.3 and Figures 14.9a and 14.9b for more information about telescoping). The result is often damaged membranes that leak feed water into the permeate. Despite the ATDs, if the pressure drop is high enough, telescoping can occur. Telescoping can be uniform, as shown in Figure 4.17a or it can involve protruding spacers (Figure 4.17b) and membranes (Figure 4.17c) (see also Figure 14.11a and b). Figure 4.18a and 4.18b show two different styles of ATDs.

Modules are connected to each other using an interconnector adaptor, as shown in Figure 4.19. The interconnector has O-rings at either end to ensure a tight seal with the module ATDs. These O-rings can roll upon installation into membrane modules, thereby allowing feed water to mingle with permeate. Great care should be exercised when loading membranes

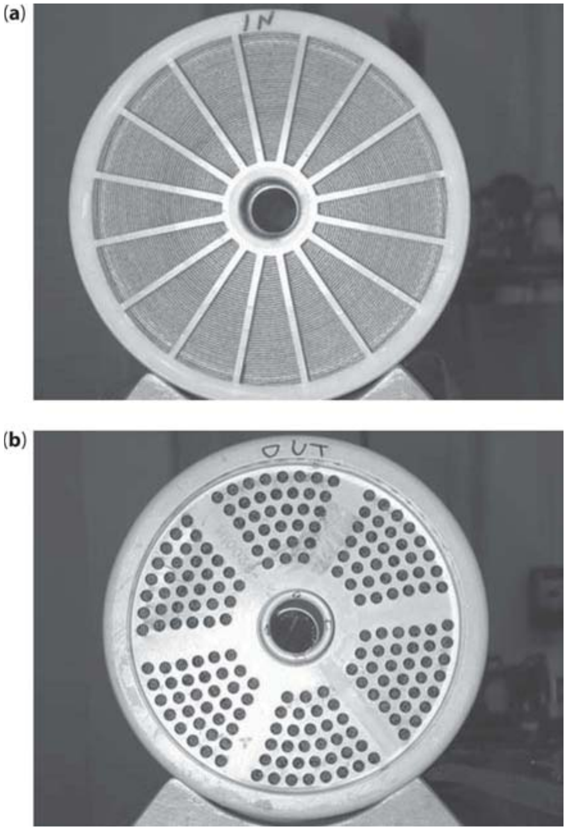

Figure 4.18 Two styles of standard anti-telescoping devices (ATDs).

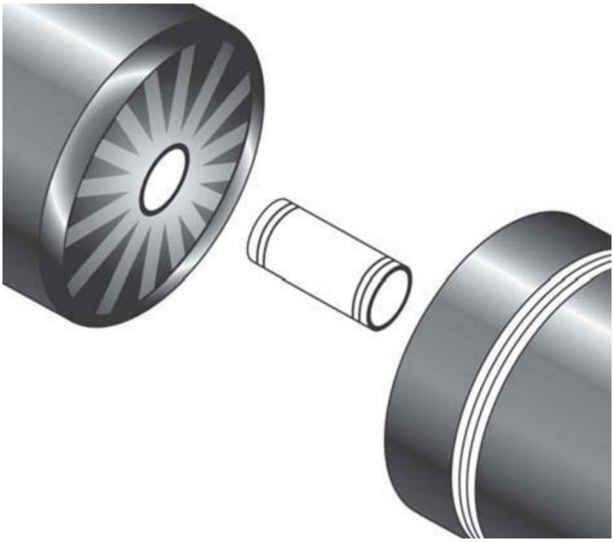

Figure 4.19 Placement of module interconnector adaptor for standard ATD end caps.

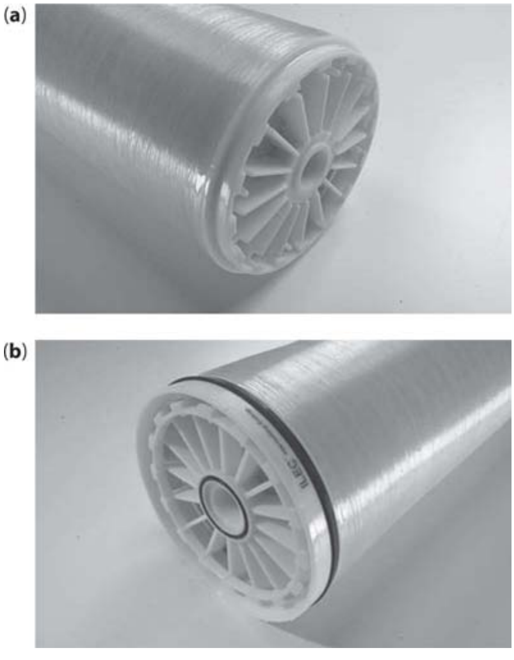

Figure 4.20 Dow Water Solutions-FilmTec *iLEC* ATDs with integral O-ring; these figures show the 2 ends that made together. *Courtesy of Dow Water and Process Solutions*.

to prevent rolling the O-rings. Lubrication can sometimes be helpful to minimize friction and rolling (see Chapter 6.3).

Figure 4.20 shows the ATDs from a new FilmTec *iLEC*™ (Interlocking End Cap) membrane module (*iLEC* is a trademark of The Dow Chemical Company, Midland, MI). The *iLEC* modules join modules by twisting them together the special *iLEC* end cans directly rather than relying on interconnector adaptors, the way standard modules are connected together. As shown in the figure, the ATD *iLEC* end cap has an integral O-ring that cannot be rolled or pinched during installation. Furthermore, water hammer cannot wear on the *iLEC* O-ring as it does on the O-rings on conventional interconnectors, which leads to fewer leaks of feed water into the permeate. In fact, Dow Water Solutions' RO design program, ROSA, projects higher-quality permeate from an *iLEC* membrane than from the same membrane material in a non-*iLEC* configuration.[25]

A strap wrench is used to hold one *iLEC* module in place as the other *iLEC* module is twisted either onto or off of the first module as illustrated in Figure 4.21.

Figure 4.21 Use of strap wrench with *iLEC* membranes. *Courtesy of Crossbow Water Technologies.*

Figure 4.22 shows the flow characteristics for standard ATDs and the *iLEC* ATD. The reduced diameter of internal couplers and vessel adapters for the standard ATDs accounts for more than 70 percent of the permeate-tube pressure drop in some systems.[26] The interlocking *iLEC* ATD design eliminates these restrictions, imposing less permeate backpressure, resulting in lower operating pressure requirements.

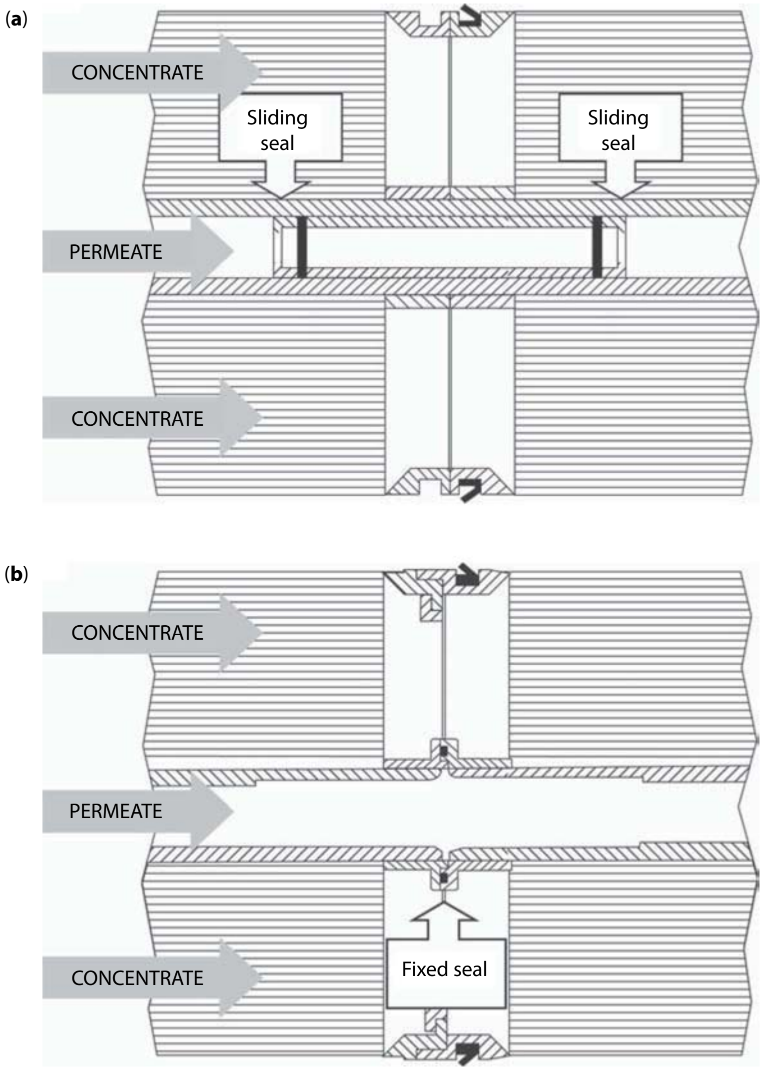

Figure 4.22 Flow characteristics through standard ADTs and *iLEC* ATDs. *Courtesy of Dow Water and Process Solutions.*

All spiral wound modules also have a brine seal (see Figures 4.23a and 4.23b). The brine seal is a U-cup-shaped rubber gasket material that is used to prevent feed water from passing by on the outside of the membrane module, thereby preventing feed water from bypassing the membranes (see Figure 4.24). The brine seal is located at the inlet end of the membrane module with the “U”facing the oncoming feed water.

The standard spiral wound module is 8 inches in diameter with a 40-inch length. There are also 4-inch and 18-inch diameter industrial membrane modules available (2.5-inch diameter modules are available for tap water or home-use applications). Koch Membrane Systems also makes a 60-inch long, 8-inch diameter module called a Magnum® and an 18-inch diameter by 60-inch length module called a MegaMagnum®

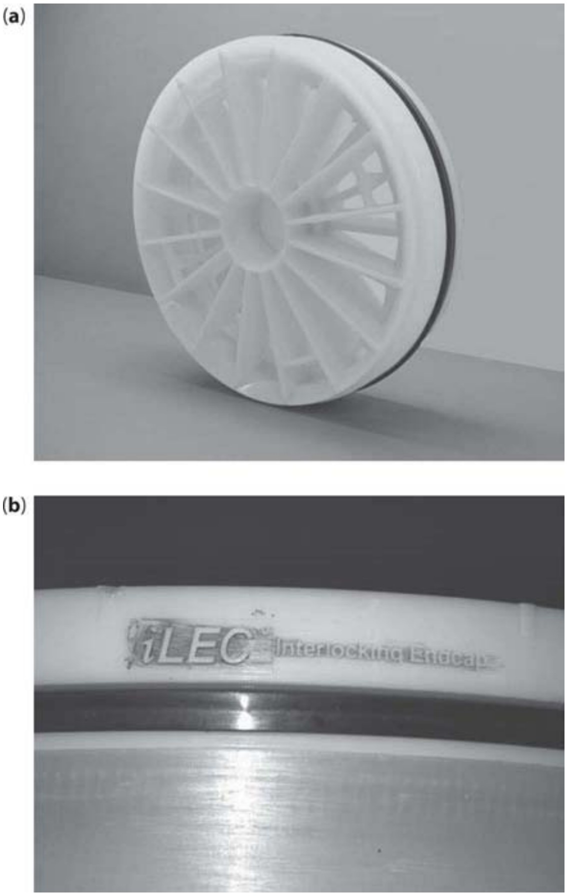

Figure 4.23 Two views of the “U cup” brine seal.

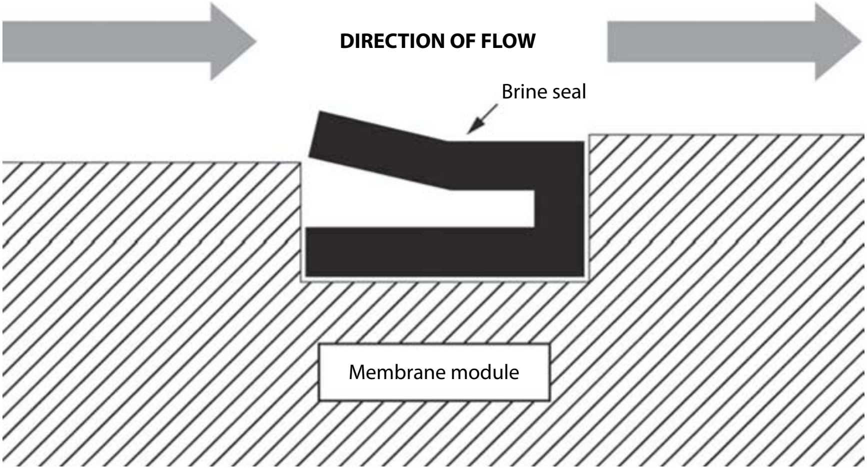

Figure 4.24 "U-cup" brine seal.

Figure 4.25 Two-train MegaMagnum RO system. Each train is capable of providing 1,390 gpm product flow when a 28-mil spacer is used, and 1,340 gpm when a 31-mil spacer is used. *Courtesy of Koch Membrane Systems.*

(Magnum and MegaMagnum are trademarks of Koch Membrane Systems, Inc., Wilmington, MA). Figure 4.25 shows two trains of MegaMagnum modules. Each train is capable of providing 1,390 gpm product flow when a 28-mil spacer is used, and 1,340 gpm when a 31-mil spacer is used (see Chapter 4.4.2.3 for details about different thicknesses of feed spacers).

Spiral wound modules are typically covered in fiberglass to protect the leaves (exceptions being sanitary modules, see Chapter 4.4.2.6). Because of the materials of construction (namely the adhesives used) and the potential for "annealing" the membrane, the maximum operating water temperature is limited to 45°C.[27]

Characteristics of spiral wound modules are described below.

- Spiral wound modules are moderately expensive due to the complexity and engineering involved. However, cost per unit membrane area is relatively low.
- Spiral wound modules can be difficult to clean. There are dead spaces within the module where high velocity cannot scour the surface of the membrane, and cleaning solution does not mix well to remove debris.
- Automated manufacturing of the membrane modules has allowed for more membrane area per unit volume and for higher-quality modules. This is because automation allows for more precise glue line application on the membrane leaves. A typical industrial module that is 8-inches in diameter and 40-inches long can hold up to 440 ft^2 of membrane area when automated manufacturing is employed (see Chapter 4.4.2.5).

Figure 4.26 Cut-away of a pressure vessel with a spiral-wound modules inside.

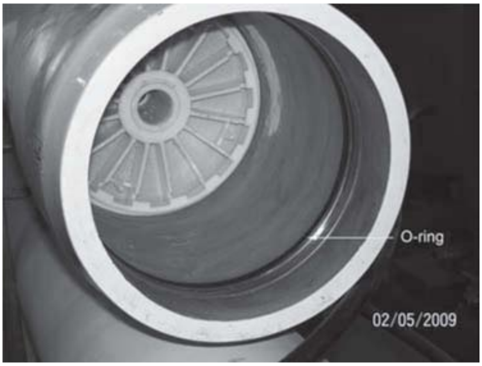

Figure 4.27 Spiral wound module in pressure vessel without pressure vessel end caps installed. The O-ring is used to seat the end cap in place. *Courtesy of Nalco-Crossbow LLC.*

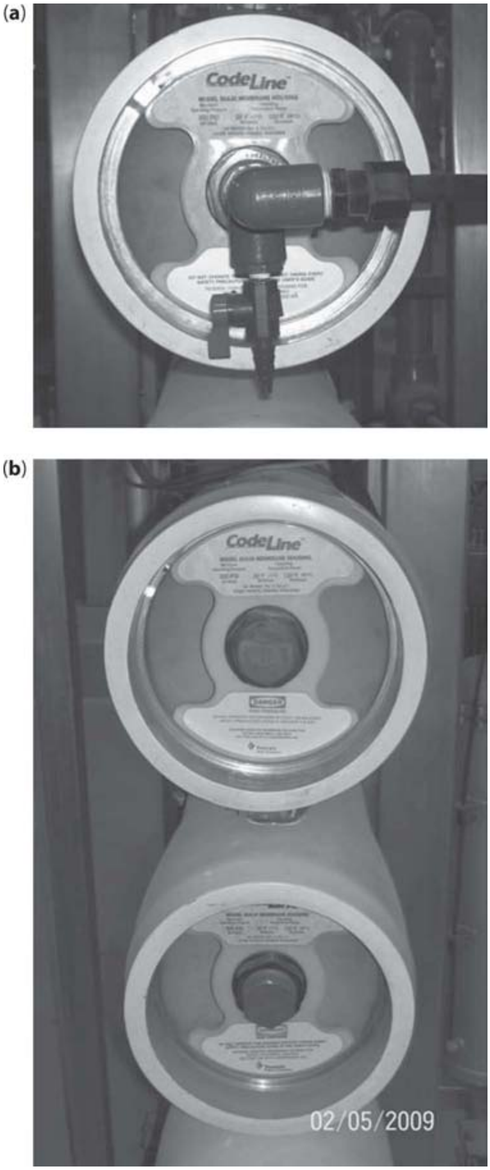

Figure 4.28 Pressure vessel end caps installed a) with permeate effluent piping and b) without permeate effluent piping (permeate exits the pressure vessel at one end only). *Courtesy of Nalco-Crossbow LLC.*

Unlike tubular or a plate- and frame modules, spiral wound modules are not themselves pressure vessels and therefore are placed in an external pressure vessel or "housing" for use. These pressure vessels are rated for the duty they will operate under, be it water softening, brackish water RO, or seawater RO (see Chapter 16.2 for membrane softening or "nanofiltration"). See Chapter 6.3 for a more detailed discussion about pressure vessels. Figure 4.26 shows a cut-away of a pressure vessel with a cut-away spiral-wound membrane module inside. Figure 4.27 shows the end of a spiral wound module in the pressure vessel without the pressure vessel end caps. Figures 4.28a and b show the pressure vessel end caps in place, one side with permeate effluent piping and one without this piping.

4.3.4 Hollow Fine Fiber Membrane Modules

Hollow fine fiber RO modules are membranes formed into very small-diameter tubes, with an outside diameter of about 85 microns and an inside diameter of about 42 microns.[15] The fibers resemble human hair and can be as flexible. See Figure "4.29" The membrane "skin" or thin film is

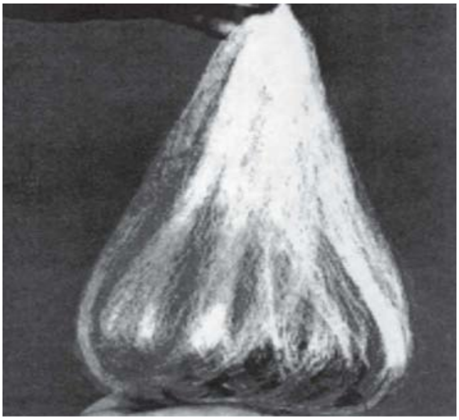

Figure 4.29 Hollow fine fiber RO membaranes.

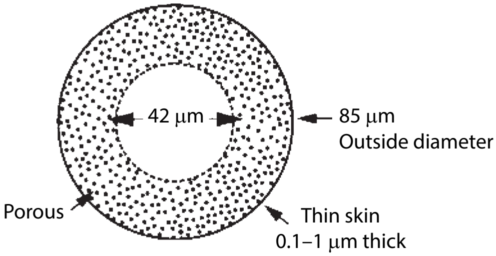

Figure 4.30 Cross section of a hollow fine fiber RO membrane.

on the outside of the fiber. This skin is about 0.1 to 1 micron thick.[15] Figure 4.30 shows a cross section of such a fiber.

Figure 4.31 shows a hollow fine fiber membrane module. The fibers are folded in half and the open end of each fiber is “potted” in epoxy “tube sheet,” while the folded end is potted in an epoxy, non-porous block. Feed to the module is outside in, which requires less strength on the part of the fiber than inside-out flow would. Also, the pressure drop on the outside of the fibers is much less than would be in the inside of the fiber (which is known as the lumen).

Characteristics of hollow fine fiber modules are described below.

- These modules are relatively inexpensive due to the high surface area per unit volume achievable with this configuration.
- These modules are relatively difficult to clean. There are several “dead” areas in and among the hollow fibers where flow does not reach well. Hence, higher-quality feed is typically required for these modules, such as seawater or brackish well water rather than high solids surface water.
- Packing density is extremely high, on the order of 150–1500 ft^2/ft^3.[22]

As discussed in Chapter 4.2.2.1, DuPont introduced linear aromatic polyamide membranes in hollow fine fiber form as the B-9 (brackish water) and B-10 (seawater) Permeators. These Permeators were available in 4-, 8- and 10-inch diameter models. The 4-, 8-, and 10- inch B-9 Permeators were capable of producing 4,200, 16,000, and 25,000 gallon per day of permeate, respectively, at 75% recovery (standard test conditions: 1,500 ppm NaCl at

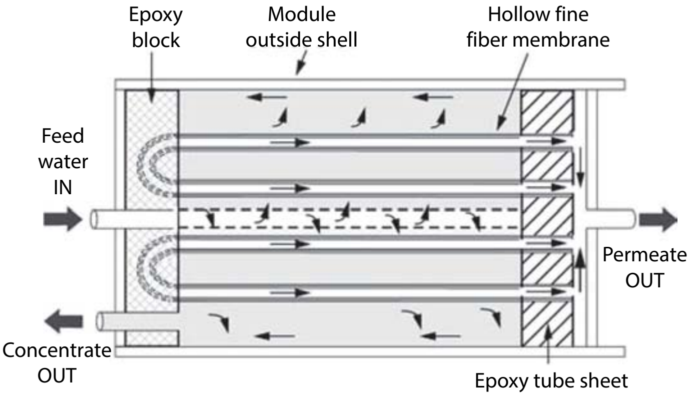

Figure 4.31 Simplified cross section of a hollow fine fiber RO membrane module.

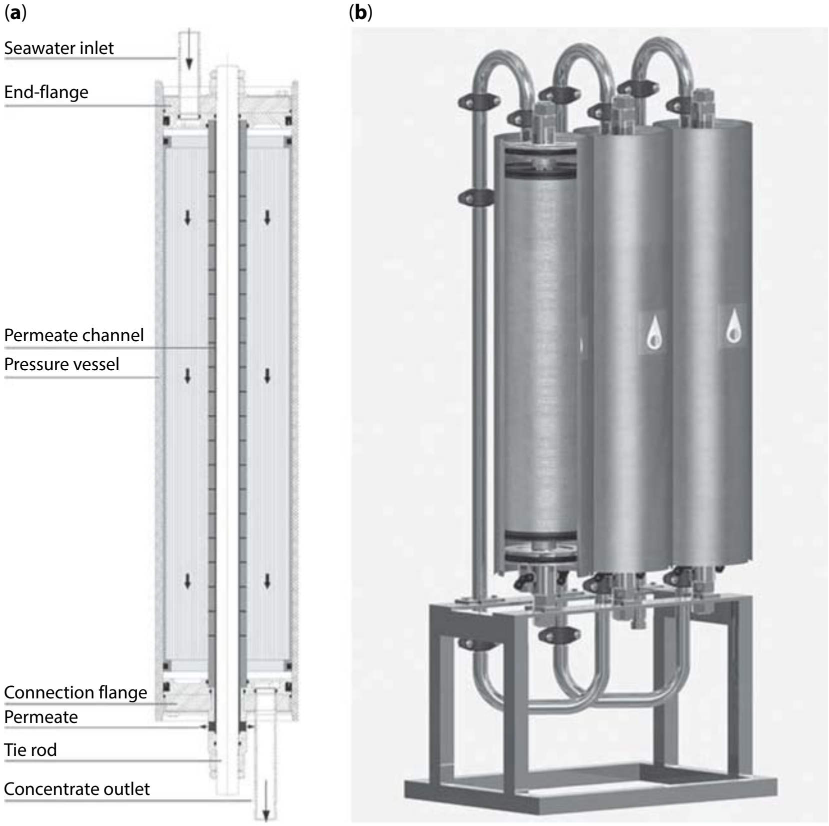

Figure 4.32 ROCHEM ST module, a modified spiral wound module, showing a) a cross-section and b) the module within a pressure vessel housing. *Courtesy ROCHEM Ultrafiltrations Systeme GmbH.*

400 psig and 25°C).[28] Permeators ranged from about 47 inches to 53 inches in length. DuPont discontinued these modules in 2001.

Currently, Toyobo markets the Hollosep® cellulose triacetate hollow fine fiber for RO applications (Hollosep is a registered trademark of Toyobo Company, Ltd, Osaka, Japan).

4.3.5 Other Module Configurations

Some manufacturers have developed unique module configurations that rely on novel methods of introducing turbulence into the feed stream as a method of minimizing concentration polarization. These configurations are generally suited to treat more difficult waters, such as waters containing high concentrations of suspended solids.

ULTURA has purchased ROCHEM RO-Wasserbehandlung GmbH (ROCHEM) who developed three module configurations which offer reduced rates of membrane fouling. This is achieved using open feed flow channels and/or short feed flow water paths followed by a 180-degree flow reversal that introduces turbulence. Figure 4.31a is a diagram of the ST module, which features an open feed channel that minimizes fouling and pretreatment requirements as well as allows for easy membrane cleaning. These modules are used to treat waters ranging from brackish and seawater to land-fill leachate. Figure 4.32b shows the ST module in its pressure vessel housing.

New Logic Research, Inc. has developed a vibrating membrane disk module using what is called the Vibratory Shear Enhanced Processing (VSEP) technique to minimizing depositions of suspended solids on the membrane surface. The VSEP membrane stack consists of parallel membrane disk "leaves" separated by gaskets. The stack vibrates at 53 Hz and the amplitude of oscillation is ¾ to 1-¼ inches thereby introducing turbulence into the pressurized feed. The VSEP system is used for a variety of applications including boiler feed water, RO reject, latex concentration, and acid mine drainage.

4.4 Commercially-Available Membranes

Several manufacturers currently supply RO membranes in the United States. Table 4.5 provides a brief description of several current US industrial RO membrane manufacturers.

Many varieties of spiral-wound, polyamide-composite membranes are available to suit different feed water conditions. Membranes discussed here include:

- Seawater membranes
- Brackish water membranes
- Brackish, low-energy membranes
- Brackish, low-differential pressure membranes
- Brackish, low-fouling membranes.

4.4.1 Seawater Water Membranes

Seawater membranes are used to treat high-salinity (35,000 to 50,000 ppm total dissolved solids (TDS)) feed waters. These membranes can operate at pressures up to 1,500 psi. Typical membrane test conditions are as follows:

Table 4.5 Current U.S. manufacturers of industrial RO membranes.

Manufacturer	Location	Brand	Membrane Material	Spiral Wound Configuration
Koch Membrane Systems, Inc.	Wilmington, MA, San Diego, CA	• Koch • Fluid Systems	PA, CA	Standard Sanitary
Toray Membrane USA	Poway, CA		PA	Standard Sanitary
Dow Water & Process Solutions	Edina, MN	• FilmTec	PA	Standard Sanitary
Hydranautics	Oceanside, CA		PA	Standard Sanitary
TriSep Corporation	Goleta, CA		PA, CA, LAPA	Standard Sanitary Custom
GE Water & Process Technologies	Vista CA, Minnetonka, MN	• Desal • Osmonics	PA, CA	Standard Sanitary
Ultura	Oceanside, OR	• SEPRO	Proprietary	Standard*
Osmosis Technology, Inc.	Buena Park, CA	• Osmotik	PA, CA	Standard Custom
TCK Membrane America, Inc.	Anaheim, CA	• CSM	PA, Polypiperatine, Polyvinylidene difluoride (PVDF)	Standard Sanitary Custom
Applied membranes INC	Vista, CA	• AMI	PA, CA	Standard**
LG NanoH_2O	EL Segundo, CA		TFN (Thin film Nano composite)	Standard

PA = Polyamide composite

CA = Cellulose acetate or cellulose triacetate

LAPA = Linear aromatic polyamide (developed by DuPont)

* also available in flat sheets

** 4" Diameter modules or smaller

- Feed water concentration: 32,000 ppm NaCl (sodium chloride)
- Operating pressure: 800 psi
- Temperature: 77°F
- Feed water pH: 6.5–8
- Recovery per module: 8–10%

Test conditions are important to take note of as these are the conditions under which rated performance is based. Operating under different conditions will result in performance that differs from the rated performance. (Chapter 9 discusses the effect of varying operating conditions on the performance of RO membranes). Notice that there is not one uniform test condition to which all membrane manufacturers adhere. Therefore, because of the difference in pH and recovery under such membranes are tested, the rated performance of seawater membranes from different manufacturers cannot be directly compared.

Within the classification of seawater membranes, there are subsets of membrane that are rated for different performance. For example, Koch Membrane Systems offers a standard high rejection seawater membrane module plus a high-flow seawater element seawater membrane module. Table 4.6 lists the productivity and rejection for three seawater membrane types. Other membrane suppliers offer similar variety in seawater membranes.

4.4.2 Brackish Water Membranes

Brackish water membranes are designed to treat lower-salinity feed waters, up to about 4,000 to 5,000 ppm (TDS). Maximum operating pressure for brackish water membranes is typically 600 psi. These membranes are usually tested at the following conditions:

- Feed water concentration: 1,500 to 2,000 ppm NaCl (low energy membranes are tested at 500–2,000 ppm NaCl)
- Operating pressure: 225 psi (low energy membranes are tested at 100–150 psi)
- Temperature: 77°F
- Feed water pH: 6.5–7
- Recovery per single module: 15%

As with seawater membranes, there is no one uniform test condition for all brackish water membranes of the same type. Thus, a direct comparison between manufacturers requires a close look at the test conditions.

Table 4.6 Comparison of seawater membranes.[28]

Manufacture	**Seawater Membrane**	**Permeate Flow* gpd**	**Rejection* (%)**
HYDRANAUTICS	SWC5 MAX	9,900	99.8
KOCH	8040-SW-400	7,200	99.75
L.G. NanoH_2O**	QFX SW 400R	9,000	99.85

* for 400 ft^2 membrane module

** Nano composite membrane

Brackish water membranes also come in various types with different performance ratings. These specific types are discussed below.

4.4.2.1 Low-Energy Membranes

Low energy membranes are designed to reduce the energy required to generate permeate. In most cases, these membranes exhibit similar productivity but at lower operating pressures than standard RO membranes. Lower operating pressure is an advantage when energy costs are high or when the feed water temperature is low (lower water temperature reduces the water throughput if pressure is held constant, as discussed in Chapter 9.2). A limitation of the low-pressure membrane is that rejection is lower than the standard brackish water membrane. In some cases the rejection drops enough to double the salt passage as compared to standard brackish water membranes.

4.4.2.2 High-Rejection Membranes

High-rejection brackish water membranes offer several tenths of a percent higher rejection than standard brackish water membranes. While the standard rejection is typically about 99.0% to 99.5%, high rejection membranes can go as high as 99.7% rejection (some newer membranes now claim 99.75% rejection). Going from 99.5% rejection (0.5% salt passage) to 99.7% rejection (0.3% salt passage) decreases the salt passage by 67%. This can be critical in high-purity applications.

4.4.2.3 Low-Fouling Membranes

Low-fouling membranes are available from some manufacturers. These membranes can be modified is several ways to reduce the potential for fouling them with contaminants in the feed water. Chapter 4.2.3 describes these modifications.

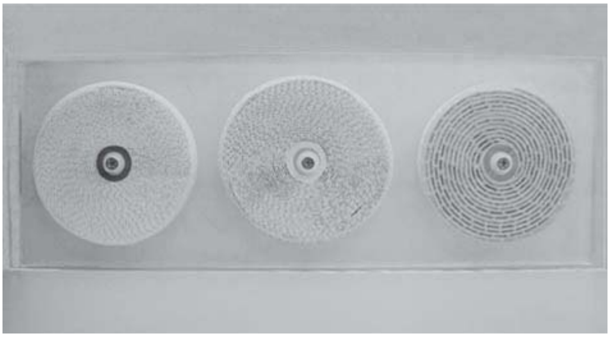

Figure 4.33 Cross section of 4-inch diameter membrane modules with feed spacers of various thicknesses, ranging from 28-mils, to 34-mils, to 50 mils-thick when viewed left to right.

An example of a low-fouling membrane is the Hydranautics low-fouling composite LFC3-LD membrane (see Chapter 4.4.2.4 for a description of the LD (low-differential-pressure) membrane). This membrane exhibits the same throughput as the standard high-rejection Hydranautics CPA3 membrane and has slightly higher rejection.[30] The difference is in the surface charge of the membrane. The standard brackish water membrane has a negative charge while the low-fouling membrane has a neutral surface charge. This will minimize fouling with cationic polymers and surfactants as well as other positively-charged species that will foul a negatively-charged membrane. Additionally, the membrane module is constructed using 31-mil feed spacers rather than the standard 28-mil spacer. Thicker feed spacers are more forgiving to fouling with suspended solids than thinner spacers. Figure 4.33 shows the cross section of 4-inch diameter membrane modules with feed spacers of various thicknesses. It is easy to see how the thinner the feed spacer, the more prone to fouling the corresponding module will be.

4.4.2.4 Low-Differential-Pressure Membrane Modules

Low-differential-pressure membrane modules can be considered a subset of low-fouling membranes. These low-differential-pressure membrane modules typically have a thicker feed spacer. Instead of the standard 28-mil thick spacer, these low-differential-pressure membranes have 31- or 34-mil thick spacers. In addition, some work on modifying the shape of the channels in the spacers has lead to lower pressure drop performance. There is less resistance to flow through the feed channels, resulting in lower pressure drops through the membrane modules. Furthermore, the feed channels will not plug as quickly with suspended solids, foulants, or scale.

Examples of low-differential-pressure membrane modules are the FilmTec BW30-400-34i (with a 34-mil feed spacer) and the Hydranautics CPA3-LD (with a 31-mil feed spacer).

4.4.2.5 High-Productivity Membrane Modules

High-productivity membrane modules contain more membrane area that standard brackish water membranes while fitting into the same size membrane module. Higher membrane area is achieved using more sophisticated module-assembly techniques. Careful positioning of the glue lines on the membrane leaves (see Chapter 4.3.3) and automated module assembly are two improvements in module assembly that have allowed for the inclusion of more membrane area. While a standard brackish water membrane typically has about 365 ft^2 of membrane area, high-productivity membrane modules may have 400 ft^2 or up to 440 ft^2 of membrane area. Productivity out of the membrane module is higher because of the additional membrane area. In general, a 400 ft^2 membrane module produces about 10% more permeate than a 365 ft^2 membrane module produces under similar operating conditions.

High productivity can also be achieved with brief, measured exposure to free chlorine (see Chapter 8.2.1.1). Membrane manufacturers will sometimes treat their membranes with a very short exposure to free chlorine. This results in membranes that exhibit higher flux with no change in salt rejection. Longer exposure to free chlorine will result in a permanent loss of salt rejection. Note that exposure to free chlorine by the end user is a violation of the membrane warranty and should not be attempted to increase flux.

4.4.2.6 Other Membrane/Module Types

There are other types of membrane and modules available. These types spring from applications where the need is different than standard membranes can handle. Two common applications are boron rejection and sanitary processing.

- Boron rejection membranes: exhibit up to 90+% rejection of boron, while standard membranes reject about 50–70%. [20,29] These membranes are typically used for seawater applications where boron removal is a concern. Boron is difficult to remove with membranes because boron, which exists as boric acid, is not ionized a typical seawater pH, 7.0–8.0, whereas the pK^a of boric acid is 9.14–9.25.[20]

Figure 4.34 Sanitary or "full fit" spiral wound membrane module. *Courtesy of Dow Water Solutions.*

- Sanitary membrane modules: these modules have a net outer wrap rather than the standard fiberglass wrap and are sometimes referred to as "full fit" modules (see Figure 4.34). The modules are designed with a bypass (no brine seal) to eliminate stagnant or "dead" areas within the module where bacteria can grow and foulants can accumulate; typically 20% of the feed flow by-passes the membrane modules.[25] Additionally, the modules are they also operated at higher vessel flows (higher cross-flow velocities) and outer module velocities to keep the sheet side of the module clean higher differential pressures to keep them clean. The trade off is that these membranes are less efficient that conventional spiral-wound RO modules. Some sanitary membrane modules can be sanitized for short periods of time at temperatures up to 85°C (recall that the maximum temperature for a standard spiral wound module is 45°C). This is because of changes in the materials of construction, including the permeate spacer. Standard permeate spacers soften as they are heated; those used for sanitary applications do not. Note that the RO membrane materials are the same and they anneal under heat, making them denser and more difficult to force water through them.[31] Thus, sanitary membrane modules last about only about one to two years on average, whereas standard RO modules last up to three to five years in use.

Sanitary applications include dairy, pharmaceutical, and biological processing. Note that pressure vessels are usually stainless steel for these applications.

- High temperature membranes: most standard, high-temperature RO membranes are basically the same as sanitary membranes. The majority of high-temperature membrane modules come with a "net" out wrap (rather than fiberglass) and operate with a bypass (no brine seal) just as the sanitary membrane modules operate.

  It is the materials of construction of the module rather than the membrane that allow for the high-temperature operation; high-temperature membrane modules use "standard" RO membranes. Standard materials of construction, such as adhesives, will soften up at high temperature, allowing for the possibility of leaking feed water into permeate.[32] Further, the nylon tricot permeate carriers have a tendency to also "soften" such that the membrane and carrier meld together decreasing productivity.[32] Many manufacturers use proprietary permeate carriers and adhesives that are tolerant to the higher temperature/pressure combination. Outer wraps can be made of polypropylene with polysulfone permeate tubes, anti-telescoping devices and interconnectors to handle the high-temperature conditions. Pressure vessels are typically stainless steel.

  High-temperature membranes allow for continuous operation at temperatures upwards of 45°C, which is the maximum for standard membrane modules. For example, Dow Filmtec high-temperature membrane modules allow for continuous operation of up to 50°C at pH less than 10, and 35°C at pH greater than 10;[33] Toray membranes have similar restrictions for continuous operation at pH greater than 10.[34] GE Duratherm® SDT membrane modules can operate continuously up to 50°C at 600 psi and 70°C at 400 psi.[35] TriSep has membrane modules that can operate up to 80°C on a continuous basis.[32]

  Some membranes can be "sanitized" at temperatures up to 90°C (at pressures less than 40 psig and pressure drops of less than 2 psi per module); it is advised that the membranes be heated and cooled slowly to prevent thermal shock. Cleaning is generally recommended at up to 50°C to prevent hydrolysis due to the combination of high temperature and pH extremes normally used during cleaning. And, just as noted above under the sanitary membrane discussion, repeated high temperature sanitation can lead to annealing of the membrane (essentially a thickening of the membrane), where flow is lost and salt rejection increases. Both Toray and GE indicate as much on the specification sheets.[34,35] Literature results of tests on the GE Duratherm STD Series high temperature membranes indicates that 30% to 50% of flow was lost before performance stabilized after repeated sanitation cycles, and that 90% of the flow loss came after the first sanitation cycle.[35] The recommendation is to pilot test the membranes to determine actual flow loss and salt rejection increase. Further, the salt rejection of high-temperature membrane modules decreases with increasing temperature, just as it does for standard membrane modules, since standard membranes used in high-temperature modules.[32] New-membrane salt rejection for the GE Duratherm membranes decreases from just over 99% at 10°C to just over 96% at 70°C.[35] Again, pilot testing is advised to determine performance under actual conditions.

Life of high-temperature membranes is a direct function of the number of cleaning cycles and the degree and speed of feed water temperature swings.[32] Because the membrane itself is virtually identical to those used in standard membrane modules, the theoretical life is the same, 3 years. Should there be many cleaning episodes where the membranes are exposed to pH extremes at high (50°C) temperature, the lifetime can be shorter.[32] Also, membranes prefer to operate at steady temperature, so temperature swings and the speed with which the temperature changes also affects life[32]; if the temperature must vary, it is best to affect the change over a longer rather than shorter period of time.[35]

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5

Basic Flow Patterns

Knowledge of the flow patterns for RO systems is fundamental to the understanding of how an RO system functions. Arrays, passes, recycle, and multiple trains are terms used to describe an RO system that are discussed in this chapter.

5.1 Arrays

Focusing on spiral wound membrane modules as the most common type of membrane modules used in industry today, an RO array or "skid" or "train" consists of a number of pressure vessels arranged in specific patterns. Figure 5.1 shows an array of 3 pressure vessels. The pressure vessels are arranged into 2 sets, with 2 pressure vessels in parallel followed by 1 single pressure vessel. The 2 sets of pressure vessels are in series. Each set of pressure vessels in parallel (even if there is only 1 vessel) is called a *STAGE*.

In theory, influent water to the RO system is split evenly among the pressure vessels in the first stage. Permeate from each pressure vessel in the first stage is combined and collected in a common header. The reject from

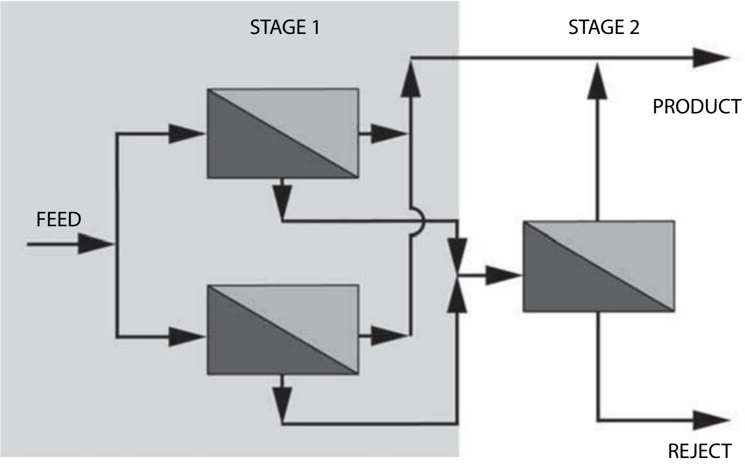


Figure 5.1 Two-by-one (2:1), 2-stage array with 2 pressure vessels in the first stage and 1 pressure vessel in the second stage.

the first stage becomes the influent to the second stage. Permeate from the pressure vessels in the second stage is collected and combined with permeate from the first stage to become the overall permeate from the system. The reject from the second stage becomes the reject for the entire system.

The RO system shown in Figure 5.1 is called a 2-stage array, or a 2:1 array, indicating that there are 2 stages (by the 2 numbers) and the first stage has 2 pressure vessels and the second stage has 1 pressure vessel. A 10:5 array would have 2 stages, the first stage would have 10 pressure vessels while the second stage would have 5 pressure vessels. A 4:2:1 array would have 3 stages, with 4 pressure vessels in the first stage, 2 pressure vessels in the second stage, and 1 pressure vessel in the third stage.

This type of array, the (n):(n/2):(n/4) is called a "taper" or "christmas tree" configuration. The reason for the tapered design involves maintaining cross-flow velocity. The number of pressure vessels required for each stage is determined by the velocity or influent flow rate to that stage. To maintain good cross-flow velocity (Chapter 2.4), influent flow rates per pressure vessel need to be about 40–60 gpm, while the reject flow rate needs to be greater than about 16 gpm, for 8-inch diameter membrane modules (see Chapter 9.1 and Tables 9.2 and 9.3 more more detailed discussions). Thus, an influent flow of 100 gpm would require 2 pressure vessels in the first stage (see Figure 5.2). Ideally, the first stage recovers about 50% of the influent water (assumes six 8-inch diameter membrane modules in series), so that 50 gpm would be permeate from the first stage and 50 gpm

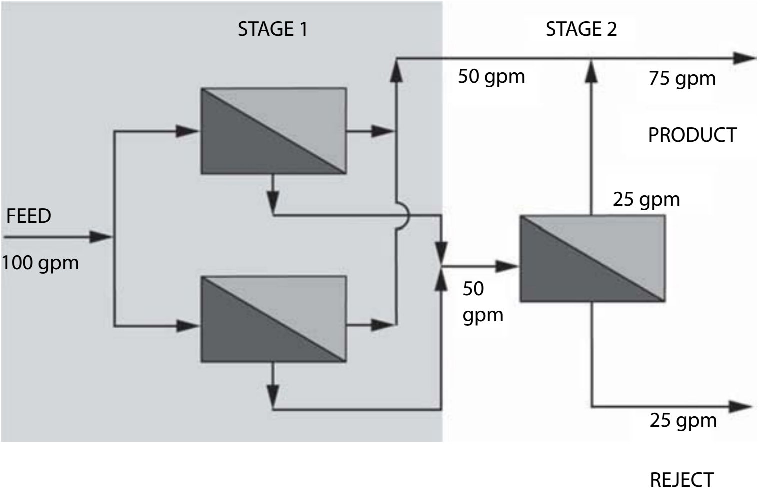


Figure 5.2 Approximate flow is distribution through a 2:1 array.

would be reject. The reject is sent on to the second stage as its feed. Since the flow now is only 50 gpm to the second stage, only 1 pressure vessel is required. (If two pressure vessels were used, the feed flow rate per pressure vessel would drop to 25 gpm each, and the eventual reject stream would have a flow rate too low to maintain good feed cross-flow velocity.) The reject from the single pressure vessel in the second stage would be 25 gpm, well above the 16-gpm minimum concentrate flow rate per pressure vessel. Permeate from the second stage would be about 25 gpm, and adding that to the 50-gpm permeate from the first stage makes the overall recovery of the system 75 gpm or 75%.

Overall recovery from a 2-stage RO is typically about 75%. Higher recoveries (80%) can be reached provided the influent water is relatively free of suspended solids and scale formers. Recoveries higher than about 80% generally require more than 2 stages (again, assuming six, 8-inch diameter modules per pressure vessel).

Figure 5.3 shows how concentration changes through an RO system (assuming 50% recovery per stage, as in Figure 5.2). In this example, assume a feed concentration of 100 ppm total dissolved solids (TDS) and a membrane rejection of 98% TDS (2% salt passage). The permeate concentration out of the first stage would be 2% of 100 ppm or 2 ppm. To calculate the reject concentration, use the concentration factor. Recall from Table 3.1 concentration factor as a function of recovery. At 50% recovery after the first stage, the concentration factor is two. Thus, the reject concentration after the first stage is approximately 2 times 100 ppm or 200 ppm. The feed to the second stage is then 200 ppm. The salt passage is still 2%, but now the concentration is double the original feed, so the permeate from the second stage is double the first stage permeate concentration, or 4 ppm. The recovery over the second stage is 50%, so the concentration factor is again two. This makes the overall reject concentration approximately 400 ppm. To calculate the permeate concentration, take 50 gpm permeate flow from the first pass and multiply by it's concentration of 2 ppm. Add this to the result of multiplying the second stage flow of 25 gpm by the second stage concentration of 4 ppm. Divide by the total permeate flow of 75 gpm and the result is 2.67 ppm. Although the individual membrane rejection is 98%, the overall *system* rejection is 97.3%. This is because the 98% rejection shown in a specification sheet in a membrane refers to an individual membrane module under test conditions (typically 10-15% recovery for brackish water membranes—see Chapter 4.4.2). Figure 5.4 shows in greater detail how the concentration changes per module through a single stage of an RO system. The data in Figure 5.4 assumes 11% recovery per module at 98% salt rejection.

It is interesting to note that higher recovery, while reducing the amount of wastewater generated, also reduced the quality of the permeate. In the previous example, Figure 5.2 shows that if a 50% recovery, single-stage system were used, the reject flow would be 50 gpm, whereas the reject flow at 7% recovery would be only 25 gpm. As shown in Figure 5.3, the

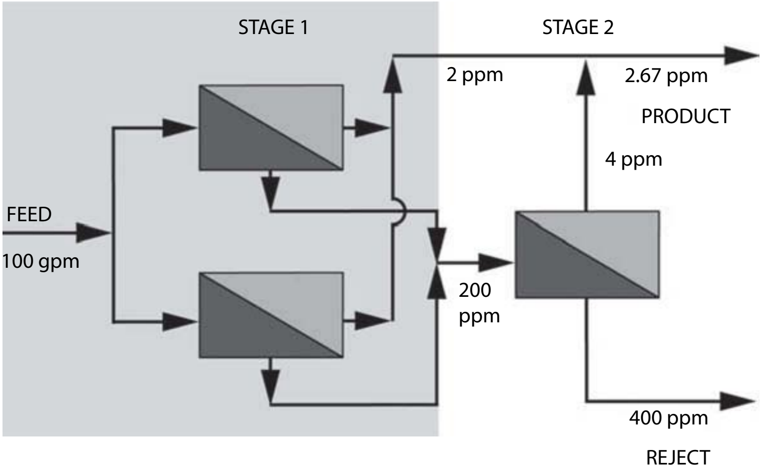


Figure 5.3 Approximate concentration changes through an RO system assuming 98% rejection by the membranes.

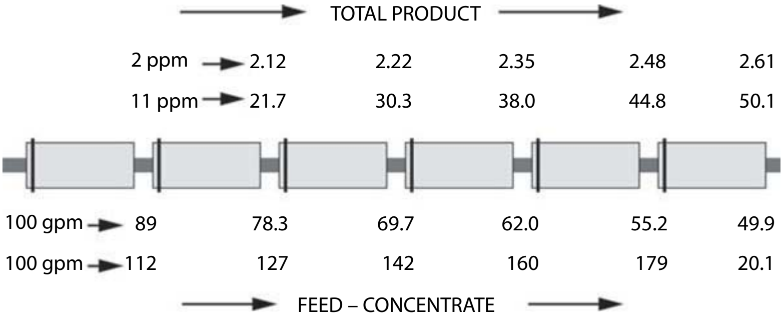


Figure 5.4 Module-by-module concentration and flow rate changes over a single RO stage. Assumes 11% recovery per module and 98% solute rejection.

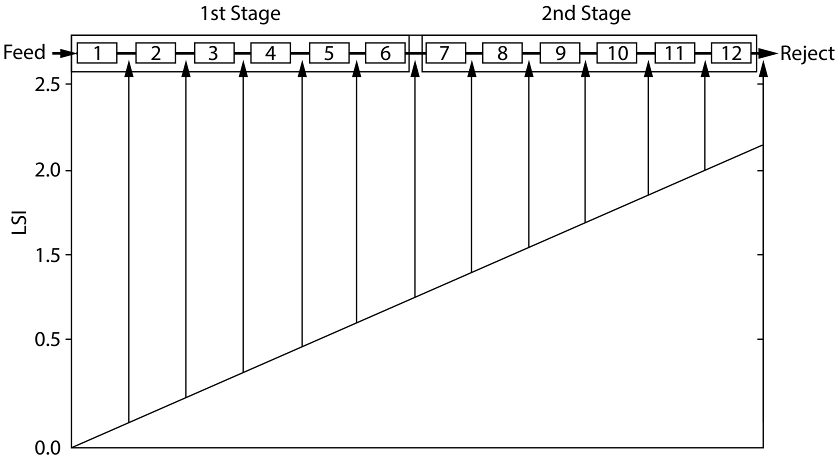


Figure 5.5 Langeleir Saturation Index (LSI) as a function of module position and recovery for a two-stage, 75%-recovery RO system. Assumes feed water conditions: 200 ppm calcium, 150 ppm bicarbonate, and pH = 7.0.

concentration of permeate at 50% recovery would be 2 ppm, while the concentration at 75% recovery would be 2.67 ppm. Hence, there is a tradeoff between high recovery and high product quality for every RO system.

In addition to observing how the flow and concentration change over a single RO stage, it is also interesting to see how the Langelier Saturation Index (LSI) changes with position in two-stage, 75%-recovery RO system (See Chapter 3.9 for a discussion about LSI). Figure 5.5 shows how concentrate LSI increases with increasing recovery through an RO system at

75% total recovery. The LSI increases linearly from zero with no recovery to greater than +2 at 75% recovery. Recall from Chapter 3.11 that if the LSI is greater than 0, the potential exists for scaling the membranes. Antiscalants, and in some cases acid feed, is required to minimize this potential (see Chapter 8.2.4).

A two- or three-stage RO *system* will usually remove about 96% to 98% of the total dissolved solids (TDS) in the water. The effluent water quality is generally high enough to send to low- to medium-pressure boilers without additional polishing. However, each application and feed water is different, and, therefore, water sampling and design projections should be conducted for every application to determine what the projected water quality will be (see Chapters 7 and 10).

5.2 Recycle

Figure 5.6 shows an RO array with concentrate recycle. A concentrate recycle is usually used in smaller RO systems, where the cross-flow velocity is not high enough to maintain good scouring of the membrane surface. The return of part of the concentrate to the feed increases the cross-flow velocity and reduces individual module recovery, thereby reducing the risk of fouling.

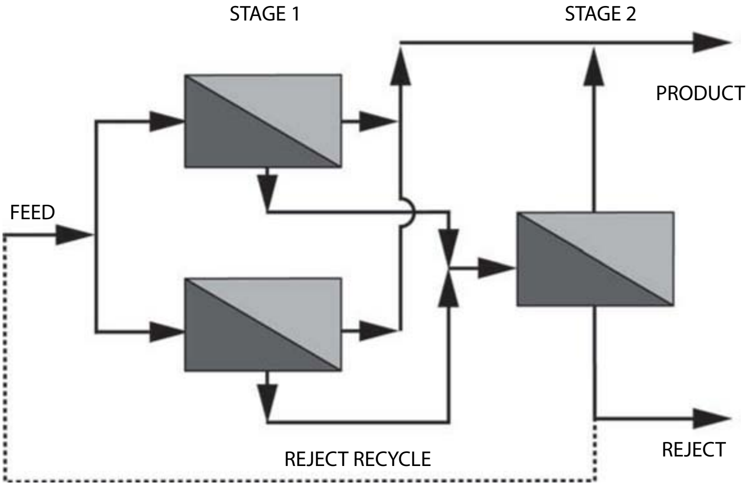


Figure 5.6 Two-by-one array with concentrate recycle.

Recycle has some disadvantages as well:

- Lower overall product quality. This is because relatively high-concentration reject is added to the lower-concentration influent.
- Larger feed-pump requirements, because the RO feed pump must now pressurize both the influent stream plus the recycled reject stream. As a result, the RO feed pump must be larger, which may mean higher capital for the RO system.
- Higher energy consumption, again because of the reject and influent streams coming together and must be repressurized. This results in higher operating costs for the system.

5.3 Double Pass

Double pass (or two-pass) refers to further purification of permeate from one RO by running it through another RO. The first RO, as described in Chapter 5.1, would be the first pass. Permeate from the first pass is then sent to another RO known as the second-pass RO. The second-pass RO "polishes" the first-pass RO product to yield higher-quality water.

Figure 5.7 shows a double-pass RO system. The design principles for the second pass are generally the same as for the first pass. However, because of the low concentration of dissolved and suspended solids in the influent to the second pass, the influent and concentrate flows can by higher and lower, respectively, than for the first-pass RO system (see Chapters 9.4 and 9.5, and Tables 9.2 and 9.3). Because the reject from the second pass is relatively clean (better quality than the influent to the first pass), it is virtually always recycled to the front of the first pass. This minimizes the waste from the system and also improves feed water quality, as the influent to the first pass is "diluted" with the relatively high-quality second-pass reject.

Recovery of the second pass can be as high as 90% with only 2 stages. This high recovery can be achieved because of the relatively low-concentration of dissolved solids in the influent to the second pass. Overall system recovery will be 73% with 75% first pass and 90% second pass recoveries (recovery would be 67.5% without recycle).

A tank is typically required between the first and second pass systems. This is so that flows can equalize between the passes. However, if the number of first-pass skids is equal to the number of second-pass skids, a tank may not be required.

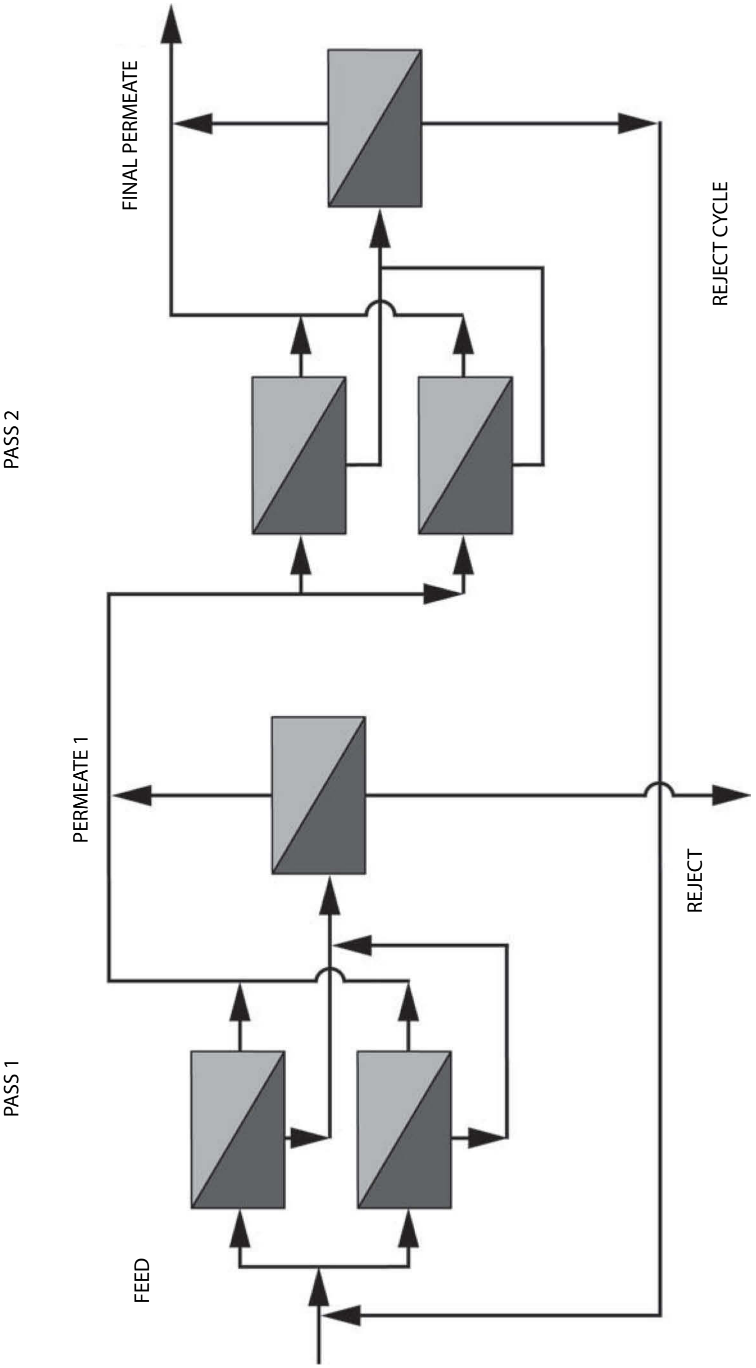


Figure 5.7 Double-pass RO.

Some vendors place both passes on a single skid, thereby eliminating the RO feed pump to the second pass RO. The backpressure from the first pass is sufficient to provide the applied pressure required of the second pass. Care must be taken so that permeate backpressure does not exceed the applied influent pressure to the first pass, or osmosis rather than reverse osmosis will occur. Additionally, high back pressure can lead to delamination of the membranes (see Chapter 12.1.2.1 and Figure 12.1)

Inter-pass caustic injection is commonly used to drive out carbon dioxide from the first-pass RO permeate/second-pass feed. Since carbon dioxide is a gas, it is not rejected by the membranes, so adding caustic converts the carbon dioxide to bicarbonate alkalinity, which is rejected (see Table 3.2). Removal of carbon dioxide is particularly important for applications that polish the second-pass RO permeate with ion exchange. The conversion and, therefore, elimination of carbon dioxide from the permeate will reduce the loading on the anion resin.

Effluent quality from a double-pass RO system is generally high enough to allow for direct use in 600 to 900 psi boilers. Higher pressure boilers (>1,000psi) and higher purity applications will still require some sort of post-treatment, typically a mixed-bed ion exchanger or electrodionization (see Chapter 16.4).

5.4 Multiple Trains

Multiple trains or "skids" placed in parallel are used when larger flow rates need to be treated. For example, an 800-gpm RO might require 1 skid, if the vendor has that size skid in their inventory. Alternatively, one could use two 400-gpm RO skids to make up the 800 gpm production rate.

There is an advantage to using multiple skids in that multiple skids provide redundancy for the system; one skid can still be on line while the other is off line for cleaning or maintenance. Additionally, multiple skids can be used to juggle variable product water demands. See Chapter 15.2 for more information about variable demands and multiple RO skids.

The drawback to multiple skids is in capital and operating costs; the greater the number of skids, the higher the capital and operating/maintenance costs. These costs must be weighed against the ability to still provide water during shut down of any one skid for cleaning or maintenance. In some cases, multiple skids will make economic sense and in others, bringing in temporary equipment during shut down will make the most economic sense.

6

Reverse Osmosis Skids

An RO skid includes the pressure vessels in which the membrane modules are contained (see Chapters 4.3.3 and 6.3 for detailed discussions about pressure vessels). Smaller skids also commonly include cartridge filters in a housing or housings and an RO feed pump. Finally, instrumentation and controls for the system are included on the skid. Figure 6.1 shows a small RO skid with these components.

Figure 6.2 shows a process flow diagram (PFD) for a 2:1 array RO system. The figure shows the major components of an RO system including instrumentation, control switches, and valves.

Components of an RO system discussed in this chapter include:

- Cartridge filters
- RO feed (booster) pumps
- Pressure vessels
- Manifolding—materials of construction
- Instrumentation
- Controls

Figure 6.1 Reverse osmosis skid. *Courtesy of Nalco-Crossbow Water LLC.*

- Data acquisition and management
- RO skid frame
- Auxiliary equipment

6.1 Cartridge Filters

Cartridge filters are usually used to directly pretreat influent water just prior to the RO feed pump and membranes. Cartridge filters are designed to prevent resin and media that may have carried over from upstream softeners and filters, from reaching the RO feed pump and damaging the impeller as well as reaching the RO membrane modules and blocking off the feed channels. They are also designed to remove macroparticles that could physically abrade or penetrate the thin film membrane layer. Cartridge filters are not intended for bulk removal of suspended solids, turbidity, or SDI (see Chapter 3.9), as is commonly believed. The rating of cartridge filters is usually 5 microns nominal (although absolute is recommended), which is much too large for removal of solids that contribute to turbidity and SDI. Cartridge filters with a rating of 1 to 3 microns absolute are sometime used when colloidal silica or metal silicates are present, but these filters can blind off quickly with bulk solids if the pretreatment prior to the cartridge filter is inadequate. In this case, the cartridge filters will require frequent replacement. This increases the operating costs for the system due to labor and material expenses.

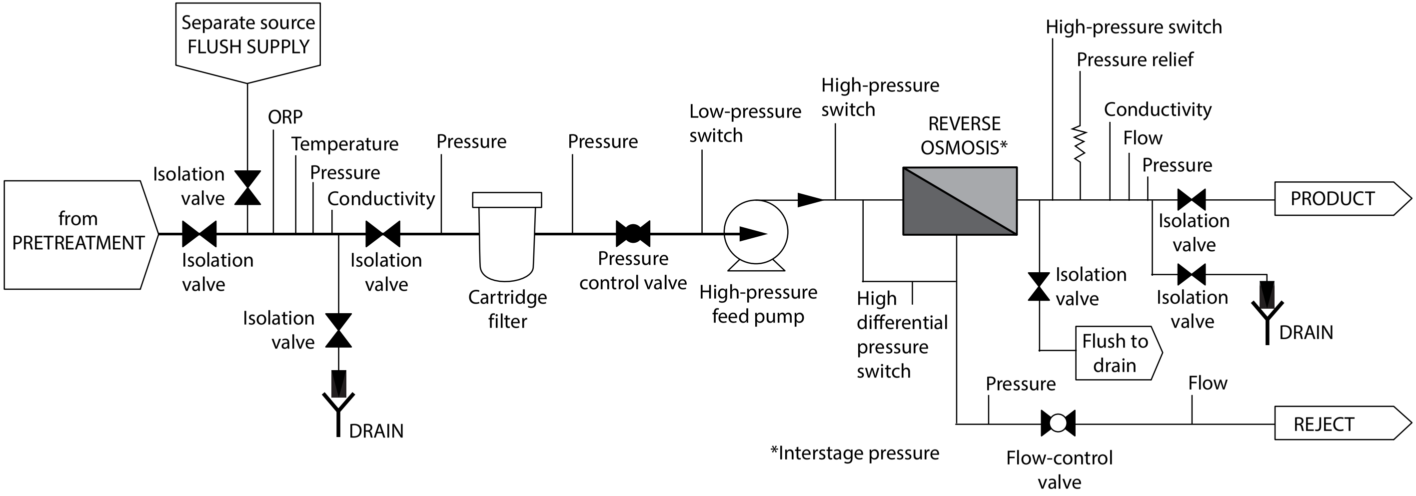


Figure 6.2 Sample RO process flow diagram (PFD) showing major equipment, valves, and instruments.

In addition to the micron rating, cartridge filters are also rated in length using 10-inch equivalents (TIE). Cartridge filters can be up to four TIE, or 40 inches in total length. Generally, RO systems use 2.5-inch diameter cartridge filters.

The number of cartridges required is determined by the flow rate of the system. Design protocol calls for a maximum flow rate of about 5 gpm per TIE (2.5-inch diameter) for optimum performance. For example, a 200-gpm flow will require forty, TIE or ten, 40-inch long cartridge filters.

Cartridge filters are generally housed in steel vessels. The largest standard housings hold about one hundred twelve, 40-inch filters. This housing can handle a flow rate of about 2000 gpm. Larger flow rates require multiple housings or a custom housing. Note that cartridge filter housings can be horizontal or vertical.

Disposable cartridge filters are recommended over back-washable filters. Back-washable filters suffer from several limitations:

- Risk of breakthrough if the backwashing mechanism fails
- Lower efficiency than disposable filters
- Higher biofouling risk

Disposable cartridge filters should be made of synthetic, non-degradable materials such as nylon or polypropylene. Their construction can be spun-bonded or melt-blown, string-wound, and pleated. These are described below.

- Spun-bonded or melt blown: These cartridge filters are manufactured by thermally either bonding or heat blowing pure polypropylene microfibers so the density is lower on the outside surface and gradually gets denser toward the center of the filter. Spun-bonded or melt-blown filters have high capacity, as particles are trapped throughout the entire cross section of the filter.
- String-wound: These cartridge filters consist of a string of polypropylene (or cotton, nylon, jute, polyester, and so forth) wound around a central core. String-wound cartridge filters rely on Van der Walls forces to capture small particles. These filters suffer from the potential to unload particles at higher pressure drops. Additionally, a slower flow rate is recommended for these filters, about 2–3 gpm per TIE.
- Pleated: These cartridge filters are typically used in higher-purity applications, such as pharmaceutical and microelectronics.

> The filters can have a multi-layered construction or be single layer. Typical materials of construction include polypropylene, polyethersulfone, and borosilicate glass fiber.

Cartridge filters come with various end cap styles, as shown in Figure 6.3. When replacing used cartridges, they should be replaced with the same end cap style so they will properly mate with the housing.

Upon start-up of new cartridge filters, the initial effluent should be sent to drain. This is necessary to prevent fouling of the RO membranes with materials used in the manufacture of the cartridge filter media. For example, lubricants and emulsifiers are used in the manufacture of the strings used in string-wound cartridge filters. These materials can coat the RO membranes and foul them. In the case of polypropylene depth filters, phthalates are used in their manufacture. As little as 50 ppb of phthalate will irreversibly foul an RO membrane.[1]

Cartridge filters should be inspected regularly during use to determine the extent of fouling of the filter. Filters should be replaced when the differential pressure across them reaches 5 psi or 2 weeks, whichever comes first. At worst, filters operating with relatively clean feed water (such as RO permeate or well water low in iron) should be replaced at least once per month to minimize biofouling risks.

Inspection of spent filters can yield useful information into the nature of foulants that may be on the RO membranes. Scrapings of the material trapped by the filter can be analyzed for elemental content. The results of this analysis can directly lead to upgrades of the pretreatment system (see Chapter 8).

6.2 Reverse Osmosis Feed Pumps

The most common type of industrial, brackish-water, RO feed pump (sometimes referred to as the "booster" pump) is a centrifugal pump, although some older units still use positive displacement pumps.[2] Centrifugal pumps are well suited to brackish-water RO applications because these pumps operate favorably at medium flows (typically less than 1,000 gpm) at relatively low pressures (up to 400 psig). Positive displacement pumps have higher hydraulic efficiencies but are plagued with higher maintenance requirements relative to centrifugal pumps.[3]

Reverse osmosis feed pumps are sized using the required flow rate and operating pressure. Pump curves, as shown in Figure 6.4, are then consulted to determine the number of stages, impeller diameter, and horsepower (hp),

Double open end
with flat gasket

Single open end
Internal O-Ring at open end

Single open end
with O-Ring with seal

Single open end
with O-Ring seal
and spear end assembly

Single open end
with O-Ring locking seal
and spear end assembly

Spring assemble,
saw cut end

Figure 6.3 Cartridge filter end cap styles. *Courtesy of Siemens Water Technologies, Inc.*

required, as well as the efficiency of the pump. For example, a 200 gpm influent flow to an RO that requires 250 psig operating pressure would need a 4-stage pump with a 6.69 in diameter impeller, and an 60 hp motor, after consulting Figure 6.4. The pump motor would operate at 3550 rpm.

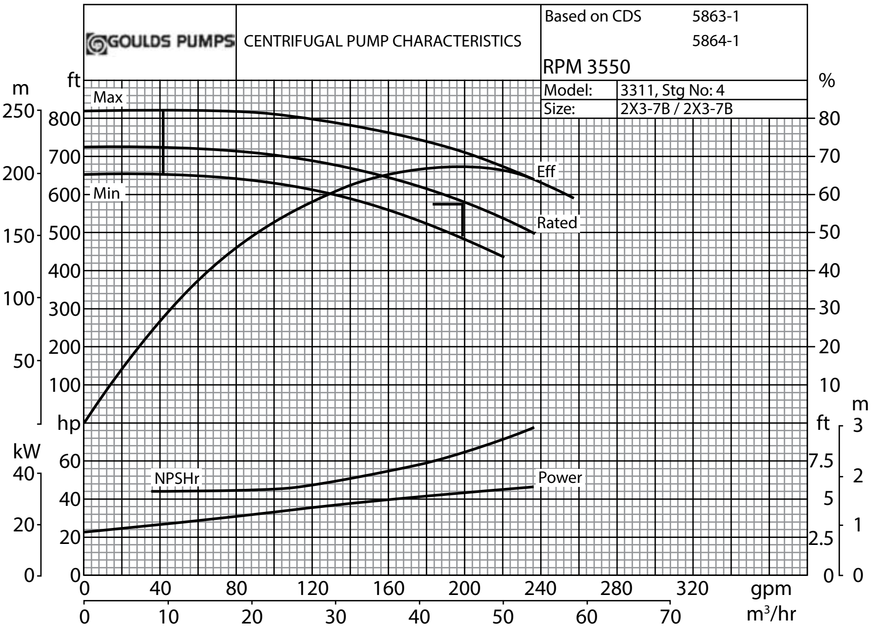


Figure 6.4 Pump curve showing stages, impeller diameter, efficiency, and horsepower. *Courtesy of ITT-Goulds Pumps.*

(Note that this pump will increase the pressure of the influent water by 250 psi over the pump suction pressure. If the suction pressure is 10 psig, the discharge pressure will be 260 psid). The curve also indicates that the net pressure suction head required (NPSHr) to prevent cavitation of the pump is about 3.45 psi (8.0 feet of water). The efficiency of the pump is about 68%, just about the maximum efficiency for this pump. This pump would be quite suitable for use in the specified RO application. However, in the case where the actual pump efficiency was far from the theoretical maximum, another pump would need to selected that would yield higher pump efficiency. Motor efficiencies run at about 90%. Each pump and motor combination has its own specific pump curve.

Variable frequency drives (VFDs) are sometime used to adjust the operation of typical (US) standard of 480VAC, 3PH, 60hz operation of the motor. The functionality of a VFD is to convert frequency measured in Hertz (Hz) to motor speed. One Hz equals 1 cycle per second. When voltage is being received (input to the VFD), it is in the sinusoidal waveform. The sine wave is converted to a digital square wave that now controls the revolutions per minute (RPM) of the motor.

The VFD should receive an analog input signal from the permeate flow sensor. This is best practice for utilizing a VFD on an RO system. Some

PLC manufactuers also make VFD controllers. This allows for eithernet cable connection from the PLC directly to the VFD. With eithernet cables an analog output is not required to control the VFD. A VFD can also be used with pressure sensors to adjust the RPM. Gaining total control of the RPM's will adjust the speed of the motor to operate at variable pressures (constant throughput) as dictated by the condition of the feed water and the membranes. This is advantageous for RO systems that operate at different water temperatures in the winter and summer. Lower pressures are required at higher water temperatures to produce the same amount of permeate (see Chapter 9.2 for more details on water temperature affects on RO performance). The VFD will reduce the speed of the motor to generate lower discharge pressure to match to lower requirements at higher water temperatures. Energy is, therefore, saved during the warmer summer months when a VFD motor is used.

If the membranes foul or scale, the VFD will automatically adjust the speed of the motor to generate higher pressure to compensate for the fouling or scaling that lowers flow through the membrane. In this manner, energy and operating cost is conserved at start up and higher energy costs do not come into play until the membranes foul or scale.

An "inverter duty" motor is required for a VFD. Unless the pump in question has this type of motor, it cannot be retrofitted with a VFD.

During operation, adjustments may be made to the VFD, but care should be taken that flow rates and recovery of the RO are not affected. Figures 6.5 and 6.6 show the outside and inside of a VFD control panel, respectively.

The discharge for centrifugal pumps is typically adjusted using a proportional pressure control valve to achieve the required operating pressure (unless a VFD is installed, in which case the pump speed is adjusted to achieved the required discharge pressure). The pressure control valve and concentrate flow control valve (also a proportioning valve) are typically throttled together to achieve the desired productivity and recovery, as shown in Figure 6.7. Manual start-up of an RO unit requires adjusting the concentrate flow control valve and then the pressure control valve, then back to the flow control valve, and so on until the desired performance setpoint is reached. The control system will automatically adjust these valves during an automated start-up. It is important to always start up the RO with the concentrate flow control valve wide open to prevent damage to the equipment or membranes upon receiving the initial pump discharge pressure blast. (Note that positive displacement pumps are adjusted using a flow control valve on a pump recycle line. The recycle line is necessary

Figure 6.5 Variable frequency drive (VFD) control cabinet. *Courtesy of Nalco-Crossbow Water LLC.*

because the pump output volume is fairly constant over the entire range of output pressures for this type of pump.[3])

As membranes age, their performance changes negatively due to the effects of fouling and scaling or degradation. These changes require adjustment in the control valve settings. For example, assuming that membrane flux declines about 15% over three years, the pressure control valve will need to be throttled to increase the discharge pressure to compensate for the loss in flux (hence, the pump must be oversized for initial conditions to allow for this increase in discharge pressure at the same flow rate).[2] RO feed pumps should be selected based on a 10% pressure premium over the 3-year membrane life pressure requirements as projected by the RO design programs (see Chapter 10). This insures that enough pressure has been built in to the pump and motor to overcome any irreversible fouling that may occur over the life of the membranes. In such cases, a VFD would save energy and operating cost by only applying the pressure that is actually needed at any given time.

Figure 6.6 Inside of a variable frequency drive (VFD) control cabinet. *Courtesy of Nalco-Crossbow Water LLC.*

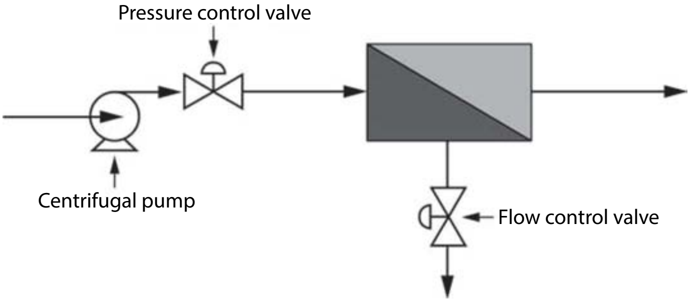


Figure 6.7 Pressure and concentrate flow control valves used to achieve desired productivity and recovery in an RO system with a centrifugal feed pump.

Pumps should be started slowly to prevent water hammer (a surge resulting from a sudden change in liquid velocity). Water hammer can cause cracks in the outer shell of the membrane modules as well as compaction of the membrane itself (compaction results in lower flux through the membrane at constant pressure). Also, water hammer causes the membrane modules to move in the vessel, which can cause wear to the O-rings used on standard interconnectors and lead to leaks of feed water into the permeate (see Chapter 4.3.3). An increase in pressure of no more than 10 psi per second is recommended.[3] Some motors may be equipped with a "soft start" that regulates the speed with which they start up. Other considerations to minimize water hammer include:

- Use centrifugal pumps. If positive displacement pumps must be used, these pumps must be fitted with approved pulsation dampening equipment; surge tanks may also be required, particularly for very short and very long pipe runs.
- Air should be vented from the system, either via the flushing cycle or mechanical vents at the uppermost section of the pipe-work in question.
- Valve operation.
  - Flow valves should be open when pumps are activated.
  - During valve change over, the closed valve should complete it's opening cycle before the open valve closes.
  - Flow valves should fail open.
  - Valves should have adequate actuation time. A solenoid valve closing in 40 milliseconds in a stream pressurized to 50 psig will generate a total pressure spike of about 490 psi.[4]

An RO feed pump requires a certain volume and pressure of make-up water to the suction side of the RO feed pump so as not to cavitate the pump, as discussed above. Low pressure and volume to the suction side of a pump are typically caused by one of the following three problems:

1. Excessive pressure drop through the pretreatment system, including the pre-filter installed on the RO.
2. Deficient pretreatment design. If pretreatment equipment is designed to backwash with service water while the RO unit is on-line, allowances must be made so that enough flow reaches the suction of the RO feed pump while the pretreatment equipment is in backwash.
3. Post installation modifications. Many times, new applications for make-up water are developed within the facility. In some cases, the easiest take-off point location is the make-up pipe to the RO system. However, if the new demand for water is significant, it will starve the RO system.

6.3 Pressure Vessels

A pressure vessel is the pressure housing for the membrane modules and contains the pressurized feed water. Various pressure ratings are available depending on the application:

- Water softening (nanofiltration—see Chapter 16.2): 50 psig up to 150 psig
- Brackish water reverse osmosis: 300 psig up to 600 psig
- Seawater reverse osmosis: 1,000 psig up to 1,500 psig

Pressure vessels are available in non-code or ASME-coded versions.

Pressure vessels are made to specifically to accommodate whatever diameter of membrane module being used, be it a 2.5-inch diameter tap water membrane module up to 18-inch diameter industrial membrane module. The length of the pressure vessel can be as short a one membrane module and as long as up to seven membrane modules in series (see Figure 6.8).

Most pressure vessels are side-entry and exit for the feed and concentrate, although some older systems employ end-entry and exit vessels. Side-entry pressure vessels are preferred over end-entry vessels because the amount of piping that must be disconnected to open the end of a pressure vessel for module replacement is minimized; only the permeate piping must be disconnected. Permeate exits out of the end of the pressure vessel in either configuration. Figure 6.9 shows side-entry pressure vessels.

Proper installation of membrane modules into a pressure vessel is critical. The membrane modules are guided into the pressure vessel in series. Membranes should be loaded into pressure vessel in the direction of flow. That is, the concentrate end of the module (the end without the brine seal)

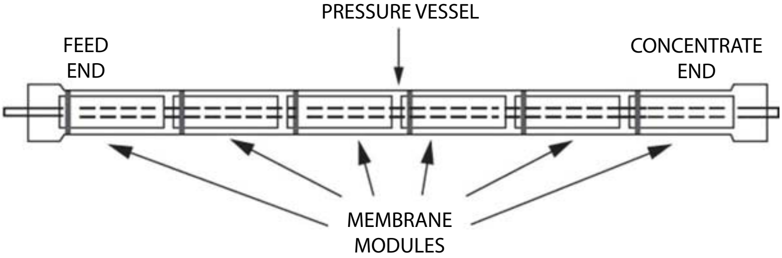


Figure 6.8 Pressure vessel containing six spiral-wound modules housed in series.

Figure 6.9 Pressure vessel showing side entry of feed water. *Courtesy of Nalco-Crossbow Water LLC.*

is inserted first into the pressure vessel. The brine seal and O-rings on the module inter-connectors can be lubricated to ease installation. They should always be lubricated using silicone, glycerin, or water; petroleum products and vegetable-based oils are not recommended as they can damage the module and membranes, and also void the membrane warranty.[5] Once the first module has been loaded into the pressure vessel, the second module is connected with its concentrate end to feed end of the first module. These two modules are then pushed into the pressure vessel using additional modules that are connected in the same manner (the final module into the pressure vessel may require additional force to push it and the other modules all the way in. Usually, a tap with a mallet on the end of the last module can move the train of modules into place). The first module into the pressure vessel becomes the last one in the series for that stage of the array.

Modules should also be removed from pressure vessel in the same direction as the flow. Hence, the first module into the vessel, which is the last one in the series, is the first module out. Figures 6.10 a, b, and c show the removal sequence for a FilmTec *iLEC* membrane module .

Pressure vessels are usually constructed of fiberglass or stainless steel. Fiberglass is typically used for industrial, non-sanitary applications.

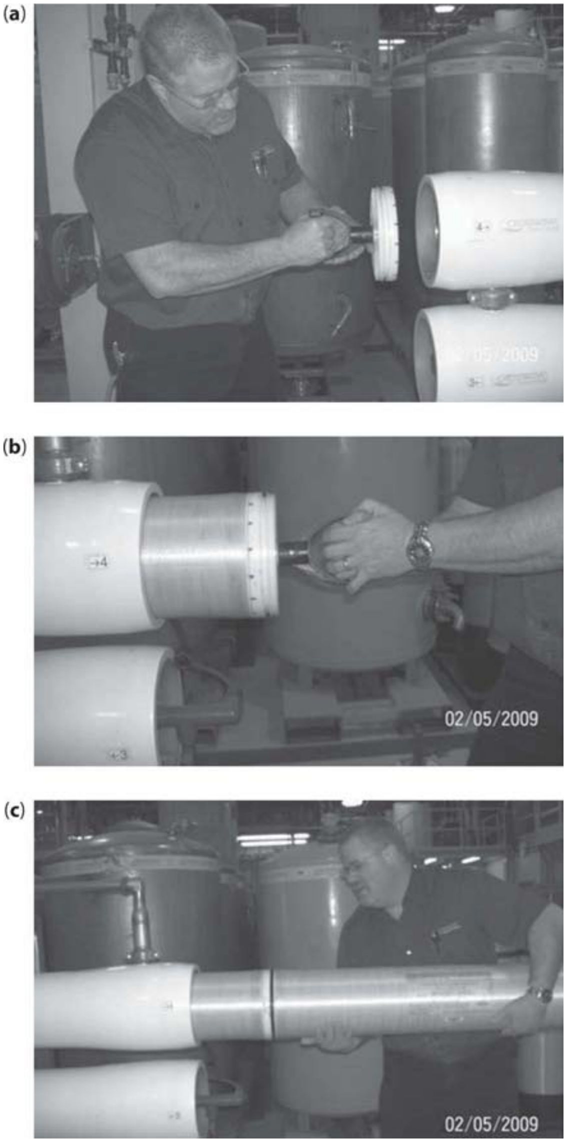


Figure 6.10 Sequence of module removal for Dow Water and Process Solutions-FilmTec *iLEC* membrane modules, (a) module removal device, (b) pulling module out of pressure vessel, (c) disconnecting 2 modules. *Courtesy of Nalco-Crossbow Water LLC.*

Stainless steel vessels are preferred for sanitary applications, where high-temperature (up to 85°C) cleaning performance may be required.

Each pressure vessel is supplied with end caps. Figure 6.11 shows an end cap with an elliptical head with the end adaptor in place. This end cap

Figure 6.11 Elliptical pressure vessel end cap with end adaptor in place for feed end of pressure vessel. Courtesy of Nalco-Crossbow Water LLC.

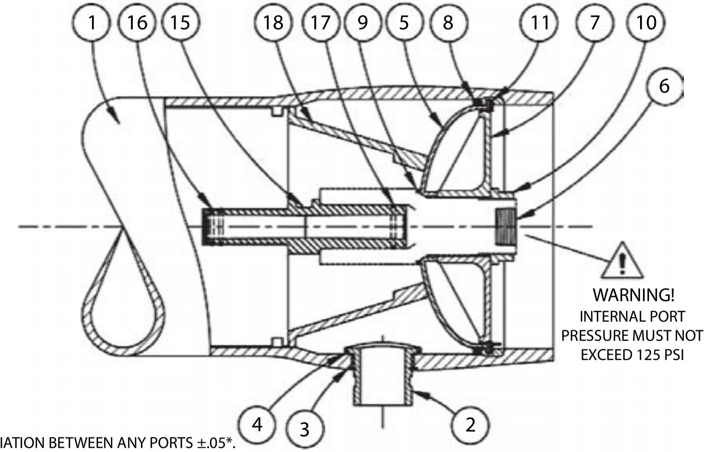
would be placed at the feed end of the pressure vessel. Figure 6.12 shows an elliptical end cap with the thrust cone (see discussion below) for a side-entry pressure vessel. Figure 6.13 shows a standard end cap with thrust ring for an end-entry pressure vessel. Thrust cones/rings are used on the concentrate end of the pressure vessel. End caps are held in place with a snap ring, shown in Figure 6.14.

Thrust rings/cones and shims are used in conjunction with pressure vessel end caps to minimize longitudinal movement of membrane modules within the pressure vessel. Movement of the membrane modules can cause the O-rings to wear as well as cause telescoping of the membranes and spacers during pressurization. Thrust rings/cones also serve to distribute the axial pressure load to the full end cap.

Correct installation of the thrust ring/cone and shims on the pressure vessel end caps and adaptors is important.

- Thrust ring/cone: the thrust ring/cone is designed to protect the end cap of the last membrane module from being destroyed during pressurized operation. It is installed at the discharge or concentrate end of the pressure vessel. Due to variations in design, the user should consult the specific vendor's specifications on how to correctly position the thrust ring. Figure 6.15 is a photo of a thrust ring as positioned on the elliptical end cap of the pressure vessel (the end adaptor

DWG REF	QTY	PART NUMBER	DESCRIPTION	MATERIAL
SHELL				
01	1	ORDER SECTION	SHELL	Fillament Wound Exoxy/Glass composiles - SS Head locking grooves integrally wound in place.
02	A/R		F/C Port	CF3M
03	A/R		Retaining Ring	300 Series Stainless Steel.
04	A/R		F/C Port Seal	Ethylene Propylene - Square Cut.
HEAD				
05	2	52025	Elliptical Head	316 Stainless Steel.
06	2	50935	Pemealse Port	Engineering Thermoplastic.
07	2	52146	Securing Plate	Engineering Thermoplastic.
08	2	45321	Head Seal	Ehtylene Propylene - Quad Seal(445)
09	2	45342	Perm Port Seal	Ehtylene Propylene - Square Cut(228)
10	2	45066	Port Nut	Engineering Thermoplastic.
HEAD INTERLOCK				
11	2	47336	Retaining Ring	316 Stainless Steel.
VESSEL SUPPORT				
12	*2	52169	Saddle	Engineering Thermoplastic.
13	*2	45042	Strap Assy.	304 Stainless Steel. PVC cushion
14	4	46265	Strap screw.	5/16-18 UNC, 18-8 Stainless Steel.
ELEMENT INTERFACE				
15	2	A/R	Adapter	Engineering Thermoplastic.
16	4	A/R	PWT Seal	Ethylene Propylene - O - Ring
17	2	52245	Adapter Seal	Ethylene Propylene - O - Ring (124)
18	1	52609	Thrust Cone	Engineering Thermoplastic.
* 3 Each Furnished With Length Code 4, 5, 6 & 7.				

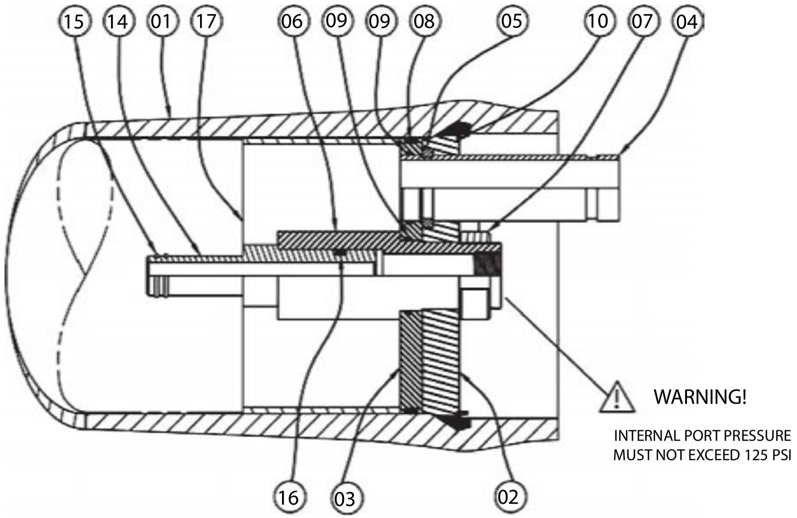


NOTES

- MAX, ANGULAR VARIATION BETWEEN ANY PORTS ±.05*.
- DIMENSION IN INCHES (MM APPROX.)
- DIMENSIONS FOR REFERENCE ONLY, NOT TO BE USED FOR CONSTRUCTION UNLESS CERTIFIED.
- SPECIFICATION SUBJECT TO CHANGE WITHOUT NOTICE.
- L.O.A REFERS TO OVERALL LENGTH OF THE VESSEL.
- EMPTY WEIGHT REFERS TO SHELL WEIGHT INCLUDING HEAD ASSEMBLIES WITHOUT MEMBRANES.

Figure 6.12 Elliptical pressure vessel end cap with thrust cone in place for concentrate end of pressure vessel. *Courtesy of Pentair Water.*

DWG REF	QTY	PART NUMBER	DESCRIPTION	MATERIAL
SHELL				
01	1	ORDER SECTION	SHELL	Fillament Wound Exoxy/Glass composiles - SS Head locking grooves integrally wound in place.
HEAD				
02	2	51051	Bearing Plate	6061-T6 Aluminium Alloy-Hard Anodized.
03	2	96003	Sealing Plate	Engineering Thermoplastic.
04	2	50567	Feed/Conc Port	316 Stainless Steel.
05	2	45090	Port Retainer Set	CF8M Cast SS. Two-piece set.
06	2	50569	Permeals Port	Engineering Thermoplastic.
07	2	45066	Port Nut	Engineering Thermoplastic.
08	2	96000	Head Seal	Ethylene Propylene - O - Ring.(442)
09	4	45312	Port Seal	Ethylene Propylene - O - Ring.(225)
HEAD INTERLOCK				
10	2	47336	Retaining Ring	316 Stainless Steel.
VESSEL SUPPORT				
11	*2	52169	Saddle	Engineering Thermoplastic.
12	*2	45042	Strap. Assy.	304 Stainless Steel. PVC cushion
13	4	46265	Strap screw.	5/16-18 UNC. 18-8 Stainless Steel.
ELEMENT INTERFACE				
14	2	A/R	Adapter	Engineering Thermoplastic.
15	4	A/R	PWT Seal	Ethylene Propylene - O - Ring
16	2	52245	Adapter Seal	Ethylene Propylene - O - Ring (124)
17	1	45069	Thrust Ring	Engineering Thermoplastic.
* 3 Each Furnished With Length Code 4, 5, 6 & 7.				



NOTES
- SHELL EXTEROR COATED WITH WHITE, HIGH GLOSS POLYURETHANE PAINT
- DIMENSIONS ARE IN INCHES [MM APPROX]
- NOT TO BE USED FOR CONSTRUCTION UNLESS CERTIFIED
- GENERAL TOLERANCES APPY, FOR DETAILS CONTACT FACTORY.
- L.O.A REFERS TO OVERALL LENGTH OF THE VESSEL.
- EMPTY WEIGHT REFERS TO SHELL WEIGHT INCLUDING HEAD ASSEMBLIES WITHOUT MEMBRANES.

SECTION THROUGH END CLOSURE

ITEM ⑰ DOWNSTREAM ONLY

Figure 6.13 Standard pressure vessel end cap with thrust ring for end-entry pressure vessel. *Courtesy of Pentair Water.*

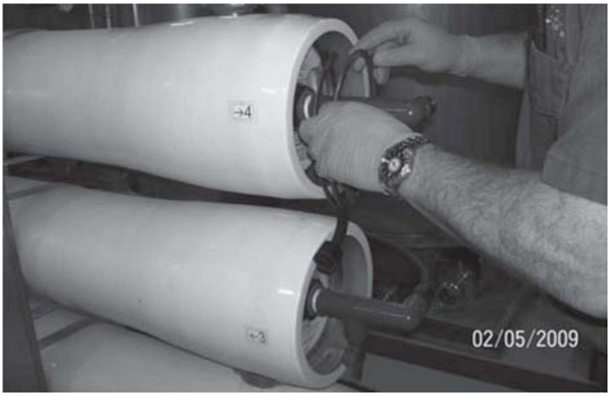


Figure 6.14 Snap ring that holds pressure vessel end cap in place. *Courtesy of Nalco-Crossbow Water LLC.*

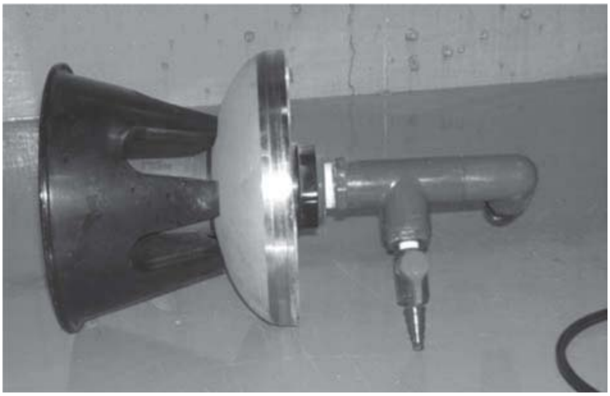


Figure 6.15 Elliptical head with thrust cone in place for concentrate end of pressure vessel. *Courtesy Nalco-Crossbow Water LLC.*

similar to the feed adaptor shown in Figure 6.11 is hidden behind the cone). The thrust cone performs the same service as the thrust ring. However, the cones are easier to install, as the cone separates from the end cap and there is no specific orientation required.

- Shims: Shims are used to prevent modules from moving back and forth during pressurization and depressurization. Such movement could wear on the internal O-ring seals. Shims are plastic spacer rings similar to washers. They are typically 0.20-inches thick, and can be purchased

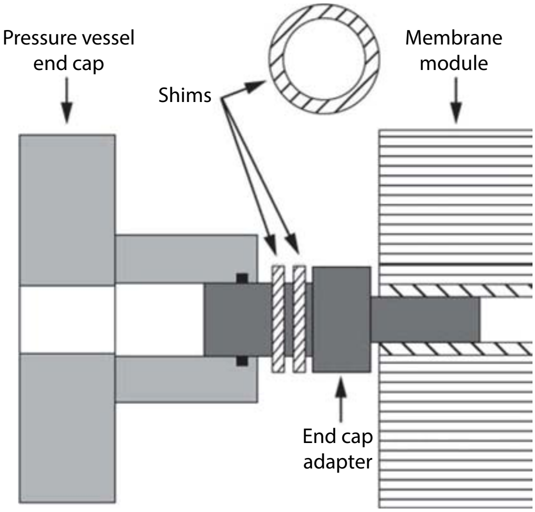


Figure 6.16 Placement of shims between the lead membrane module and the adapter hub. *Courtesy of Dow Water and Process Solutions.*

> from the manufacturer of the pressure vessel or fashioned from polyvinylchloride (PVC) pipe. Shims fashioned from PVC pipe must be cut parallel and free of burrs to work correctly. They are installed between the face of the lead membrane module and the adapter hub (see Figure 6.16) after all the membrane modules have been loaded into the pressure vessel. Prior to installation of the shims, the membrane modules should be pushed completely into the pressure vessel so that the modules seat firmly against the thrust ring.

Prior to installation of the end caps, the head seal should be installed. The head seal is an O-ring to prevent feed/concentrate from leaking out of the end caps. Figure 4.27 shows the location of this O-ring, as do Figures 6.12 and 6.13.

6.4 Manifolding—Materials of Construction

The low pressure piping on an RO skid is typically schedule 80 PVC. This includes the feed, low-pressure concentrate, and product piping. High pressure piping is typically schedule 10, 316L stainless steel (suitable for waters with concentrate streams below 7,000 ppm TDS). Sanitary applications (such as food, pharmaceutical, or biotechnical processing—See Chapter 4.4.2.6) are generally all stainless to allow for disinfection of the system.

RO permeate distribution piping considerations need to be mindful of the fact that the permeate is highly corrosive. Retrofitting an RO system into a facility with carbon steel permeate piping is difficult, as the piping will corrode. Nonmetallic materials such as plastics and fiberglass are recommended for low-pressure RO product distribution piping.

6.5 Instrumentation

Instrumentation is key to operating and monitoring an RO system. Unfortunately, there is little uniformity among RO equipment vendors in the instrumentation they provide. Table 6.1 lists basic instrumentation that should be part of each RO system. Most vendors do supply the influent, reject, and permeate instrumentation listed with the exception of the pH, temperature, and chlorine or ORP monitors, which are sometimes available as options. However, many vendors do not include the interstage instrumentation. This is an important omission, as this instrumentation is vital during troubleshooting to determining whether problems with an RO system are due to fouling in the first stage of an RO or scaling in the last stage of an RO.

Alarms and shutdowns are necessary to prevent damage to RO and pretreatment equipment and to personnel near the unit. Common shutdown alarms are listed below:

- *Low influent flow*—insufficient flow is available to keep the RO feed pump flooded and operating properly.

Table 6.1 Basic recommended RO instrumentation.

Parameter	Raw Feed	Pressurized Feed	Interstage	Product	Reject
Pressure	X	X	X	X	X
Flow	X		X**	X	
Conductivity	X		X**	X	X
Temperature	X*				
ORP	X*				
pH	X*				

* Typically installed off skid

** Generally not provided

- *Low reject flow*—the recovery of the RO system is too high; this shutdown alarm also protects against completely closing the reject flow control valve, which could damage the membranes.
- *Low permeate flow*—not enough flow is available for downstream processes such as polishers.
- *Low permeate quality*—permeate should be diverted as the RO shuts down.
- *Low influent pressure*—this could lead to cavitation of the RO feed pump.
- *High pump discharge pressure*—this is to protect the RO membranes from high-pressure water.
- *High influent temperature*—this is to protect the membrane module materials of construction that can be deformed or fail at high temperatures.
- *High oxidation potential*—this is to prevent membrane degradation by free chlorine or other oxidizers.

6.6 Controls

Most RO skids are equipped with either a microprocessor or programmable logic controller (PLC). Both the microprocessor and the PLC replaced mechanical relay panels, that were very large in size, and had tendencies for difficult troubleshooting. From the early time of RO manufacturing, control panels in most cases were large enough for the average-sized human to stand in. Today's technology allows for controls to be mounted directly to the RO units, and save a great deal of space. The PLC and microprocessor offer digital relay technology that are connected within a base moduals, other wise known as bricks (or chipsets). This is opposed to the electromechanical relay.

Microprocessors are usually found on smaller or lower-priced RO systems, while PLC controls are used for larger, more complicated systems that require greater control over process conditions. Major suppliers of PLC units for RO systems include Allen-Bradley, and Siemens.

Microprocessors boards are used on smaller RO units that require minimum input/output (I/O) function. In general, standard manufactured microprocessor boards, that are inexpensive, are used. Trouble-shooting a microprocessor board can be difficult without proper documentation and experience. In many cases, it would be quicker and more cost effective to replace a mal-functioning control board. Damage is usually caused by human errors on field wiring.

The PLC provides more expanded options for control and changes to control. They are provided with many different (I/O) cards such as, digital, analog, device net, modbus, and Internet Protocal (IP). Along with a human machine interface (HMI), the combination makes a solid control system for water treatment. High end PLC RO systems offer pretreatment control, along with multiple external valve option, post-treatment DI, and external pumps.

Systems that are fully automated also include several proportional plus integral plus derivative (PID) controllers. The PID controllers control individual set-point functions and can monitor alarm conditions. Independent PID controllers can control their specific function without a PLC. Should an independent PID controller fail, only the specific function it controlled cannot be adjusted.

Larger, commercial installations will also be equipped with a Supervisory Control And Data Acquisition system (SCADA). The SCADA system is connected via a data highway with the PLC(s) used in the system.

The basic function of a control system is to keep the RO system functioning and on-line. At start-up, the control system will automatically adjust the pressure and flow control valves to achieve the desired productivity and recovery of the system (provided the system is in automated start-up mode). It is highly recommended that an trained RO specialist be on-site for start-up. This will ensure that manufactures warranties are not compromised by human errors. The control system will also automatically turn RO skids on and off according to the demand for product water. This is typically accomplished via level control in the permeate tank. On/off (optional) divert valves can be automatically controlled to divert unsuitable feed water from the RO membranes. Examples of when divert valves spring into action include high temperature, high pH and free chlorine present in the feed water. There may also be product divert valves to dispose of high-conductivity permeate. Waste flush valves can cycle water in between long down time to prevent bacteria growth (see Chapter 13.1.3).

Control systems also include features to protect the membranes and the feed pump. Pressure switches are used on the pump suction for low inlet pressure and on the discharge for high pressure. A pressure-relief valve is installed on the permeate line to prevent backpressure from damaging the membranes. Back pressure shouldn't be considered an option for the membranes. Check with the manufacturer to see limitations on the membranes regarding back pressure. Some systems may have a high membrane differential pressure switch to prevent crushing of the membranes during conditions of excessive membrane fouling or scaling.

Administrative functions in the PLC are typically set at the factory or during installation by factory-trained personnel. These functions should not be adjusted except by those trained to do so. Changing the functions without understanding how all components of the RO system are interdependent can be disastrous for operation of the RO.

Reverse osmosis systems operate best when the flows and, therefore, recovery of the system are held constant. Both were designed with attention to other variables such as Beta, minimum velocity through a pressure vessel, and maximum velocity through a pressure vessel (see Chapters 3.5, 9.4, and 9.5). These variables and others are important to minimize fouling and scaling of the RO membranes; adjustment without regard to all of the other engineering design considerations will lead to accelerated fouling, scaling, cleaning frequencies, and membrane replacement.

When operating conditions change, for example, such as when the feed water temperature decreases or membrane fouling occurs, performance such as the permeate flux also changes. Adjusting the feed pressure compensates for such changes in performance. This adjustment can be manually initiated, but generally occurs automatically through the PLC if such a unit has been purchased. Careful observation of the system is required to ensure that the maximum allowable feed pressure is not surpassed or that fouling does not become excessive.

There is a tendency to want to increase throughput shortly after start up or after a successful membrane cleaning, when membranes are performing their best. However, if changes are made without regard to consideration of the other variables in the system that depend on flow and recovery, that will hasten fouling and scaling as a result.

6.7 Data Acquisition and Management

An operator interface is used to record data gathered by the PLC.[1] The operator interface is usually another computer (sometime called the human-machine interface or HMI). The HMI uses process displays with real-time sensor readings so that the operator can quickly assess the status of the system (see Figure 6.17). The operator uses the control panel to adjust alarm settings and to turn on and off process equipment. Once

Figure 6.17 Human-Machine Interface (HMI) showing status of the reverse osmosis system, including pretreatment.

running, however, the PLC controls and runs the system automatically, without further input from the operator. Common HMI status indicators are listed below:

- All shutdown alarms
- Total run time
- RO operating mode
- Recovery
- Influent flow
- Reject flow
- Permeate flow
- Pump status
- Valve status
    - Influent
    - Reject
    - Permeate to tank
    - Permeate to drain
    - Permeate flush

Data management typically means normalization. Normalization software is available from several sources to help interpret RO operating data (see Chapters 11.3.1 and 12 for more detail about "normalized" data). Membrane manufacturers have normalization software that requires manual input of operating data, but that run the calculations. Some chemical and equipment vendors have software/ hardware packages that collect data and perform all the normalization calculations automatically. In general, smaller and/or less expensive RO control packages and PLCs do not come with normalization software.

6.8 Reverse Osmosis Skid

Reverse osmosis skids are typically contained within a frame of galvanized or urethane-coated steel. Skids should be designed for easy access for monitoring and maintenance. Access to controls, instruments, valves, the pump and motor, and membranes is essential. Access to the permeate from each pressure vessel is often overlooked. Without such access, profiling and probing used to troubleshoot poor performance is not possible (see Chapter 14.7).

When locating space for an RO skid, attention should be given to space needed for access to controls and the membranes. Multiple skids are usually put in face to face. Four feet should be allowed between the face on a skid and neighboring equipment (one to two feet is acceptable for the back side of the skid). Each end of the skid should have at least four feet and preferably six feet of free space so that membranes can be installed and removed from the pressure vessels.

There are advantages to hard piping most of the RO system, but some piping needs to remain open so that flows can be observed and measured. In particular, waste flows to drain, such as filter backwash waste, RO reject, and RO permeate divert streams, should be accessible before they enter the drain so that they can be easily observed and sampled if needed; waste-flow piping should end 6 to 10 inches above the drain.

6.9 Auxiliary Equipment

Some RO skids come equipped with “on board” integrated cleaning equipment. The main process pump and cartridge filter are used for the cleaning system. The skid also includes valves and hoses that are used for the cleaning. A free-standing cleaning tank is placed next to the RO skid. Note that on-board cleaning systems are limited in their ability to properly clean membranes, particularly if they do not allow for cleaning each stage individually, which is difficult if not impossible to do when using the main RO feed pump. It is difficult to achieve the proper cross flow using the on-board system when the stages are not individually cleaned: each stage requires different flow rates to adequately scour the membrane surface to remove foulants and debris. See Chapter 13.2 for more details about cleaning membranes.

If an RO skid does not come with an integrated cleaning system, a free-standing cleaning skid is required (alternatively, the membranes must be shipped out for off-site cleaning—see Chapter 13.2). The cleaning skid should include a cartridge filter housing, low-pressure recirculating pump, and tank. The tank may or may not be equipped with a mixer and heating element. If a mixer and heating element are not included, the cleaning solution must be recirculated within the cleaning skid until the cleaning chemicals are well mixed and the recirculation pump imparts enough heat to the cleaning solution that an effective cleaning can be conducted.

Automated SDI kits are available that can be installed on the RO influent line (see Chapter 3.8 for more information about SDI). These kits provide the hardware and software to run up to 5 consecutive SDI tests and perform the SDI calculations without operator attention. Should an automated kit not be available, manual SDI equipment should be installed. Equipment required for a manual SDI system is shown in Figure 3.7.

6.10 Other Design Considerations

6.10.1 Access to Profile and Probe RO Membranes

Profiling and probing are two techniques use to sample the performance of individual membranes *in situ* (see Chapter 14.7). Access for profiling and probing is important to assist with troubleshooting an RO system. Profiling requires that permeate sample port be installed on the effluent from each pressure vessel. Probing requires that the sample port be such that a section of flexible tubing can be snaked down the through the port into the permeate tubes of the membranes while installed in the pressure vessel. Many commercially-available standard skids do not include proper valves to allow for either profiling or probing.

6.10.2 Interstage Performance Monitoring Instrumentation

Data normalization over individual stages is important to allow for determination of the type of fouling or scaling that is occurring and where in the system is it occurring. Interstage instrumentation that is required includes flow indicators, pressure sensors, and conductivity meters.

6.10.3 Stage-by-Stage Membrane Cleaning

The ability to clean each stage individually in an RO system is very important. This prevents scale from the last stages to be mixed with the other stages, and foulants from the first stage being mixed with other stages. It also allows for proper flow rates through the pressure vessels to maximize cleaning efficacy. Valves should be installed to allow for cleaning of each stage individually. Additionally, if multiple skids are cleaned with the same cleaning skid, provisions should be made to allow return piping to drain completely between cleaning of each RO skid. This will eliminate cross contamination from one skid to the next.

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2

PRETREATMENT

7

Water Quality Guidelines

The performance and successful operation of an RO system depends directly on the quality of water feeding the RO. The nature of feed water constituents can influence membrane performance by causing scaling, fouling, or degradation of the membrane. Table 7.1 lists water quality guidelines against which RO influent (and, in some cases, concentrate) should be contrasted, to determine whether membrane fouling, scaling, or degradation is possible. This chapter details various feed water constituents that affect the performance of RO membranes.

7.1 Suspended Solids

Suspended solids are typically measured using turbidity. Turbidity measures the light-scattering ability of particles in water. The water quality guidelines call for an influent turbidity of less than 1 Nephelometric Turbidity Units (NTU), which also happens to be a warranty requirement of membrane manufacturers. Exceed 1 NTU and the membrane warranty is voided. The

Table 7.1 Generally-accepted water quality guidelines for RO influent and concentrate waters.

Species	**Units**	**Guideline Value/Range**
Colloids	SDI (unit-less)	<5*
Suspended Solids	NTU	<1
Calcium Carbonate	LSI	<0**
Metals: iron, manganese, aluminum	ppm	<0.05
Barium, Strontium	ppm	<0.05
Hydrogen Sulfide	ppm	<0.1
Microbes	CFU/ml	<1,000[†]
Silica (soluble)	ppm	140–200[††]
Organics (TOC)	ppm	<3
Color	APHA	<3
Chemical Oxygen Demand (COD)	ppm	<10
pH—CA Membranes	pH units	4–6
pH—PA Membranes	pH units	2–12[†††]
Chlorine, free—CA Membranes	ppm	<1
Chlorine, free—PA Membranes	ppm	<0.02
Temperature—CA Membranes	°C	<35
Temperature—PA Membranes	°C	<45

* Silt density index (see Chapter 3.8)

** Can be up to +2.0 to +2.5 depending of the type of antiscalant used; membrane manufactures allow up to + 1.8 in their warranties.

[†] In RO reject stream

[††] In RO reject stream, varies as functions of pH and temperature (see Figures 7.2 and 7.3)

[†††] General guideline—check with membrane manufacturer for limits for specific membranes

lower the turbidity, the less likely the membranes are to foul with suspended solids. RO best practices call for feed water turbidity less than 0.5 NTU.

Another measure of suspended solids is particle size distribution. However, there are no recommendations on particle size distribution in RO feed water that have been established. In general, particle size distributions have a lower limit of 0.5μm, while the particles of importance with respect to membrane following may be much smaller in size.

Silt density index measures suspended solids, particularly colloids, such as alumina-or iron-silicates, clay, iron corrosion products, and microbes, that have a great potential for fouling RO membranes (see Chapter 3.9 for more details about SDI). The SDI should be as low as possible to minimize fouling of the membranes, but must be less than 5 to meet warranty requirements set by the membrane manufacturers (best practices call for SDI in RO feed water to be less than 3). Note that there is no direct correlation of turbidity to SDI, other than high turbidity usually means high SDI (the converse is not always true).

Membranes fouled with suspended solids will exhibit lower productivity and an increase in pressure drop. Sometimes there is also a decrease in salt rejection.

Suspended solids can be removed or reduced in RO feed water using coagulation, clarification, and filtration (see chapter 8.1).

7.2 Microbes

Microbial fouling of RO membranes is a significant issue. Bacterial colonies will grow virtually anywhere in the membrane module where the conditions are favorable. Concentration polarization provides an environment next to the membrane surface that is enriched in nutrients for microbes. Satellite colonies can break off and begin to grow elsewhere within the membrane module, increasing the surface area of membrane that is covered with microbes and their associated biofilm. Satellite colonies can lead to uneven growth of colonies, thereby developing localized areas of lower flow velocity where scaling can occur, resulting in a subsequent increase in salt passage; this also can occur prior to an appreciable increase in differential pressure. For a more complete discussion on membrane biofilms, see chapter 8.5 and Ridgeway[1]. Microbial fouling will lower membrane productivity, increase operating pressure, and, increase pressure drop and in some cases, lead to higher product concentration of dissolved solids.

The potential for biological fouling of a membrane can be determined by considering the assimilable organic carbon (AOC). This test is a bioassay that measures the growth potential of microorganisms in a sample. The test procedure is described in part 9217 of the Standard Methods.[2] A value of 10 micrograms per liter is a proposed standard to minimize biological fouling of membranes, but in some cases, fouling may still occur even at this low value.[3] Dow Water Solutions recommends an AOC value of less than 5.[4]

The degree of membrane fouling with microbes that has already occurred is determined by checking the number of colonies that slough off the membrane into the RO reject stream. This is typically determined using one of two methods:

- Culture: This technique is easy to perform and does not require expensive equipment. It is used to determine the number of colony-forming units (CFU) in a water sample using part 9000 of the Standard Methods[3]. The number of CFU in a sample is an expression of the number of culturable microorganisms present. Note that while this technique is relatively inexpensive, the counted colonies may represent only about 1 – 10% of the total bacterial count (TBC). Never-the-less, this technique can be useful in tracking microbial fouling. Concentrations of 1,000 CFU per milliliter or greater in an RO concentrate stream are considered a fouling problem that can significantly and negatively effect performance of the RO system.
- Total Bacteria Count: The TBC is determine by directly counting the actual number of microorganisms collected on a filter after it is used to filter a sample of the water in question.[5] The sample is stained with acridine orange and viewed with an epi-illuminated fluorescent microscope. This technique is more accurate and quicker than the culture technique, but is not as practical for field work.

Microbial fouling is best dealt with before biofilm becomes mature. Biofilm protects the microorganisms from the action of shear forces and biocidal chemicals used to attack them. Microbes can be destroyed using chlorine, ozone, ultraviolet radiation, or some non-oxidizing biocides (see Chapters 8.2.1, 8.2.2, and 8.1.8). An effective method to control bacteria and biofilm growth usually involves a combination of these measures. Specifically, chlorination or ozonation of the pretreatment system, followed by dechlorination to protect the membranes, or UV distruction followed by periodic disinfection with a non-oxidizing biocide used directly on the membranes to keep the membranes clean.

7.3 Organics

Organics adsorb to the membrane surface resulting in flux loss that can be permanent in some cases.[4] Adsorption is favored at pH less than 9 and where the organic compounds are positively charged. Particularly troublesome are emulsified organics, which can form an organic film on the membrane surface. Organic fouling exacerbates microbial fouling, as many organics are nutrients for microbes. It is recommended that the organic concentration, as measured by total organic carbon (TOC) be less than 3 ppm to minimize fouling potential. Organic fouling of the membrane will decrease productivity of the membrane.

The concentration of oils (both hydrocarbon and silicone-based) and greases should be less than 0.1 ppm in RO feed water. These materials will readily adsorb onto polyamide membranes and result in a decrease in membrane throughput. However, they can be removed from the membrane using alkaline cleaners if the flux has not declined by more than 15% from start-up.[4] Note that some hydrocarbon solvents are also solvents for the RO membrane and exposure should be avoided.

Organics can be reduced in RO feed water using coagulation/clarification, ultraviolet radiation, or activated carbon filtration (see Chapters 8.1.1, 8.1.8, and 8.1.4, respectively). Lower molecular weight organics such as urea, isopropyl alcohol, and acetone are not easily removed using these techniques. However, oxidation of these organics using persulfate activated by UV light has been shown to be successful.[6] Oils and greases can be removed from RO feed water using coagulation/clarification, carbon filtration, with special carbon or, in the of wastewater reuse, dissolved or induced air flotation. Operation at pH 9 or higher also helps to minimize following by converting the organic compounts to salts.

7.4 Color

Color adsorbs onto the surface of the RO membrane. Color is typically made up of naturally occurring humic substances that form when organic substances, such as leaves, decay. Humic substances are themselves composed of three different types of organic compounds. Humic acid is that color which precipitates during acidification; these organics are dark brown to black in color. Fulvic acid does not precipitate during acidification; these substances are yellow to yellow-brown in color. Finally, humin is not soluble at any pH and is black in color.

Color can be true or apparent. Apparent color is essentially total color, composed of dissolved and suspended organics and other suspended solids such as iron oxidizes. True color is measured by filtering out the suspended matter through a 0.45µm filter so that the only color present is due to dissolved organics. Color is measured using APHA (American Public Health Association) or the Pt-Co (Platinum-Cobalt) method dimensionless units.

Adsorption of color onto an RO membrane is favored when the compounds are hydrophobic or positively charged. As with other organics, a high pH (>9) helps to minimize fouling with color, but causes other concerns, including calcium carbonate scaling.

True color should be less than 3 APHA or 3Pt-Co units to minimize fouling due to color adsorption. Adsorption of color onto the membrane will decrease productivity of the membrane.

Color can be reduced in RO feed water using coagulation/clarification with hydroxide flocculants, ultrafiltration and nanofiltration, adsorption of activated carbon, and ultraviolet radiation (see Chapters 8.1.1, 8.1.9, 8.1.4, and 8.1.8, respectively).

Note that exposure to chlorine can result in color forming trihalomethanes (THMs), which are known to posses carcinogenic properties (see Chapter 8.2.1 for more information about THMs and chlorination). This is a particular concern to potable or municipal RO systems.

7.5 Metals

RO membranes will readily foul with precipitated metals, including iron, manganese, and aluminum. Further, iron and manganese (and cobalt present in some bisulfite solutions used for dechlorination) are also a problem for RO membranes. These metals will catalyze the oxidation of the RO membrane resulting in damage to the membrane. By dropping the pH and reducing the oxygen concentration, higher concentrations of soluble iron can be tolerated. Metal fouling will increase pressure drop and decrease productivity. Oxidization of the membrane with metals will result in lower salt rejection and higher productivity.

Iron and manganese are naturally occurring in well water, although they can be found in surface waters in lower concentrations (the exceptions include mine drainage water where concentrations can be very high). Typically, iron and manganese will be soluble while in the well, but upon exposure to oxygen in air, they precipitate, forming oxides. These oxides collect on the membrane surface, fouling the membrane.

Iron and manganese can be removed from RO feed water using sodium softening or iron filters (see Chapters 8.1.6 and 8.1.5, respectively). In some cases, it may be desirable to operate with soluble iron and/or manganese through the RO system, if the entire system can be kept air tight to prevent oxidation of the metals into suspended solids.

Carry-over and overfed of alum (aluminum sulfate) coagulants, post-precipitation of alum coagulants due to poor pH control, and naturally-occurring aluminum silicates are responsible for aluminum fouling of RO membranes. Alum feed is usually employed on surface waters where clarification is the first pretreatment step. The overfed of alum occurs when the raw water turbidity increases. Many operators will continue to add alum past the point called for by stoichiometry. Carry over also occurs when the clarifier is not operated properly.

Aluminum can react with silica in water to form aluminum silicates. This reaction can occur at silica concentrations much below saturation, for example, as low as 10 ppm.[7]

Alum's minimum solubility is at pH 6.5. If the RO is run at pH 7–9, this should keep the alum in solution through the RO. Alum is generally addressed either by operating at appropriate pH (7–9), or by replacing the alum with another coagulant.

7.6 Hydrogen Sulfide

Hydrogen sulfide is a gas typically found in well water that is devoid of oxygen. It is the result of sulfate-reducing bacteria oxidizing organic matter, which releases hydrogen sulfide gas. Hydrogen sulfide is a weak acid whose speciation depends on pH as follows:

$$H_2S + H_2O \rightarrow \leftarrow H_3O^+ + HS^- \quad pK_a = 7 \qquad (7.1)$$

$$HS^- + H_2O \rightarrow \leftarrow H_3O^+ + S^{2-} \quad pK_a = 17 \qquad (7.2)^*$$

The chemistry of sulfur dioxide is not fully understood, but does involve several intermediates; the mechanisms are not as clean as the equations imply.[8] For example, hydrogen sulfide is chemically oxidized by dissolved oxygen:

$$H_2S + 2O_2 \rightarrow H_2SO_4 \qquad (7.3)$$

*there is considerable disagreement in the literature as to the actual pKa for this equation; estimates range from 12–19.8

But, this reaction passes through several intermediates of different oxidation states, including sulfite (SO_3^-), which can further react with hydrogen sulfide ion (HS^-) to yield thiosulfate.[8] The thiosulfate can be oxidized to yield sulfate via production of tetrathionate, $S_4O_6^{2-}$. In the presence of trace metals, the formation of elemental sulfur occurs in the initial step of sulfide oxidation, where S° is elemental sulfur[8]:

$$2HS^- + O_2 \rightarrow 2S^\circ + 2OH^- \tag{7.4}$$

Elemental sulfur can react with sulfite and sulfide to yield thiosulfate and polysulfides (which are unstable in oxic conditions and decomposes to elemental sulfur and thiosulfate), respectively[8]:

$$S^\circ + SO_3^{2-} \rightarrow S_2O^{32-} \tag{7.5}$$

$$(n-1)S^\circ + HS^- \rightarrow HS_n^- \tag{7.6}$$

Elemental sulfur is a yellow-white substance, as shown on the brine seal and on the *iLEC* interconnecting O-ring seal in Figures 7.1 and 7.2, respectively.

Hydrogen sulfide can also react with metal salts, such as iron and manganese which are also present in most well water sources.

Metal salts, such as iron sulfate, which may also be present in most well water sources, also react with hydrogen sulfide to yield metal sulfides:

$$Fe(SO_4) + H_2S \leftrightarrow H_2SO_4 + FeS_{(s)} \tag{7.7}$$

Metal sulfides are quite insoluble; the solubility product (K_{sp}) of FeS is only 8 X 10^{-19}. By comparison, the K_{sp} for barium sulfate is 1 X 10^{-10} and

Figure 7.1 Elemental sulfur deposit on brine seal.

the K_{sp} for calcium fluoride is $3.5 \text{ X } 10^{-11}$. Deposits can be sooty-black or a pasty-gray, that resemble sludge in appearance (see Figure 7.3).[9]

In many cases, well water is chlorinated prior to RO to help oxidize and removal metals such as iron and manganese. Hydrogen sulfide reacts with chlorine to form acids. The overall equation is shown in Equation 7.8, but, just as with the reaction of oxygen with hydrogen sulfide, there are intermediates, which include elemental sulfur (Equation 7.9):

$$H_2S + 4Cl_2 + 4\ H_2O\ H_2SO_4 + 8\ HCl \tag{7.8}$$

$$H_2S + Cl_2\ S^o + H^+ + 2Cl^- \tag{7.9}$$

Figure 7.2 Elemental sulfur on *iLEC* interconnector O-ring seal.

Figure 7.3 Gray deposit of elemental sulfur on the surface of the membrane. Note the incomplete scraping even with manual means.

Thus, oxygen, chlorine, and metals all react with hydrogen sulfide to yield solid elemental sulfur and insoluble metal sulfides, respectively. Fouling with elemental sulfur or metallic sulfides will cause a decrease in water flux due to membrane surface fouling and an increase in salt passage due to scale which is attracted to and held on to by the solid sulfur compounds.

Treatment recommendations are polar opposite for hydrogen sulfide. Some professionals recommend that no treatment to remove hydrogen sulfide be used, and all efforts should be focused on keeping the RO feed water free of oxygen or other oxidizers. This may be possible. However, any back flow of water into the well will create a vacuum on the system which can lead air can entering through system voids and oxidizing the hydrogen sulfide. Submersible pumps with check valves located on the discharge of the pump or a procedure to waste the initial flow from the well are techniques that can be used to minimize potential for oxidation into elemental sulfur. The percentage of hydrogen sulfide as gas and as ion (from equation 7.1) is shown in Figure 7.4. For this technique to work, the pH of the feed to the RO must be keep at 5 or lower. The permeate and concentrate streams should then be scrubbed of the hydrogen sulfide gas passing through the RO system due to corrosion of piping and system downstream.

Others recommend treatment to remove hydrogen sulfide. Most techniques involve oxidation of the hydrogen sulfide and filtration of the insoluble sulfur and metal oxides. Suitable oxidizers include chlorine, potassium permanganate, and peroxide. Chlorination is generally used

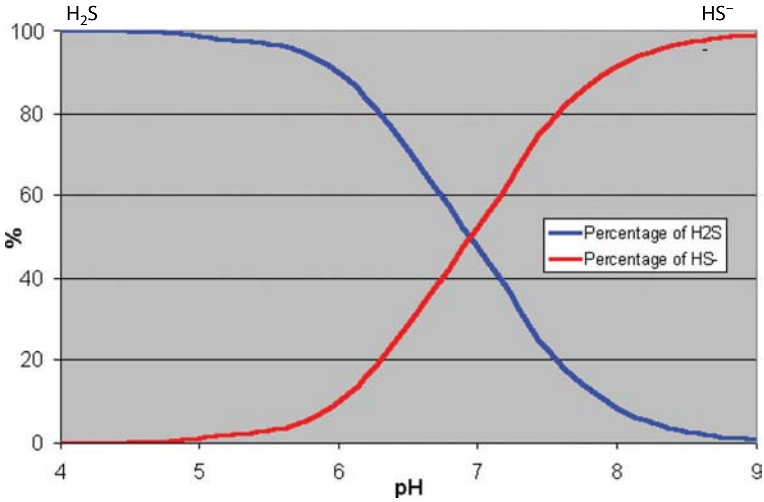

Figure 7.4 Hydrogen sulfide speciation as a function of pH.

when the hydrogen sulfide concentration exceeds 6 ppm. Dosing rations range from 2 to 3 ppm chlorine per ppm of hydrogen sulfide. A minimum of 20 minutes contact time should be allowed for adequate oxidation. Manganese dioxide (pyrolusite) filters following oxidation can be used for filtration and also catalytic oxidation of any hydrogen sulfide that did not get oxidized by the chlorine (see Chapter 8.1.5). Aeration without chemical feed is sometimes used when the hydrogen sulfide concentration is less than about 2 ppm.

Because hydrogen sulfide is a gas, it is not rejected by an RO membrane. For systems that do not remove the compound prior to the RO membranes, hydrogen sulfide will be present in the permeate. Exposure to air on the permeate side of the membrane, such as during shut down of the system, can result in an ivory to yellow precipitate of sulfur on the permeate side of the membrane. This will result in a loss of flux (increase in operating pressure) over time. It is not possible to remove the precipitate on the permeate side with manual techniques. However, due to the corrosive nature of the RO permeate, the precipitate will eventually be remove by the permeate stream, provided no additional sulfur precipitate is added.

7.7 Silica

Silica, in its various forms, can cause serious problems for an RO system. Silica scaling and fouling can occur via a number of ways and is not well understood due to the number of different mechanisms that can take place.[10] The concentration of silica, the speciation of silica, and temperature, pH, and the general chemistry of the water all affect the chemistry of silica scaling and fouling. In general, the silica issues that affect RO systems can be summarized as deposition of silicates, polymerization of silicic acid to amorphous silica, and the accumulation of amorphous colloidal particles.[11] To understand the potential problems, it is first necessary to understand a little about the chemistry of silica.

Silica as SiO_2 is generally used in water–related discussions, when, in fact, more than 22 phases of silica, as silicic acid and silicates, have been identified.[12] For example, H_4SiO_4 is recognized as ortho (or mono) silicic acid and H_4SiO_3 is metasilicic acid, with the difference being the degree of hydration. Crystalline silica, as SiO_2, dissolves in water to form silicic acid, as shown in Equation 7.10:

$$(x)\ SiO_2 + 2H_2O \longleftrightarrow (x - 1)\ SiO_2 + H_4SiO_4 \tag{7.10}$$

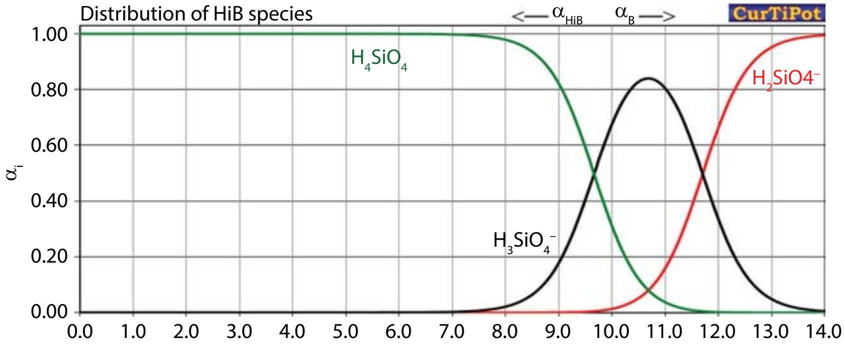

Figure 7.5 Silicic acid distribution as a function of pH.

This equation is an overly simplified but accurate description of the process.[11] As mentioned previously, the chemistry of silica is quite complex. Hence, the mechanisms of membrane scaling and fouling with silica are complex. The mechanisms depend on many factors, including the speciation of silica and interactions of the various species with each other, temperature, pH, and the presence of multivalent ions and their interactions with the assorted silica species in the feed water to an RO.[11]

The speciation of silica generally depends on pH. Figure 7.5 shows the distribution of silicic acid and silicate as a function of pH. As the figure shows, the pK_a of silicic acid is 9.84. This means that at pH 9.84, the concentration of silicic acid and silicate compounds is the same, so a 50/50 blend of the compounds coexist. Hence, at the pH of most RO systems, generally 7–8.5, the form of silica present is primarily silicic acid.

The solubility of silicic acid as a function of temperature is shown in Figure 7.6. Once the concentration of silicic acid exceeds saturation, it begins to form amorphous silica, a soft, gel-like substance, by means of a condensation-polymerization reaction. Amorphous silica is sometimes referred to as colloidal silica, although amorphous silica more correctly described as shown in Table 7.2. One can see by this classification that colloidal silica will pass through a 0.45-micron filter used in the silt density index (SDI) tests typically used to determine the fouling potential of feed water to an RO. Thus, the SDI test is not a good predictor of fouling with colloidal silica, but the test will pick up the larger, "filterable" silica. Also, note that the larger the particle of amorphous silica, the lower its solubility.[13]

The solubility of amorphous silica is also a function of pH, as shown in Figure 7.7. The solubility of amorphous silica stays relatively constant below about pH 8.5 to 9.0, but then rapidly increases at higher pH. This increase in solubility at pH about 8.5 and higher, corresponds directly to

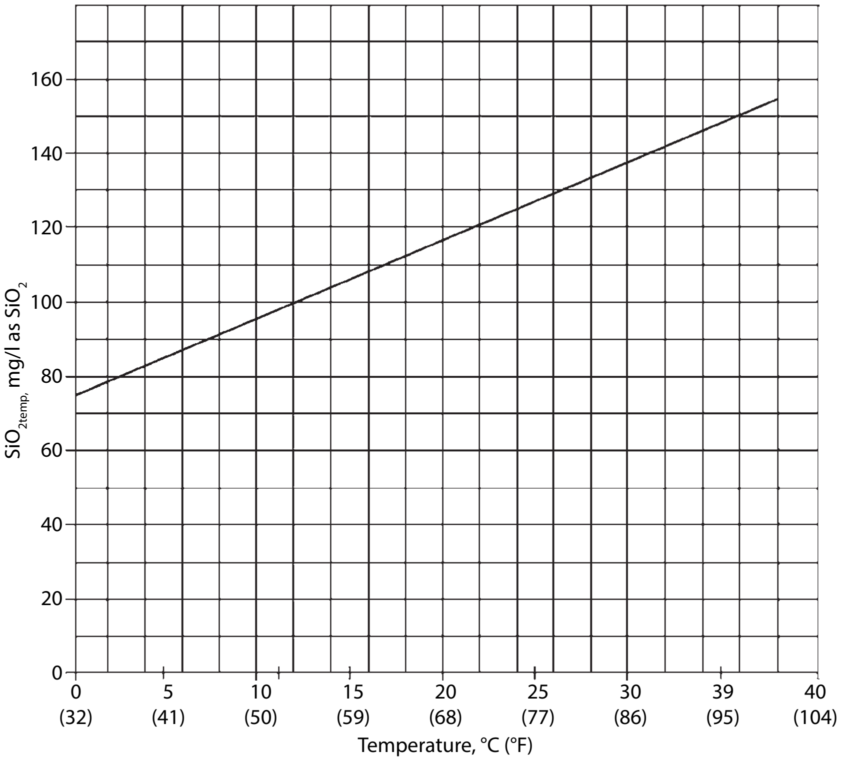

Figure 7.6 Silica solubility as a function of temperature.a

Table 7.2 General classification of amorphous silicic acid.[14]

Type of Amorphous Silica	"Particle" Size (microns)
Filterable	>0.45
Colloidal	0.01–0.45
Polymeric	<0.01
Silicic Acid Monomer	<0.0001

the increase in the presence of silicates that this pH and higher. It has been reported that the silicate solubility at pH 11 is 5000 ppm.[15] Note that these silica solubilities of are in the *absence of metals*.

The presence of metals, including hardness, aluminum, iron, and manganese, can greatly reduce the solubility of silicates (data also suggests that metals may also react with amorphous silica at neutral pH, and limit

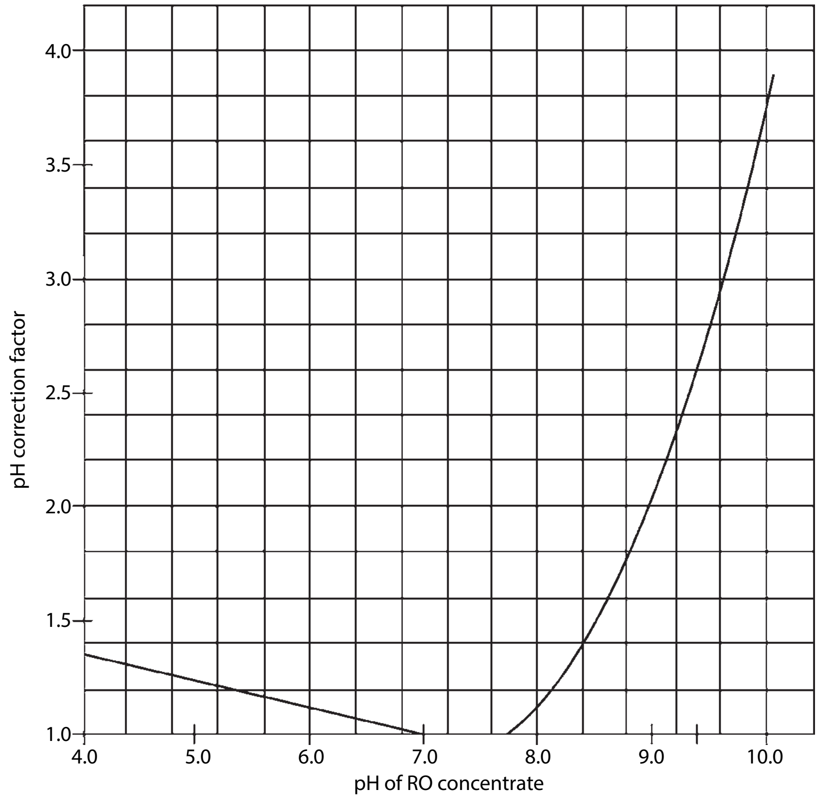

Figure 7.7 Silica solubility as a function of pH. To determine silica solubility at a given pH, multiply the solubility as a function of temperature by the pH correction factor of the given pH of the concentrate solution.

solubility).[4,16] Metals specifically react rapidly with silicates to form silicate compounds such as iron silicate ($FeSiO_4$) and calcium magnesium silicate ($CaMgSiO_6$) that can foul RO membranes. Silicate compounds can form even when the silica concentration is significantly below saturation. Silicate compounds have inverse solubility, in that they precipitate at elevated pH and temperature.[16] The issue of high pH and high temperature should not be significant for most RO systems, however, since they are operated at temperature and pH values that favor the presence of amorphous silica. But, given that even low concentrations of silica in the form of silicate can react with metals to form metal silicates which can deposit on membranes, RO operations at a pH greater than 7.8 need to be cognizant of the potential issue with silicates and metals.

The High Efficiency Reverse Osmosis, or HERO™ (HERO is a trademark of Debasish Mukhopadhyay) takes advantage of the elevated concentrations of silicates at very high pH (Figure 7.5) and removes metals as part of the HERO process to eliminate the potential for forming metals silicates at high pH on the RO membranes. See Chapter 16.5 for more on the HERO process.

As mentioned at the beginning of this section, silica, whether amorphous or silicate, can seriously affect the performance of an RO system. Silica fouling and scaling leads to low productivity (and higher operating pressures as a result). It can also result in high pressure drop, and an increase in silica passage (and perhaps other ions) into the permeate. The key is controlling the issues associated with silica:

1. Elimination: eliminating silica through lime softening with magnesium chloride or magnesium hydroxide is very effective a reducing the concentration of amorphous silica and silicates.
2. Inhibition/dispersion: for parctical applications, antiscalants today are useful at silica concentrations of up to about 180–200 ppm, depending on the conditions, type, and manufacturer. Due to the co-precipitation with metals, the effective antiscalants should disperse silicates and amorphous silica, as well as other scales, such as calcium carbonate, that provide nucleation sites for silica scale, all at the same time. This can be a difficult task, so it is generally recommended that the typical RO system limits its concentrate silica concentration to about 180 ppm.
3. Concentration: limiting the concentration of silica in an RO system is another rather common method for dealing with silica. Reducing the recovery of the RO system to keep the concentrate concentration within saturation limits (either with or without an antiscalant) has been used successfully to deal with the problem of silica scaling on RO membranes. The disadvantage of this technique is that the waste flow from the RO system will increase at the lower recovery.
4. HERO™ Process: As described previously and in Chapter 16.5, the HERO process first removes hardness and then takes advantage of the very high solubility of silicates at high pH to allow for treatment of high silica feed waters without the formation of metal silicates.

7.8 Calcium Carbonate

Calcium carbonate scaling is perhaps the most common type of problem, with the possible exception of microbial fouling, that RO membranes experience. Fortunately, it is fairly easy to detect and handle. Basically, if the ion product (IP) of calcium carbonate in the RO reject is greater than the solubility constant (K_{sp}) under reject conditions, then calcium carbonate scale will form. If $IP < K_{sp}$, scaling in unlikely. The ion product *at any degree of saturation* is defined as:

$$IP = [cation]^a[anion]^b \tag{7.11}$$

where:

IP = ion product
[cation] = cation concentration
[anion] = anion concentration
superscripts:
a = quantity of cation within the salt
b = quantity of anion within the salt

The solubility product *at saturation* is defined as:

$$K_{sp} = [cation]^a[anion]^b \tag{7.12}$$

where:

K_{sp} = solubility product

Langelier Saturation Index (LSI) is used to determine the scaling potential of calcium carbonate. (Note that LSI is used up to about 4,000 ppm TDS; higher concentrations rely on the Stiff-Davis Saturation Index.) The LSI is calculated using the following formulas (note that the concentrate concentration is used to calculate the LSI, as this is where the concentrations of solutes is the greatest):

$$LSI = pH - pH_a \tag{7.13}$$

where:

$$pH_a = (9.30 + A + B) - (C + D) \tag{7.14}$$

where:

$A = (\log_{10}[TDS] - 1)/10$
$B = -13.12 \times \log_{10}(^{o}C + 273) + 34.55$
$C = \log_{10}[Ca^{2+}] - 0.4$, where $[Ca^{2+}]$ is in ppm as $CaCO_3$
$D = \log_{10}[alkalinity]$, where [alkalinity] is in ppm as $CaCO_3$

A positive LSI means that scaling is favored; a negative LSI means that corrosion is favored. It is desirable to keep the LSI near zero (or below) in the RO concentrate to minimize calcium carbonate scaling. This is usually accomplished by feeding acid to lower the pH or feeding an antiscalant (see Chapter 8.2.4). Care must be given if sulfuric acid is used to adjust the pH, as this may exacerbate sulfate-based scales, such as calcium sulfate, barium sulfate, and strontium sulfate.

Alternatively, antiscalants can be used to control calcium carbonate scale at LSI values as high as +2.0 to +2.5, depending on the specific antiscalants. However, membrane manufacturers' warranties require that the LSI be less than +1.8, even with antiscalant dosing. Thus, many applications will require adding both an antiscalant and acid to control calcium carbonate scaling.

Calcium also forms scales with fluoride, sulfate, and phosphate. The LSI will not help predict these scales; analysis of water quality, using the ion product and solubility constants, is required to determine the potential for scaling with calcium fluoride or calcium phosphate. Antiscalants currently available can address calcium fluoride and calcium sulfate scale; some also address calcium phosphate scale.

Scaled membranes exhibit lower productivity and lower salt rejection. This lower salt rejection is a function of the concentration polarization phenomenon (see Chapter 3.5). When membranes are scaled, the surface of the membrane has a higher concentration of solutes than in the bulk solution. Since the membrane rejects based on the concentration at the membrane surface, the passage of salts will be higher, due to scale on the membrane surface even though the absolute or true rejection of the membrane stays constant.

Calcium is removed from RO feed water using sodium softening, or reduced using lime softening (see Chapters 8.1.6 and 8.3, respectively). Dropping the LSI using acid is used to address calcium scaling without removing or reducing the concentration of calcium. Antiscalants are also used to address the issue without reducing the amount of calcium present (see Chapter 8.2.4).

7.9 Trace Metals—Barium and Strontium

Barium and strontium form sulfate scales that are not readily soluble. In fact, barium is the least soluble of all the alkaline-earth sulfates. It can act as a catalyst for strontium and calcium sulfate scales.[4] Analyses of the ion product with the solubility constants for barium and strontium sulfates is necessary to determine the potential for scaling with these species. If the ion product (IP) for barium sulfate exceeds the solubility constant, scale will form. Note that in the case of strontium sulfate, if IP > $0.8K_{sp}$, scaling is likely. However, the induction period (the time it takes for scale to form) is longer for these sulfate-based scales than it is for calcium carbonate scale.

Barium and strontium can be reduced in RO feed water using sodium softening (see Chapter 8.1.6). Antiscalant can be used to control or inhibit scaling without reducing the concentration of either species (see Chapter 8.2.4).

7.10 Chlorine

Polyamide, composite membranes are very sensitive to free chlorine (recall from Chapter 4.2.1 that cellulose acetate membranes can tolerate up to 1 ppm free chlorine continuously) while polyamide membranes cannot tolerate chlorine (4.2.2.2)). Degradation of the polyamide composite membrane occurs almost immediately upon exposure and can result in significant reduction in rejection after 200 and 1,000-ppm hours of exposure to free chlorine (in other words after 200–1,000 hours exposure to 1 ppm free chlorine). The rate of degradation depends on two important factors: 1) degradation is more rapid at high pH than at neutral or low pH, and 2) the presence of transition metals such as iron, will catalyze the oxidation of the membrane.

The mechanism of degradation is the loss of polymer crosslinking[17]. This results in the membrane polymer dissolving, similar to a nylon stocking when exposed to chlorine bleach. Damage is irreversible and will continue as long as the membrane is exposed to the oxidizer.

Chloramines also pose a risk to polyamide, composite membranes (see Chapter 8.5.2.1.2). Chloramines are virtually always in equilibrium with free chlorine. Although the tolerance of the FilmTec FT30 membrane to pure chloramines is 300,000 ppm-hrs, FilmTec still recommends that influent water with chloramines be dechlorinated prior to the membrane.[4] In most cases, ammonia is added to chlorine to generate chloramines. This leaves open the possibility that there is still some free chlorine available. The most successful chloramine applications seem to be found in wastewater systems with a resident concentration of ammonia, to which chlorine is added to make the chloramines.

Another note of caution with chloramines is the need for good pH control. If the pH gets up to 9, dissolved ammonia gas is present as $NH_3(g)$, which swells at least some polyamide composite membranes. This swelling can be enough to drop the salt rejection from 98% down to about 85%.[18] Dropping the pH back to about 7 converts the ammonia gas to ammonium ion, which does not swell the membrane and rejection returns to nominal.

The use of chlorine dioxide is not recommended for use with polyamide, composite membranes.[4] This is because free chlorine is always present with chlorine dioxide that is generated on site from chlorine and sodium chlorate (see Chapter 8.2.1.1). (Note that other formation techniques have been developed that do not rely on chlorine, which may improve on the compatibility of the membranes with chlorine dioxide. (see chapter 8.5.2.1.3))

Initially, polyamide composite membranes that have been degraded due to chlorine attack will exhibit a loss in flux.[4] This drop in flux is followed by an increase in flux and salt passage.

Chlorine can be removed from RO feed water using sodium bisulfite or carbon filtration (see Chapters 8.2.3 and 8.1.4, respectively). As discussed in Chapter 8.1.4, carbon in carbon filters can aide the growth of microbes so carbon filtration is typically not recommended for dechlorination of RO feed water unless the concentrations of organics is high enough to warrant its use, or if the dosage of sodium bisulfite is too low for accurate control.

7.11 Calcium

Besides calcium carbonate, there are three other calcium–based compounds that will scale RO membranes. These compounds are calcium sulfate, phosphate, and fluoride. Although there are no specified feed water guidelines for these compounds, they are worth investigating.

- Calcium sulfate is a sparingly-soluble salt. As with barium and strontium sulfate, the potential to scale with calcium sulfate is high when the ion product exceeds 80% of the solubility constant. Antiscalants or sodium softening to remove calcium can be used to control calcium sulfate scale.
- Calcium phosphate has become a common problem with the increase in treatment of municipal waste-water for reuse. Surface waters can also contain phosphate. Calcium phosphate compounds can also contain hydroxyl, chloride, fluoride, aluminum, and/ or iron. Several calcium phosphate compounds have low solubility, as shown in Table 7.3. Solubility for calcium carbonate and barium sulfate are also shown by comparison. The potential for scaling RO

Table 7.3 Solubility of calcium phosphate compounds as compared to calcium carbonate and barium sulfate.

Compound	**Formula**	**pK$_{sp}$**
Calcium Phosphate	$Ca_3(PO_4)_2$	28.9
Brushite	$CaHPO_4{\cdot}2H_2O$	6.68
Octacalcium Phosphate	$Ca_4H(PO_4)_3{\cdot}3H_2O$	49.6
Hydroxyapatite	$Ca_5(PO_4)_3OH$	57.74
Fluoroapatite	$Ca_5(PO_4)_3F$	60
Calcium Carbonate	$CaCO_3$	8.42
Barium Sulfate	$BaSO_4$	9.97

membranes with the calcium phosphate compounds listed in Table 7.3 is high and will occur when the ion product exceeds the solubility constant. This can occur at orthophosphate concentrations as low as 0.5 ppm. Sodium softening or antiscalants together with low pH help to control phosphate-based scaling.

- Calcium fluoride scale can form when the concentration of fluoride is as low as 0.1 ppm if the concentration of calcium is high. Scaling will occur when the ion product exceeds the solubility constant. Antiscalants or sodium softening can be used to control calcium fluoride scale.

Calcium has also been shown to affect the deposition of natural organic matter (NOM).[19] Work by Schafer et al., demonstrated that NOM in the form of humic substances deposit preferentially on hydrophilic membranes, such as polyamide-based membranes.[19] The presence of calcium resulted in high flux decline due to precipitation of primarily humic acids (due to their relatively low molecular weight and hence lower diffusion away from the membrane in the concentration polarization boundary layer). The higher the calcium concentration, the faster the flux declined.[20] Calcium binds to the acidic functional groups of NOM resulting in a compact fouling layer on the membrane surface. Bridging between deposited NOM molecules is enhanced in the presence of calcium, leading to additional compactness of the fouling layer.[20] Operation at low flux, low trans-membrane pressure, and high shear was shown to reduce the deposition of NOM on membrane surfaces and, therefore, fouling of the membrane.[19,20]

As described previously, calcium can be removed or reduced in RO feed water using sodium softening or lime softening (see Chapters 8.1.6 and 8.3, respectively).

7.12 Exposure to Other Chemicals

Exposure of a thin-film composite membrane to a variety of organic compounds can result in swelling or dissolution of the polysulfone microporous support layer.[21] Suspect chemicals include:

- Solvents: dimethyl formamide, dimethyl acdimide, n-methyl pyrrolidone, dimethyl sulfoxide, etc.
- Aromatic compounds: benzene, toluene, xylene, phenol, diesel fuel, gasoline
- Others: ketones, aldehydes, esters, strong ethers

Note that only low-molecular solvents such as alcohols (isopropanol and smaller) are acceptable.

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8

Techniques and Technologies

Adequate pretreatment is one of the fundamental keys to successful and cost-effective operation of an RO system. Pretreatment is designed to prevent or minimize membrane fouling, scaling and degradation of membrane performance and materials. This chapter covers mechanical and chemical techniques and technologies that are commonly used to pretreat RO systems. Also included in chapter 8.5 which is a detailed discussion about membrane biofouling and materials to minimize membrane biofouling.

Figure 8.1 Shows the projected performance of an RO membrane system with ideal, marginal and inadequate pretreatment.[1] After an initial period over which time new membranes stabilize performance, a system with ideal performance will show only a slight decline in performance with time due to compaction and the inevitable fouling and scaling that will occur despite good pretreatment and system hydraulics. Marginal pretreatment exhibits more rapid decline in performance than the system with ideal pretreatment. Initial cleaning may be able to revive most of the performance, but after time, foulants and scale that were not removed become irreversibly attached to the membrane and cannot be cleaned away. The RO system

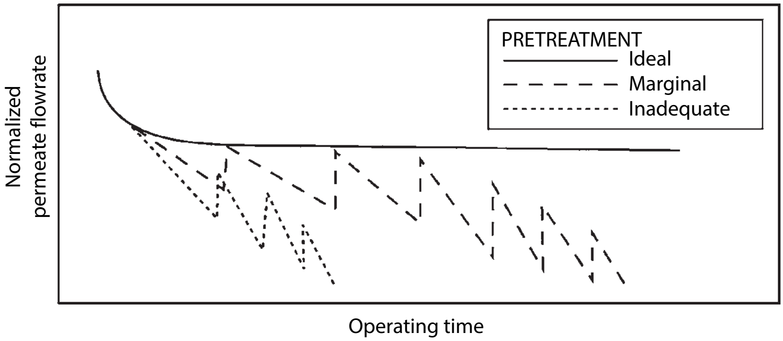

Figure 8.1 Projected performance of an RO system as a function of the quality of feed water pretreatment.

with inadequate pretreatment will show very rapid decline in performance that typically cannot be recovered by cleaning the membranes. An RO system with less than ideal pretreatment faces frequent cleaning intervals and short membrane life. Frequent cleaning and membrane replacement costs money, time, and the environment.

Once optimized, the pretreatment system must be continuously evaluated and re-optimized to adjust to changes in performance of each unit operation, due to mechanical difficulties or changes in the influent water quality.

Pretreatment techniques and technologies can be categorized into three general types:

- Mechanical
- Chemical
- Mechanical plus chemical

Appropriate pretreatment techniques and/or technologies for a given RO application need to be selected based on the quality of the influent water to be treated by RO. Some water, such as well water with low concentrations of iron and manganese, may require very little, if any, pretreatment, while other water, such as river or lake water, may require extensive pretreatment using sequenced techniques and technologies.

Obtaining historical influent water quality data as well as pilot testing of proposed pretreatment unit operations are both good practice in designing and optimizing the pretreatment system.

8.1 Mechanical Pretreatment

Mechanical pretreatment involves physical techniques to reduce turbidity, suspended solids, SDI, bacteria, hardness, and heavy metals present in RO influent water. Table 8.1 lists some mechanical treatments and what species they will treat. It is important to reduce or eliminate these species from RO influent water to minimize fouling and scaling of the membranes.

8.1.1 Clarifiers

Clarifiers are used to remove large suspended solids, colloids, organics, and color from surface water supplies. Coagulation and flocculation using chemical treatments, and sedimentation or "settling" are the three primary steps used to achieve reduction of contaminants. However, the typical effluent quality from a clarifier is not low enough in turbidity and suspended solids to send directly to an RO. Still, clarification is a good bulk removal technology for reducing the majority of suspended solids and turbidity. Multimedia filtration is generally required to polish clarifier effluent to reduce the turbidity (and SDI) so that it is low enough to meet RO influent standards. See Chapter 7 for more information about RO influent water specifications.

Table 8.1 Mechanical RO pretreatment techniques and species that these techniques address.

Mechanical Pretreatment	Species Addressed
Clarification	Suspended solids, Colloids, Organics, Color, SDI
Multimedia Filtration	Turbidity, Suspended solids down to 2–10 microns, SDI
High-Efficiency Filtration	Suspended solids down to 0.25 microns
Carbon Filters	Total organic carbon, Chlorine
Iron Filters	Iron, Manganese, Hydrogen sulfide
Sodium Softeners	Hardness, Soluble iron
UV Radiation	Organics, Microbes
Membrane	Microbes, Algae, Color

There are three basic designs for clarifiers (also known as “gravity clarifiers”): solids-contact, inclined-plate settlers, and sedimentation. The advantages of each type of unit are:

- Solids contact: lowest chemical demand and higher effluent quality
- Inclined-plate: smallest footprint
- Sedimentation: least sensitive to fluctuations in influent flow rates—typically used for wastewater treatment.

All designs share some common design characteristics:[2]

- Rise Rate: Rise rate of water is the flow rate (total hydraulic load) divided by the surface area of the clarifier. Most clarifiers operate between 0.75 gpm/ft^2 and 1.25 gpm/ft^2, with the exceptions of inclined-plate settlers, which operate at higher rise rates, as high as 2.0 gpm/ft^2 and the Actiflo® recirculation clarifier which operates at a rise rate of at least 16 gpm/ft^2 (Actiflo is a registered trademark of Veolia Water North America, Chicago, IL).
- Rapid Mix Zone: This is the area of the clarifier (or just immediately prior to the clarifier) where coagulation takes place.
- Slow Mix Zone: This is the area of the clarifier where flocculation takes place.
- Rake: The purpose of the rake is twofold: direct the settled solids to the blowdown and to control the character of the sludge bed. High rake speed results in a fluffier bed while low speed hinders the contact between newly-formed floc (agglomerated suspended solids) and the bed. Note that most inclined-plate clarifiers do not have this feature.
- Sludge Bed: The sludge bed provides filtering for floc, thereby improving the effluent quality. The height of the bed depends on the specific clarifier design, the type of chemical treatment program used, and the operating protocol.

8.1.1.1 Solids-Contact Clarifiers

Solids-contact clarifiers (also known as “upflow” clarifiers) typically have four treatment zones:

- Rapid mix zone: sludge is recirculated to this zone to improve coagulation,

- Slow mix zone: this is the zone where particle flocculate and settle,
- Sedimentation zone: the sludge bed forms in this zone,
- Clarifier water zone: this zone is where the clarified water exits the unit.

Solids-contact clarifiers may be circular or rectangular in design. Typical rise rates for circular clarifiers range from about 0.75–1.25 gpm/ft^2; residence time is about one to two hours. In the rectangular Actiflo® clarifier, rise rate is significantly higher, as described above, which yields a higher throughput for this type of clarifier. As a result, the residence time is shorter and the footprint is significantly smaller for an Actiflo® than that of a conventional circular clarifier.

Solids-contact clarifiers are characterized as either recirculation or sludge blanket clarifiers (Figures 8.2, 8.3 and 8.4). In a circular recirculation clarifier, high floc volume is maintained by recirculation from the slow mix zone to the rapid mix zone. In the rectangular Actiflo® recirculation clarifier, microsand is recirculated through the unit to provide a ballast for flocs formed during the coagulation stage. The sand acts as a seed for floc formation and provides weight to speed settling of the floc. The clarification tank is fitted with lamella to speed the settling of the microsand-ballasted sludge (see Chapter 8.1.1.2 for more discussion about lamella used in

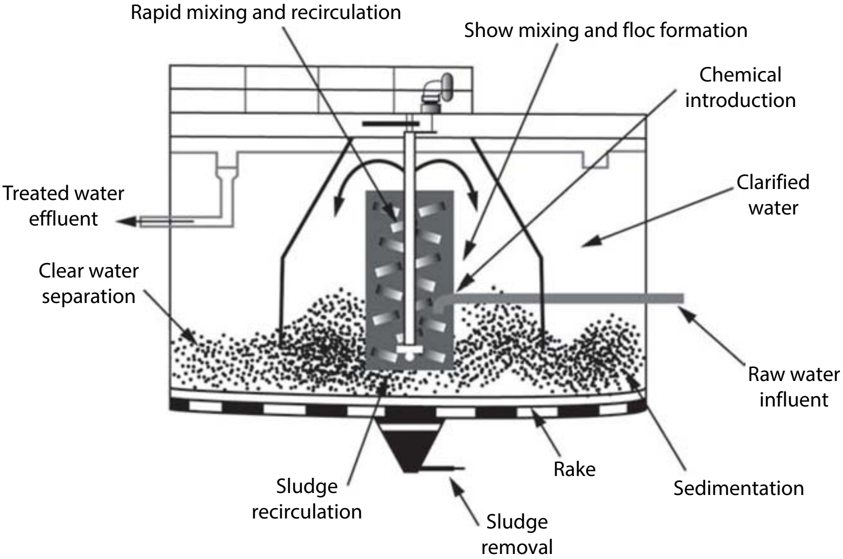

Figure 8.2 Recirculation solids-contact clarifier. *Courtesy of Ecodyne Limited.*

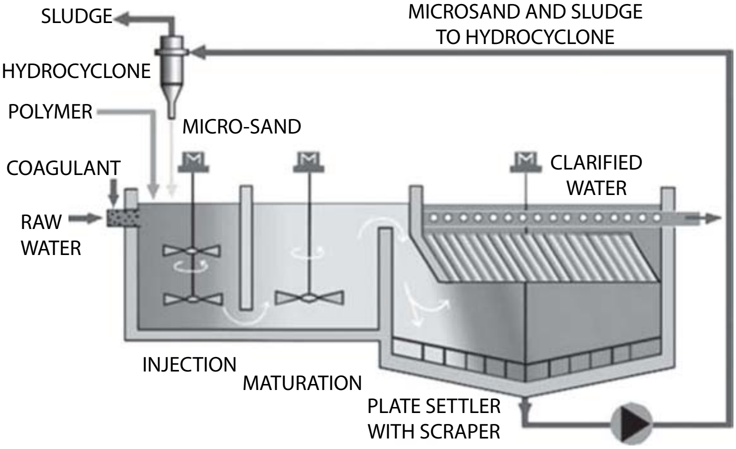

Figure 8.3 Actiflo® rectangular recirculation clarifier. *Courtesy and registered trademark of Veolia Water North America, Chicago, IL.*

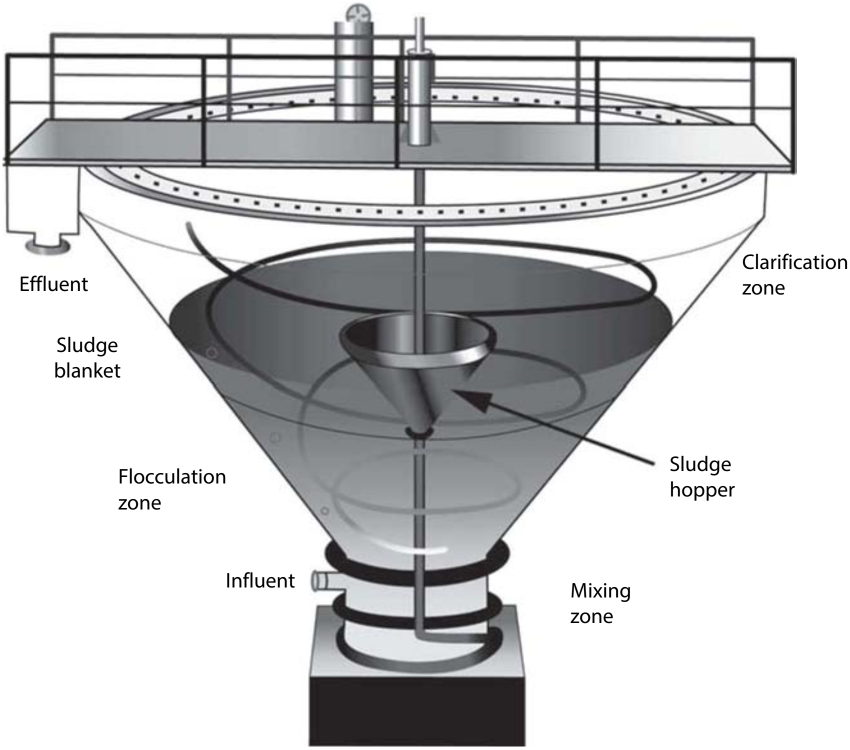

Figure 8.4 Spiracone® sludge-blanket clarifier. *Courtesy and registered trademark of Siemens Water Technologies Corp., Warrendale, PA.*

clarifiers). Finally, with a sludge blanket clarifier, high floc solids are maintained by flowing water through a fluidized blanket of solids.

8.1.1.2 Inclined-Plate Clarifiers

Inclined plate clarifiers, also known as Lamella® clarifiers, use several inclined plates (or sometimes tubes) to maximize the settling area for a given floor area (Lamella is a registered trademark of Parkson Corporation, Ft. Lauderdale, FL). Figure 8.5 shows a diagram of an inclined-plate clarifier.

Inclined-plate clarifiers have five treatment zones:

- Flash mix tank: coagulant is feed in this rapid-mix zone
- Flocculation tank: flocculants are fed in this tank

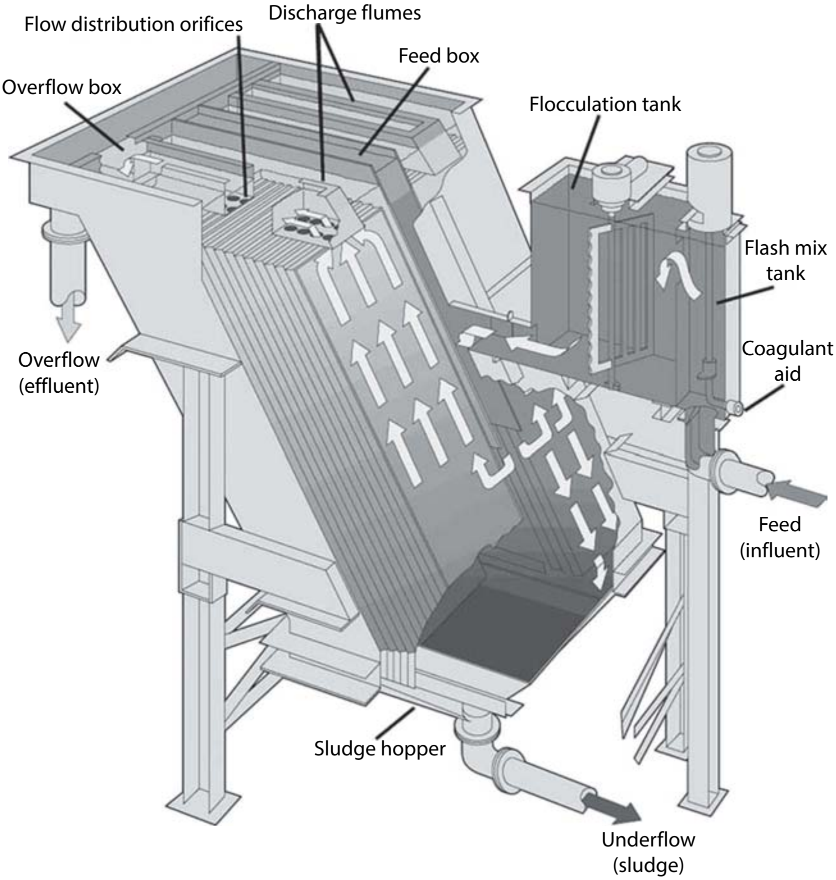

Figure 8.5 Inclined-plate clarifier. *Courtesy of Parkson Corporation.*

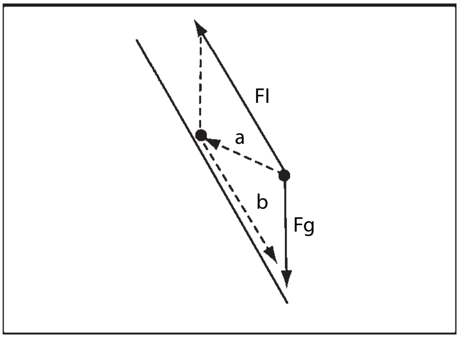

Figure 8.6 Particle motion in a lamella clarifier, where Fl is the convective flow force vector and Fg is the gravitational force vector. Particles first move toward the lamella (a) and then move toward the sludge zone (b).

- Settling zone: plates (or tubes) on which the solids settle,
- Outlet (Overflow) zone: this is where clarified water exits the unit,
- Sludge (Underflow) zone: area where sludge collects and exits the unit

Rise rate is about 2.0 gpm/ft^2 in an inclined plate clarifier.

The plates or "lamella" collect solids. The incline of the plates is a function of the density of the solids; typical set point is about 55^o from horizontal. The settling distance varies from a few inches to a maximum of a few feet, unlike conventional clarifiers, where the settling distance can be several feet. Figure 8.6 shows how the particles between the lamella plates migrate to the plate surface (a) following the resultant vector of the fluid drag (Fl) and gravity (Fg) forces. Once on the plates, the particles slide down to the sludge zone (b).

The advantages of this arrangement over conventional, circular clarifiers include:

1. the footprint of the system is much smaller
2. the plates minimize sludge carry over
3. the unit is ready to start up and stop at any time without operational delays
4. the unit provides high efficiency separation with minimum-density floc
5. the unit exhibits, good performance in low-turbidity water, with dirty-water recycle

8.1.1.3 Sedimentation Clarifiers

Sedimentation clarifiers are generally used for secondary clarification of wastewater. They are characterized by having four treatment sections:

- Inlet zone: coagulant is fed into the influent of this mixing zone,
- Settling zone: this is the zone where particles settle,
- Outlet zone: Weirs direct effluent out of the clarifier,
- Sludge zone: This zone is where solids settle, and are collected for removal.

Sedimentation clarifiers may be circular or rectangular in configuration. In a circular sedimentation clarifier, the influent enters into the center or the perimeter ("peripheral feed") of the unit. In a center-fed unit, the effluent water is collected in the perimeter. It is difficult to control the recirculation in a perimeter-fed unit, and hence, is not common. In a rectangular sedimentation unit, the flow is linear. Rise rate is about 1 gpm/ft^2 with a residence time of two to six hours.

8.1.1.4 Chemical Treatment for Clarifiers

The settling rate of particles in a clarifier follows Stoke's Law:

$$V = \frac{2gr^2 (d_1 - d_2)}{9\mu} \tag{8.1}$$

where
V = settling rate
g = gravity constant
r = particle radius
d_1 = particle density
d_2 = liquid density
μ = liquid viscosity

As shown in the equation, the settling rate of a particle depends on the square of the radius: the larger the particle, the faster it will settle, and the settling rate grows exponentially with the particle size.

Chemical addition is typically used with clarification to improve both the utility and performance of the unit operation. Coagulants and flocculants are generally used to improve the ability to settle particles in the clarifier by increasing the size of the particle. Jar tests are used to determine the proper dosage of chemicals and streaming current detectors or turbidity monitors are used to monitor performance and control chemical dosage. Chlorine is often used to improve the removal of organics and color in the clarifier. Chlorine also provides disinfection of the make-up water to prevent the clarifiers from going septic.

8.1.1.4.1 Coagulation

Coagulation involves using cationic compounds to charge neutralize the net negative charge of suspended particles in water. Charge neutralization of the net negative charge on particles allows the particles to move closer together in anticipation of creating larger particles that settle faster as shown by Equation 8.1. Coagulation requires rapid mixing and occurs immediately upstream or in the influent well of the clarifier, depending on design.

Coagulants can be inorganic salts or organic compounds. Inorganic salts include aluminum sulfate (alum), ferric sulfate, and ferric chloride. Organic polymers used for coagulation such as polyamines and poly (diallyl-dimethyl-ammonium chloride), commonly known as poly-DADMACS, are generally lower-molecular weight (<500,000), high-charge cationic polymers.

The performance of inorganic coagulants depends on pH. The performance of alum is optimum at pH 6.0–7.0 (with an optimum at pH = 6), while ferric coagulants can be used over a broader pH range, from 5.0–11.0 (with an optimum at pH = 8).

The performance of polymeric coagulants depends on the amount of turbidity present in the water. At less than 10 NTU, an inorganic or combination inorganic/organic polymer is preferred. At 10–60 NTU, a combination of inorganic and organic coagulants are generally used. At greater than 60 NTU, a polymeric coagulant alone is sufficient.

Caution must be used whenever coagulants are used upstream of an RO due to the potential for fouling the membrane with the coagulant its constituents. Alum and ferric carryover is common and the aluminum and iron will foul the RO membranes. Under conditions of poor pH control or high surface water turbidity, high doses of alum can result in post precipitation of aluminum. Aluminum hydroxide is difficult to remove through filtration and will foul RO membranes. Operators of RO systems that are located downstream of an alum feed need to be extra vigilant in monitoring membrane performance for signs of fouling. Membranes need to be cleaned when normalized product flow or pressure drop data indicate that performance has dropped by 10% to 15% from start-up (see Chapter 13.2.1).

Cationic polymeric coagulants have a natural affinity for the negatively-charged polyamide composite membranes, leading to irreversible fouling of the membrane. Therefore, overfeed and carryover of polymeric cationonic coagulants must avoided by carefully monitored the application of such coagulants. Additionally, cationic polymers can co-precipitate with negatively-charged antiscalants and further foul an RO membrane.

8.1.1.4.2 Flocculation

Flocculation is the agglomeration of charge-neutralized particles into larger particles. Unlike coagulation, rapid mixing is not required for flocculation to take place. It typically occurs in the reaction chamber or “slow mix” zone of the clarifier.

In general, very high molecular-weight, anionic polyacrylamides are the most effective flocculants. Some flocculation success may occur using non-ionic polymers. Typical anionic flocculants are 1,000,000 to 2,000,000 molecular weight, while non-ionics can be up to 20,000,000 molecular weight. Flocculants, due to their anionic or non-ionic nature, do not cause the same degree of fouling of negatively-charged polyamide composite membranes that cationic coagulants do, but overfeed can lead to organic fouling of the membranes by the flocculant polymer that can usually be removed if addressed in a timely manner.

8.1.1.4.3 Chlorine

Chlorine is usually added upstream of a clarifier to oxidize organics, to improve the removal of color in the clarifier, and to control microbial growth in the clarifier and downstream equipment. Chlorine along with an alum feed at pH 4.5 to 5.5 is optimum for color removal. This is important for RO pretreatment, as color can irreversibly foul a polyamide composite membrane (see Chapter 8.2.1.1 and 8.5.2.1.1 for a more detailed discussions about chlorine for RO pretreatment).

8.1.2 Multimedia Pressure Filters

Multimedia pressure filters are designed to reduce turbidity and some colloids (measured as SDI) in water. These filters can remove particles down to about 10 microns in size. If a coagulant is added to the filter influent stream, reduction of particles down to 1-2 microns can sometimes be accomplished. Typical removal efficiency for multimedia pressure filters is about 50% of particles in the 10–15 micron size range. Influent turbidity for RO pretreatment is limited to about 10 NTU. At turbidity greater than 10 NTU, these filters may backwash too frequently to provide consistent effluent quality at reasonable run lengths.

Multimedia pressure filters contain graduated layers of anthracite on top of sand on top of garnet. Figure 8.7 shows a cross section of a multimedia

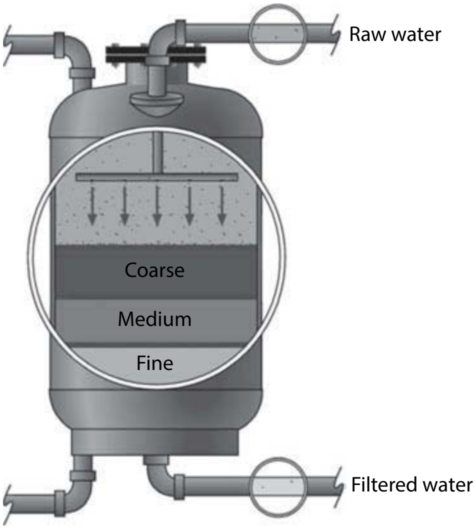

Figure 8.7 Multimedia pressure filter showing coarse, medium and fine media, typically anthracite, sand, and garnet, respectively.

filter. The fine garnet material is denser than the coarse anthracite material. There is no discrete boundary between each of the layers; there is a gradual transition from one material density and coarseness to the next. Otherwise, there would be a build up of particles at each interface. Particles are subsequently removed through the filter using physical entrapment. Larger particles are removed on top through the anthracite, while smaller particles are subsequently removed through the sand and garnet. Multimedia filters offer finer filtration than dual media (anthracite and sand) filters due to the relatively fine nature of the additional garnet.

Service flow rates for RO pretreatment should be about 5 gpm/ft^2 of media. Throughput can be estimated using a filter about 0.45 lb of suspended solids per square foot of filter loading of area. Backwash rates should be 15 gpm/ft^2 at 60°F. Lower water temperatures require higher flow rates to adequately raise the bed for a complete backwash. A 30–50% bed expansion is necessary to achieve good backwashing of the media. Raw, unfiltered water can be used for backwash. Alternatively, a filtered product tank can be provided that also acts as a reservoir for backwash water. Some operators choose to recover RO reject by using this water to backwash filters. However, for best results, use of RO reject water to backwash a multimedia filter is not recommended. In some applications where there is heavy use of coagulants, an air scour during backwash is recommended.

An air scour involves air that is bubbled up through the bed to help release some stubborn solids from the media.

Multimedia pressure filters operate best when they are continuously on line. When multiple filters are required, all filters will be on line except during backwash, when only one filter is off line for backwashing. During backwash of one filter, the remaining filters on line will handle the full influent flow rate. To achieve the 5 gpm/ ft^2 design flux as an average service flow rate, the diameter of the filters should be such that when all filters are on line, the flux is slightly less than 5 gpm/ft^2, and during backwash of one filter, the flux through the remaining filters on line should be less than about 7.5 gpm/ft^2.

Multimedia pressure filters can be vertically or horizontally oriented. Figure 8.7 shows a vertical filter while Figure 8.8 shows a horizontal multimedia pressure filter. Horizontal multimedia filters are separated internally into “cells” or compartments. Each cell acts as an individual filter. When it is time to backwash one of the cells, the effluent from the other cells provides the backwash water. The key in selecting horizontal filters is that the filter should have enough internal cells so that productivity (required effluent flow rate plus the flow rate needed to backwash one tank) can be maintained even when one cell is in backwash. Given the design of a horizontal filter, effluent from all tanks is combined and a portion of this total becomes backwash water for one tank. Horizontal filters are used for higher flow rates, as the footprint for the horizontal filters is smaller than that for several vertical filters for the same throughput.

Figure 8.8 Horizontal multimedia pressure filter with 4 internal cells. *Courtesy of Siemens Water Technologies Corp.*

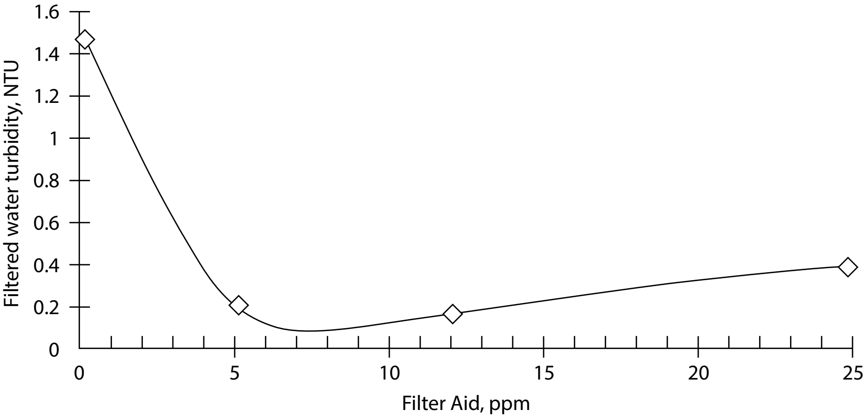

Figure 8.9 Effect of filter aid dosage on effluent turbidity from a multimedia pressure filter. Too little cationic coagulant feed does not charge neutralize the net negative charge on the particles thereby not reducing turbidity enough. Too much cationic coagulant changes the charge surrounding the particles from a net negative to a net positive, resulting in charge repulsion and higher effluent turbidity.

Multimedia pressure filters can be used as stand alone treatment, when the feed sources is relatively clean water, such as a potable municipal supply, or in series with clarification, for river and other surface waters.

Multimedia pressure filters can be used in conjunction with filter aids (typically polymeric coagulants) to increase the removal efficiency of the media. In essence, the coagulant "bridges" particles to overcome the net surface negative charge to allow them to agglomerate so that they are more easily removed by the filter media. There is an optimum dosage of filter aid at which the turbidity removal is optimum. Too much or too little filter aid will decrease the performance, as shown in Figure 8.9. The optimum dosage is found empirically for each application, with ranges from about 3–10 ppm for inorganic coagulants and 0.25–2.0 ppm for organic and inorganic/organic blends. Higher dosages will result in swinging the net negative charge on the particle to a net positive charge which will also result in particles repelling each other.

8.1.3 High-Efficiency Filters

High-efficiency filters (HEF) are pressure filters designed to remove turbidity and SDI in water. They were originally applied to cooling towers, to reduce the concentration of suspended solids in those systems.

Table 8.2 shows a typical cooling water particle size distribution. As seen in the table, nearly 98% of all particles are smaller than 1.0 microns,

Table 8.2 Typical cooling water particle size distribution.

Size (micron)	**Particle Count**		
	Per 100ml	**Percent of Particles in this Size**	**Cumulative Percent of all Particles**
0.5–<1.0	30,277,895	97.7	97.7
1.0–<5.0	614,664	2.0	99.7
5.0–<10	72,178	0.2	99.9
10–<15	21,561	0.1	100.0
15–<20	8,186	0.0	100.0
>20	5,765	0.0	100.0
Total	31,000,249	100.0	100.0

and greater than 99% of all particles are smaller than 5 microns. Recall that multimedia filters were only about 50% efficient at 10–15 microns. By comparison, HEFs can remove 50% of particles a small as 0.25 microns in size.

There are two basic HEF designs, the top-over-bottom design and the vortex design. Figures 8.10 and 8.11 show cross sections of each of these types of HEFs.

Vortex filters use centrifugal force to swirl raw water above the surface of the media in a cross-flow manner. Large suspended solids are collected on the sidewall of the filter tank. The smaller solids drop down to the surface of the fine sand media and are filtered out through this media. When the pressure drop reaches about 15 psig, the vortex filters are backwashed.

Vortex filters operate at high flow rates, typically 15 –20 gpm/ft^2. Backwash flow rate is about 2.5–5 gpm/ft^2 and requires only 4–8 minutes of backwash time.

Vortex filters supplied by Sonitec, Inc., ("Vortisand®" filters—Vortisand is a registered trademark of Sonitec, Inc., Holyoke, MA) come complete with a chemical cleaning system. This system is used every 3–8 backwash sequences to reduce filter media fouling and maintain filtration effectiveness. Dispersants are typically used in the spring when high run off can result in fouling of the filter media with silt. Chlorine is necessary during the summer and fall to reduce biofouling.

Top-over-bottom HEFs rely on tangential flow across the surface of the media to affect filtration. Raw water enters the filter tangentially to the surface of the media, thereby creating turbulence over the bed and a

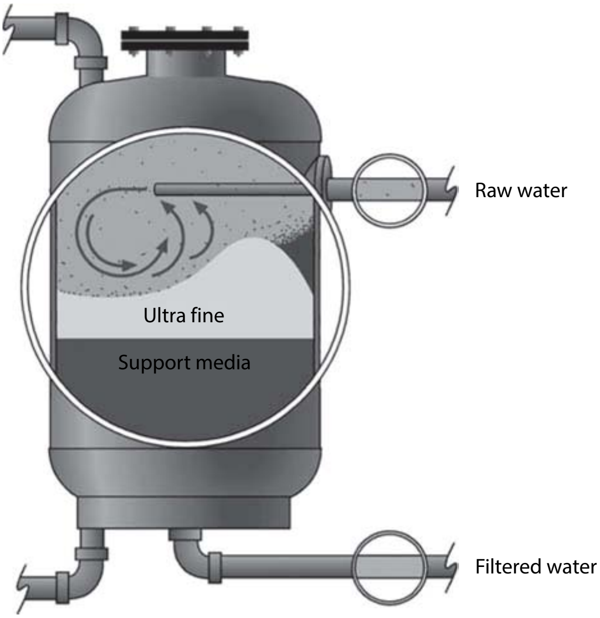

Figure 8.10 Top-over-bottom high efficiency filter.

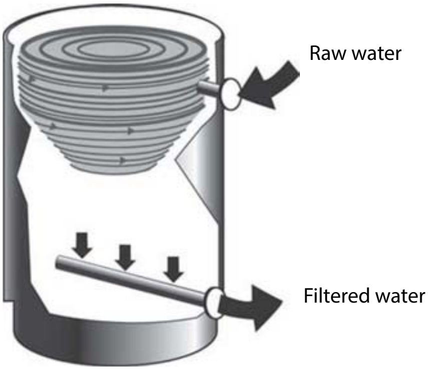

Figure 8.11 Vortex high efficiency filter. Courtesy of Sonitec, Inc.

tangential force that scrubs suspended solids off on to the surface of the media. The tangential force also causes some of the sand in the filter bed to collect near the inlet of the filter into what looks like a "camel hump." Solids that have been swept off of the filter surface collect behind this hump, as this area, right underneath the inlet to the filter, is an area of low

Table 8.3 Performance comparison of multimedia and high-efficiency filters as used FG for RO pretreatment.

Parameter	**MMF**	**HEF**
Service flow, gpm/ft^2	5	10–15
Max differential pressure, psig	15–25	18
Capacity, lb/ft^3	0.45	NA
Inlet turbidity, NTU	10*–30	1–200
Backwash flow rate, gpm/ft^2	15	10
Backwash time per backwash, minutes	30–60	5

* Maximum turbidity for RO pretreatment

N/A = not available

turbulence. Solids continue to collect here until they spill over the hump on to the high-turbulent area of the bed. As more solids collect on the turbulent side of the filter bed, the pressure drop through the filter increases. When the pressure drop reaches about 18 psig, the filters should be backwashed. Note that the filters should be backwashed at least once per day to avoid fouling of the bed.

Top-over-bottom HEFs operate at lower flow rates, than vortex filters, typically as 10–15 gpm/ft^2. Backwash flow rate is about 10 gpm/ft^2 at about 5 minutes per backwash.

Table 8.3 compares performance parameters or multimedia pressure filters (MMF) and HEFs. The higher throughput of HEFs reduces the footprint of the system required when compared to multimedia filters as used for RO pretreatment. Also, the lower backwash flow requirements for HEFs leads to less waste water to dispose of and smaller backwash components on these filters.

High-efficiency filters are gaining in acceptance for RO pretreatment.[3] These filters offer some advantages over conventional multimedia filters, the most important of which may be the ability to remove particles down to 0.25 microns in size for the top-over-bottom filters, and 0.45 microns for the vortex filters.

The downside of HEF is that some solids, particularlly those that are organic in nature or loosely held, can actually break apart due to the high velocities in the filter and quater smaller particles that are not removed in the filter. These particles will increases the SDI Hence, pilot testing is recommended.

8.1.4 Carbon Filters

Activated carbon filters are used to reduce the concentration of organics in RO feed water. These filters are also used to remove oxidants such as free chlorine from RO feed water.

Activated carbon is derived from natural materials such as bituminous coal, lignite, wood, fruit pits, bones, and coconut shells, to name a few. The raw materials are fired in a low oxygen environment to create char, which is then activated by steam, carbon dioxide or oxygen. For most industrial applications, bituminous carbon is used. This is because of the smaller pores size, higher surface area, and higher density than other forms of carbon give bituminous carbon higher capacity for chlorine. Carbon can also come in one of 3 forms: powdered (PAC), extruded block (CB), and granular (GAC). Most industrial applications used GAC as this is the lowest cost of the 3 types of carbon media and this type of carbon can be reused.

All carbon is characterized by high surface area. A gram of carbon can have surface area in excess of 500m^2, with 1,500 m^2 being achievable.[4] High surface area is necessary for reduction of organics and chlorine within reasonable contact time.

Chlorine and other oxidants are removed using activated carbon by an oxidation/reduction reaction. Chlorine oxidizes the carbon while the chlorine is being reduced. Chlorine ends up forming hydrochloric acid via equation 8.2.

$$Cl_2 + H_2O + C^* \Rightarrow 2HCl + C^*O \tag{8.2}$$

where:
C* = carbon
C*O = oxidized carbon

The reaction in equation 8.2 is virtually instantaneous. Effluent concentrations of chlorine are typically less than 0.05 ppm, which is adequate quality for feed to a downstream RO.

Activated carbon can also be used for chloramine removal, but the reaction time is much longer, about 5–10 minutes in a new bed and up to 30 minutes in a bed near equilibrium. The reaction with chloramine is a two-step process:

$$NH_2Cl + H_2O + C^* \Rightarrow NH_3 + HCl + C^*O \tag{8.3}$$

$$2NH_2Cl + C^*O \Rightarrow N_2 + 2HCl + H_2O + C^* \tag{8.4}$$

Note that the carbon filtration removal of chloramines leaves behind some residual ammonia. Recall from Chapter 3, Table 3.2, that ammonia as the gas is not rejected by polyamide RO membranes. The pH of the solution must be below about 7.5 for the ionized form of ammonia (ammonium) to be present in much greater proportion than ammonia gas. Furthermore, ammonia gas swells the RO membrane leading to lower rejection of dissolved solids by the membrane. See Chapter 8.2.1.1 and 8.5.2.1.2 for more discussions about chloramines.

The removal of organics (typically measured by total organic carbon or TOC), is an adsorption process. The surface of activated carbon is both hydrophobic and oleophilic, conditions favorable for good removal of TOC. The capacity for organics is a function of temperature, pH, nature of the organic, and concentration such that accurate capacity predictions are not possible. In general, typically 25% to 80% of TOC is removed through a carbon filter.

The iodine and molasses numbers are used to determine the capacity of carbon for micro- and macro-molecules, respectively. Iodine number is a measure of the micropore (0 to 20 angstroms) content of the carbon. It is equivalent to about 900 to 1,100 m^2/g. Typical range for iodine number is 500–1,200 mg/g. A high number indicates a greater capacity for small molecules. The molasses number is a measure of the macropore (greater than 20 angstroms) content of the carbon. Typical range for molasses number is 95–600, with higher numbers indicative of a higher adsorption capacity for large molecules. Note that the European molasses number is inversely related to the North American molasses number.

Carbon filters are not designed to remove suspended solids or bacteria. In fact, carbon filters encourage the growth of bacteria, with the organics removed through the media providing nutrients for the microbes.[4,5] This invites caution when using carbon for pretreatment prior to RO. Further carbon fines are continuously sloughing off of the bed. These fines that may be infected with bacteria, they can get into the RO system and can foul the membranes. Periodic servicing of the carbon by hot water or steam sanitization is required to destroy bacteria in the bed. Note that using carbon as an oxidant removal mechanism does not eliminate or reduce the need to service the carbon unit for biofouling.

Carbon filters have the following influent water requirements to assure optimal operation of the filter:

- Turbidity < 5 NTU
- Free chlorine: <10 ppm
- TOC: <5 ppm

Service flow rates for carbon filters when used to pretreat RO feed water are as follows:

- TOC removal: 1 gpm/ft^3
- Chlorine removal (pre RO): 2 gpm/ft^3

The filters are backwashed occasionally to remove any suspended solids that may have accumulated on the surface of the bed. Backwashing does not remove material adsorbed in the pores of the carbon. Although a few installations regenerate their carbon using thermal, steam, solvent extraction, or other techniques, most applications see replacement of carbon when exhausted. Typical "life" of carbon used for TOC removal is 6–12 months. For chlorine removal, the typical "life" is 12–18 months.

Carbon filters were once the standard method for removing chlorine from RO influent water. However, due to the microbial fouling that occurs downstream of a carbon filter, the current primary RO application is for the reduction of TOC only.

8.1.5 Iron Filters

Many well waters contain soluble iron, manganese, and hydrogen sulfide that oxidize in the presence of oxygen or chlorine to form insoluble hydroxides and metal sulfur compounds, all of which foul RO membranes.[5] Manganese dioxide media is used to oxidize and filter out the oxidized metals. Specifically, manganese greensand and alternatives such as BIRM® (sometimes called better iron removal media) and pyrolusite, are three types of media containing manganese dioxide that are used to oxidize and filter iron, manganese and the like (BIRM is a registered trademark of Clack Corporation, Windsor, Wisconsin). Table 8.4 compares properties of these media. As the table shows, pyrolusite contains the most manganese dioxide and has the longest life expectancy of the media. Table 8.5 compares some additional properties of pyrolusite, BIRM®, and manganese greensand media.

8.1.5.1 Manganese Greensand Filters

Manganese greensand has been used in the United States since the 1920's. Manganese greensand is a natural zeolite with an exchange capacity of about 3,000 grains/ft^3. It was used extensively for softening applications until the development of synthetic gel-type resins following World War II. It is commonly known as New Jersey greensand and is derived from glauconite (an iron-potassium-silicate zeolite of marine origin). Stabilized glauconite is coated with manganese oxide in various valence states. It is the coating that provides the oxidative properties of the material.

Manganese greensand requires the use of oxidizers to aid in the oxidation and removal of iron, manganese, and hydrogen sulfite. Iron can be removed with the use of chlorine as the oxidizer. Manganese removal via

Table 8.4 General properties of manganese greensand, Greensand Plus™ BIRM®, and pyrolusite.

Parameter	**BIRM®**	**Manganese Greensand**	**Greensand Plus™**	**Pyrolusite**
Optimal Operational pH	6.5 for iron 8–9 for manganese	>6.8	6.2–8.8	5.0–9.0*
Hydrogen Sulfide Removal	Not compatible	OK	OK	OK
Feed Water Turbidity	<10 NTU	<4 NTU	NA	NA
Flow Rate, gpm/ft²	4			
Typical		3–5	3–5	7–8
Range		2–12	5–12	5–15
Minimum Bed Depth, in	30–36	24	20–24 + 15 anthracite OR 30 for single media	24**
Backwash, gpm/ft²				
Without air scour	12	12 @ 55°F	12 @ 55°F	25–30 @ 60°F
With air scour	NR	NR	NR	15 @ 60°F
Typical Service Life, yrs	1	5	5	10

NA = not available

NR = not recommended

*LayneOx

**DMI-65

manganese greensand requires the use of potassium permanganate to adequately oxidize the metal.

Manganese greensand can become exhausted and therefore, require regeneration. Regeneration can be on a continuous or intermittent basis. For continuous regeneration without manganese present, iron can be removed with 1 ppm of chlorine per ppm of iron. For iron and manganese

Table 8.5 Technical properties of BIRM®, manganese greensand, Greensand Plus™ and Pyrolusite.

Specification	**BIRM®**	**Manganese Greensand**	**Greensand Plus™**	**Pyrolusite**
Manganese Dioxide %	<0.01	0.5	NA	80
Base Material	NA	Glauconite	Sand	Manganese Dioxide
Color	Black	Black	Black	Grey-Black
Form	NA	Granular	Granular	Granular
Screen Size, mesh	9 × 35	18 × 60	18 × 60	8 × 20*
Density, lb/ft^3	44–50	85	88	120*
Effluent Quality, ppm	NA	0.1 or 98% reduction	0.1 or 98% reduction	0.05*
Influent TDS Limit, ppm	NA	850	NA	>1100
Removal Capacity, grains	NA			NA
➢Iron		550	585	
➢Manganese		400	292	
➢Hydrogen Sulfide		175	117	
Feed Water Limit, ppm		NA	NA	
➢Iron	10			27**
➢Manganese	5			11**
➢Hydrogen Sulfide	0			17**
Preconditioning	No	Yes	Yes	No

NA = not available

NR = not recommended

*LayneOx

**Filox

removal, the potassium permanganate demand is about 1 ppm per 1 ppm of iron plus 2 ppm per 1 ppm of manganese (pH should be greater than about 7.5 for optimum manganese oxidation). For intermittent regeneration, the dosage of potassium permanganate should be 1.5–2.0 ounces per cubic foot of media.

Effluent concentrations of iron and manganese are limited to 2% of the influent concentration (98% removal) or 0.1 ppm iron, whichever is greater.

Greensand is a relatively soft material that can crush at service flow rates as low as 5 gpm/ft^2. Ten States Standards (Great Lakes-Upper Mississippi River Board) require a flow rate of no greater than 3 gpm/ft^2 to minimize damage to the medium.[6] Thus, in practice, the useful flow rate for service is 2–5 gpm/ft^2.

Manganese greensand filters are periodically backwashed to remove the precipitated metals. Backwashing should be initiated at 10 psig pressure drop or at a filter loading of 700 grains of iron removed per square foot of vessel area, whichever comes first (see Table 8.5 for capacity of manganese greensand). Backwash flow rate is 12 gpm/ft^2 at 55°F. Backwash duration can be as long as 25 minutes or until the backwash water runs clear. Although specifications for greensand indicates that air scour during backwash is allowed, it is not actually practiced. This is because any abrasion might remove the manganese dioxide coating, leaving nothing but an inert glauconite particle filter.

The manganese dioxide coating on glauconite is fragile. It can be removed via air scour (as described above), high pressure drop during service, general abrasion, or if the material is not regularly and properly regenerated with chlorine or permanganate. Any attrition of the coating exposes the base glauconite, which provides no catalytic properties, and at that point the media becomes merely a particle filter.

Low concentrations of hydrogen sulfide can be treated with manganese greensand. However, the greensand will degrade at a rate proportional to the concentration of hydrogen sulfide. At some point in time, the greensand will need to be replaced due to loss of functionality.

Waters that may be contaminated with high concentrations of turbidity may want to consider a top layer of anthracite to capture these solids. This protects the greensand and ensures that the greensand is free and clear to proceed with oxidation and filtration of metals. A 15–18-inch layer of anthracite is recommended.

Because of the popularity of manganese greensand, and result of a single supplier Inversand company, occasional shortages and long lead times have been experienced. Hence, the development of alternatives to manganese greensand. These alternatives include Greensand Plus™ and Pyrolusite. In general, some of these alternatives to manganese greensand exhibit higher capacity, efficiency, and life. Alternatives to manganese greensand are discussed below.

8.1.5.2. Greensand Plus™

Greensand Plus™, also available from Inversand Company, is similar to manganese greensand, but instead of coated glauconite, the base material is sand that is coated with manganese dioxide. Many of the properties of Greensand Plus™ are similar to those of manganese greensand, including the potential for removal of the coating due to abrasion, high service or backwash flow rate, and high pressure drop, which would expose the inert sand that has no catalytic properties. Service and backwash flow rates are also similar.

8.1.5.3 BIRM® Filters

BIRM® or "better iron removal media" filters are used to oxidize and filter out iron and manganese. BIRM® is a man-made granular zeolite coated with a fine dusting of manganese dioxide. BIRM® acts as a catalyst and uses the dissolved oxygen in the water to affect the oxidation of iron and manganese. The dissolved oxygen content in the water must be at least 15% of the iron content. Chlorine is not recommended as this may deplete the coating on the media. BIRM® is not compatible with hydrogen sulfide.

8.1.5.4 Pyrolusite Filters

Pyrolusite is a naturally-occurring, mined ore used for the removal of iron, manganese, and hydrogen sulfide from water. Pyrolusite media contains upwards of 80% manganese dioxide in a cluster format that enhances performance, including its capacity. While relatively new to the United States, pyrolusite has been used for decades in Europe due to a lack of supply of manganese greensand, which is limited to North America because the glauconite is mined in New Jersey. There are several pyrolusite media available in the marketplace, including AD26 (AdEdge Technologies), LayneOx (Layne Christensen), Filox-R (Watts) and DMI65 (Itochu Chemicals America), among others, that are effective for iron, manganese, and even arsenic and hydrogen sulfide removal. The performance characteristics of these bands vary, slightly and they have operating characteristics that also vary slightly. Some require more oxidizers than others. Pyrolusite media are very heavy and require significant back wash flow rates and/or air scour to clear metal oxides from the bed. The best recommendation is to pilot the media of interest prior to installing a full-scale system. Also, when considering the full-scale system, the designers needs to be aware of the required backwash flow rate which can be significant and determine whether this flow is available at the site.

Some forms of pyrolusite claim to be capable of removing up to 15 ppm of iron, 7 ppm of hydrogen sulfide, and 3 ppm of manganese without additional oxidizers. However, it is recommended in all cases that chemical regeneration be employed to ensure performance. The need for oxidants can be determined by measuring the oxidation reduction potential (ORP) of the water to be treated. If the ORP measures above negative 170 millivolts, some pyrolusite bands can be used without the use of additional oxidants. Lower than negative 170 millivolts will require additional oxidants. Air, hypochlorite, hydrogen peroxide, ozone, and potassium permanganate are all suitable oxidants to use. Note that weaker oxidants, such as air and hypochlorite will be sufficient for most applications.

Effluent concentrations of iron and manganese from a pyrolusite filter can be as low as 0.05 ppm.

Backwashing of the pyrolusite media is critical to successful operations. Inadequate backwashing will lead to bed fouling and eventual failure of the bed. About 20% to 50% bed expansion is required to ensure adequate backwashing. Pyrolusite is a heavy medium at 114 lb/ft^3. Hence, a high backwash flow of 25 gpm/ft^2, without air scour at 60°F, is required for 5 minutes or until the backwash water runs clear. Pyrolusite can tolerate higher backwash flow rates than either manganese greensand or Greensand Plus™ due to the fact that pyrolusite is solid manganese dioxide and not just a coating. Consequently, attrition or abrasion of the media particle merely exposes more active manganese dioxide. Air scour is also possible with pyrolusite. Air scour, at about 3 scfm/ft^2, drops the required backwash flow rate to 12–15 gpm/ft^2 at 60°F; backwash duration, at the lower backwash flow rate, increases to 10 minutes or until the water runs clear.

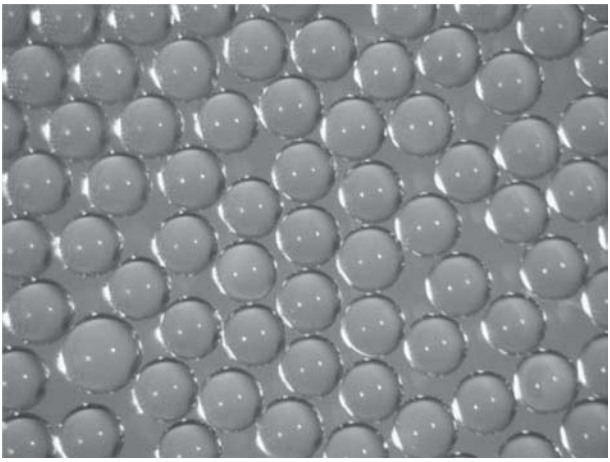

Figure 8.12 Dowex™ Upcore™ Monosphere C-600, styrene-divinylbenzene gel cation resin (Dowex and Upcore are trademarks of Dow Chemical Company, Midland, MI).

8.1.6 Sodium Softeners

Sodium softeners are used to treat RO influent water to remove soluble hardness (calcium, magnesium, barium, and strontium) that can form scale on RO membranes. Once known as sodium zeolite softeners, zeolites have been replaced with synthetic plastic resin beads. For sodium softeners, these resin beads are strongly acidic cation (SAC) polystyrene resin in the sodium form. The active group is benzene sulfonic acid, in the sodium, not free acid, form. Figure 8.12 shows styrene-divinylbenzene gel cation resin.

Equation 8.5 shows the softening reaction for calcium exchange:

$$\mathrm{Ca(HCO_3)_2 + SAC - Na \Leftrightarrow 2NaHCO_3 + SAC - Ca} \qquad (8.5)$$

Figure 8.13 illustrates equation 8.5.[7] Calcium exchanges with sodium because the resin has selectivity for calcium over sodium. The relative selectivity of SAC resin is shown below:

$$\mathrm{Fe^{3+} > Al^{3+} > Ba^{2+} > Sr^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} >}$$
$$\mathrm{K^{+} > Na^{+} > H^{+} > Li^{+}}$$

Assuming the selectivity of the resin for sodium is 1, the relative selectivity for magnesium, calcium, and strontium would be 1.7, 2.6, and 3.3, respectively. Selectivity is related to valence or charge on the ion. The higher the valence, the higher the SAC resin selectivity for that ion.

Note that the resin shows a preference for iron and manganese over hardness. Although sodium softeners will remove these metals, they are not adequately removed from the resin during regeneration. Therefore, sodium softeners operating on well waters with high iron or manganese

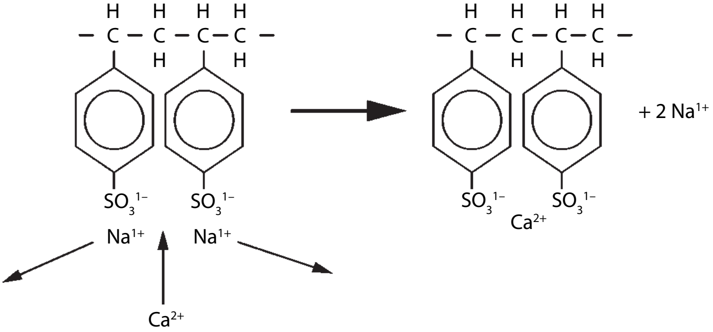

Figure 8.13 Sodium softening reaction for calcium exchange.

must be periodically cleaned. The same is true of aluminum, when alum is used ahead of sodium softeners. Cleaning the resin of iron or aluminum typically involves the use of an acid such as hydrochloric, phosphoric, or citric. Following cleaning with acid, a double regeneration with salt is required to return all sites back to the sodium form (otherwise, a low pH can result during the first service run after a cleaning).

Theoretically, hardness in the effluent from a sodium softener can be less than 1.0 ppm as $CaCO_3$. In practice, effluent quality from a sodium softener is dependent on the influent water quality. Higher influent hardness leads to higher effluent hardness. The total dissolved solids (TDS) concentration in the effluent from the softeners should be equivalent to that of the influent water since no TDS is removed through the softener; instead sodium replaces hardness in the treated stream. The effluent will have a much higher concentration of sodium and lower concentration of hardness than the influent has.

Effluent hardness is nearly constant for most of the service run. As the resin nears exhaustion, the hardness in the effluent begins to increase. At this point, it is time to regenerate the resin.

Regeneration of the resin involves replacing the hardness ions that have exchanged onto the resin with sodium. This is possible for two reasons: first, exchange Equation 8.5 is reversible and second, an excess of sodium will drive Equation 8.5 in the reverse direction. A 10% sodium chloride solution is used to regenerate resin. The dosage of salt used during regeneration will determine the capacity of the resin for hardness. Table 8.6 lists the theoretical capacity of the resin for hardness as a function of salt dosage used in regeneration. The higher the salt dosage, the higher the resin capacity is for hardness. Maximum salt dosage used in industrial applications is 15 lb/ft^{3}of resin. This is because the curve of resin capacity as a function of

Table 8.6 Hardness leakage and resin capacity as a function of regenerant salt dosage.

Salt Dosage, lb/ft^3	**Theoretical Capacity (grains)**	**Hardness Leakage (ppm)**		
		100 ppm total electrolyte	**250 ppm total electrolyte**	**500 ppm total electrolyte**
6	20,000	0.1–0.3	0.5–2	3–6
10	24,000	0.1	0.3–0.5	1–3
15	30,000	0.1	0.1–0.2	0.5–1

salt dosage is asymptotic; the curve tends to flatten out at higher salt dosages resulting in little increase in capacity as the salt dosage is increased.

Regeneration of softener resin is a 4-step process.

1. Backwashing: Backwashing the resin removes suspended solids and resin fines that may have collected in the vessel. Typical flow rates for backwashing range from about 4 to 8 gpm/ft^2 for a minimum of 10 minutes or until the backwash water runs clear. The target is to expand the bed by 50% for adequate backwash. Backwash water is usually sent to drain.
2. Brining: This step involves the injection of brine into the resin bed. A brine maker or day tank is used to dissolve salt into a 25% solution. This solution is then diluted in line with service water to 10% and either pumped or educted into the resin bed. Flow rates range from 0.5 to 1.0 gpm/ft^3. The low flow rate is necessary to give ions time to diffuse into and out of the resin beads. Duration of backwash is typically 20 to 30 minutes. Effluent is sent to drain.
3. Slow rinse: A slow or “displacement” rinse is used to remove traces of brine from the bed. Dilution water from the brining step continues to run at the same total flow rate as the brining step. Duration of the low rinse step ranges from 8 to 25 minutes. The water is sent to drain.
4. Fast Rinse: The fast rinse is conducted using service water at the service flow rate, typically 6 to 8 gpm/ft^2. The objective is to rinse out traces of brine and hardness. Duration of the fast rinse is 15 to 20 minutes or until effluent hardness returns to nominal concentration. The fast rinse is usually sent to drain.

For optimal operating of the sodium softener, the feed water to the system should adhere to these guidelines:

- Temperature: 45°F–250°F
- Total dissolved solids: < 750 ppm
- Total hardness: < 350 ppm as $CaCO_3$
- TOC: < 2 ppm
- Color: < 5 APHA
- Turbidity: < 6 NTU
- Iron: < 0.2 ppm
- Manganese: < 0.1 ppm

- Free chlorine: < 0.5 ppm
- Service flow rate: 8 gpm/ft^2 nominal, up to 25 gpm/ft^2 for some polishing applications

Softening water prior to RO helps to minimize the potential for scaling the membranes with hardness. However, more and more facilities are being faced with chloride-discharge limitations, making the use of sodium softeners prior to RO undesirable. To achieve hardness-free product water while minimizing the chloride discharge, sodium softeners are being used as polishers for RO effluent. See Chapter 15.1.1 for a discussion on the merits of pre- and post-RO softening.

8.1.7 Spent Resin Filters

Spent or exhausted resin has been used on occasion to filter RO influent water. These filters are designed to remove silt and reduce SDI from surface water sources. All evidence to the effect of such filters on the suspended solids in RO influent is anecdotal; there appears to be no data in the literature attesting to the efficacy of such filters for RO influent filtration applications.

8.1.8 Ultraviolet Irradiation

Ultraviolet (UV) irradiation is used to destroy bacteria and reduce organic compounds (measured as TOC) as well as destruction of chlorine and chloramines. This technique involves passing water over a UV lamp that is operating at a specific wavelength of energy.

Bacteria require a dosage of radiation equivalent to about 10,000–30,000 microwatt-seconds/square centimeter. This can achieved by using a 254-nanometer wavelength. This wavelength alters the DNA of microbes, causing them to be unable to reproduce, leading to their death.

A significant advantage of UV over use of chemical oxidizers for microbial control is that no trihalomethane (THM) compounds are generated. Additionally, the need to store and feed a hazardous chemical oxidizer is avoided.

A limitation in using UV irradiation for microbial growth control is that there is no residual. Unlike with chemical oxidizers, there is no down-stream protection against microbial growth once the treated water leaves the UV unit. Any viable material that happens to make it through the UV process is then free to grow and foul down-stream equipment including the RO membranes. Also, introduction of microbes into the RO influent stream via, for example, chemical feeds, are also free to proliferate and foul piping, equipment, and membranes downstream of the introduction point.

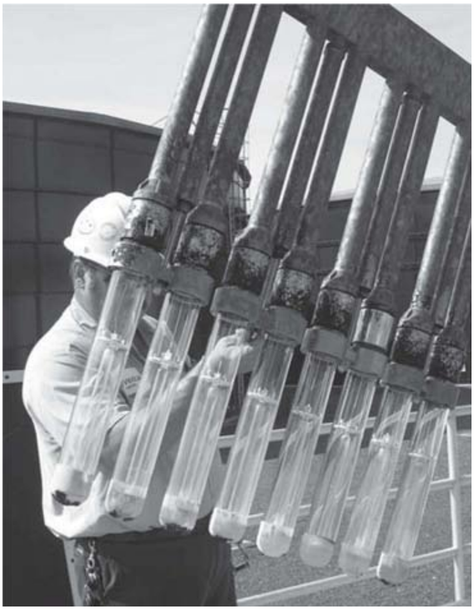

Figure 8.14 Ultraviolet light bulbs.

Total organic carbon destruction requires more energy then bacterial destruction, typically around 90,000 microwatt-seconds/square centimeter. Since lower wavelengths correspond to higher energies, a wavelength of 185 nanometers is used for TOC removal. At this wavelength, organics are oxidized to form organic acids, carbon dioxide, and water.[9]

Ultraviolet radiation can also be used as an alternative to carbon or sodium metabisulfite for the destruction of chlorine and chloramines in RO feed water. The UV radiation breaks the molecular bonds of these compounds, reducing them to basic elements. For example, the typical end products of chloramine destruction using UV are chloride, hydrogen, nitrate, and ammonia. Ultraviolet radiation offers advantages over conventional dechlorination techniques, including being chemical free and without the potential for increased microbial fouling that is associated with carbon filters. Limitations of the technology include high energy requirements and capital investment.

Low-pressure mercury vapor lamps are used to produce the UV light (see Figure 8.14). An electric current is passed through an inert gas. This vaporizes mercury contained in the lamp, which then emits UV radiation. The lamp is encased in a quartz sleeve and water is in contact with the quartz. Quartz is used instead of glass because quartz does not absorb UV radiation while glass does.

Maximum contact between the water and the quartz sleeve is achieved by using plug flow with a tangential flow pattern for the water. Retention time of water in a UV unit is designed to be at least 15 minutes.

For UV to be effective, certain water conditions must be met. The water must be free of suspended solids, which can foul quartz sleeves, thereby reducing the amount of radiation reaching the water. Some UV systems include cleaning mechanisms for quartz sleeves. The water should also be free of taste, odor, iron, and manganese. Furthermore, chloride, bicarbonate, and sulfates should be reduced, as these affect the absorption of UV radiation.[10] Thus, some pretreatment is required prior to sending water to a UV system.

8.1.9 Membrane

Membrane pretreatment includes microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF). Microfiltration and UF membrane processes can remove microbes and algae. However, the pores of MF and UF membranes are too large to remove the smaller, low-molecular weight organics that provide nutrients for microbes. As a result, MF and UF can remove microbes in the source water, but any microbes that are introduced downstream of these membranes will have nutrients to metabolize. Therefore, chlorination along with MF and UF is often recommended to minimize the potential for microbial fouling of RO membranes. The MF or UF membranes used should be chlorine resistant to tolerate chlorine treatment. It is suggested that chlorine be fed prior to the MF or UF membrane and then after the membrane (into the clearwell), with dechlorination just prior to the RO membranes. See Chapter 16.1 for additional discussion about MF and UF membranes for RO pretreatment.

Nanofiltration membranes are "tighter" then either MF or UF membranes but "looser" than RO membranes. They can be used to remove dissolved species, such as hardness and color. Recent developments in NF membranes have made them applicable to de-color feed water without chlorination and with minimal membrane fouling (see Chapter 16.2).

8.2 Chemical Pretreatment

Chemical pretreatment focuses on bacteria, hardness scale, and oxidizing agents. Chemicals are used to remove, destroy, inhibit, or chemically reduce these species. Table 8.7 lists chemical treatments and what species they treat.

Table 8.7 Chemical RO pretreatment techniques and the species each technique treat.

Chemical Pretreatment	Species Addressed
Chlorine	Microbes, Total Organic Carbon, Color
Ozone	Microbes, Total Organic Carbon, Color
Antiscalants	Hardness, Silica
Sodium Metabisulfite	Oxidizers (free chlorine)
Non-Oxidizing Biocides	Microbes

Table 8.8 Oxidation-reduction potential for various compounds.[11]

Species	Oxidation Reduction Potential (volts)
Hydroxyl	2.8
Ozone	2.1
Peroxide	1.8
Chlorine gas	1.4
Monochloramine	1.4
Hypochlorite	0.9

This chapter also includes a copy of a paper written in the International Water Conference (IWC) in 2014. This papers covers the basics of membrane Bio fouling and alternatives to chlorine to address this fouling. Some information is presented twice in this chapter but since this is such an important topic, a double take is worthwhile.

8.2.1 Chemical Oxidizers for Disinfection of Reverse Osmosis Systems

Chemical oxidizers used to disinfect RO systems include hydrogen peroxide (peroxide), halogens, and ozone. Although halogens (and specifically chlorine) are the most popular oxidizers using in conjunction with RO pretreatment, they do not have the highest oxidization-reduction potential (ORP). Table 8.8 lists the ORP for several oxidizers. As the table shows, ozone and peroxide have nearly twice the ORP or oxidative power as chlorine. Despite the relatively low ORP, chlorine is the most commonly used disinfectant in brackish water RO pretreatment due to its ease of use and its ability to provide residual disinfection (for seawater desalination using RO, bromine (as HOBr) is predominantly used because the high bromine concentration in typical seawater would rapidly form hypobromous acid if hypochlrous acid were used).

8.2.1.1 Chlorine

Chlorine is commonly used to kill microbes in pretreatment prior to RO and to break up organics that may foul RO membranes. It is used rather than other halogens because of its higher ORP. Chlorine is available in many forms, such as chlorine gas, sodium hypochlorite (bleach), chloramines, and chlorine dioxide. Chlorine gas and sodium hypochlorite each react with water to form hypochlorous acid, as shown in Equations 8.6 and 8.7, respectively.

$$Cl_2 + 2H_2O \Rightarrow HOCl + H^+ + Cl^- \quad (8.6)$$

$$NaOCl + H_2O \Rightarrow HOCl + NaOH \quad (8.7)$$

where:
NaOCl = sodium hypochlorite
HOCl = hypochlorous acid

Hypochlorous acid then dissociates in water to form hydrogen ions and hypochlorite ions (Equation 8.8):

$$HOCl \Leftrightarrow H^+ + OCl^- \quad (8.8)$$

where:
OCl^- = hypochlorite ion

The equilibrium in Equation 8.8 is a function of pH. Figure 8.15 shows how the presence of hydrochlorous acid, chlorine gas, and hypochlorite

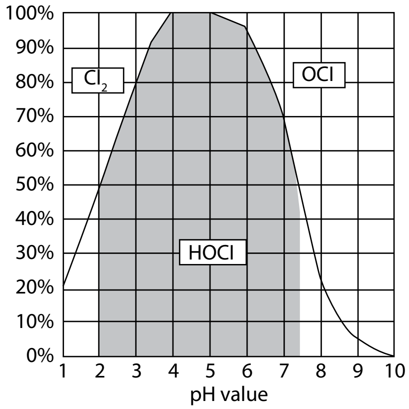

Figure 8.15 Presence of hydrochlorous acid, chlorine gas, and hypochlorite ion as functions of pH.

ion are functions of pH. Hydochlorous acid is predominant at pH 4–5. At pH 7.3 or so, the concentrations of hydrochlorous acid and hypochlorite ion are the same, and above pH 8, hypochlorite ion is the only species present.

Hydrochlorous acid has the highest disinfecting capability of the 3 species; it is 100 times more active than hypochlorite ion.[12] Chlorine gas contains 100% available chlorine (hydochlorous acid) while industrial-grade bleach has about 12%–15% available chlorine.

The sum of chlorine gas, sodium hypochlorite, calcium hypochlorite, hydochlorous acid, and hypochlorite ion is known as the free or free available chlorine. Most polyamide composite membranes have little tolerance for free chlorine; they can tolerate about 200–1,000 ppm-hrs of exposure (e.g., 200 hours at 1 ppm of free chlorine) before rejection drops to unacceptable levels. While the pretreatment to RO should have a free chlorine residual of about 0.5 to 1ppm, the influent to the RO must be dechlorinated to bring the free chlorine concentration down to less than 0.02 ppm.

Note that some membrane manufacturers treat some of their membranes with a measured amount of chlorine prior to shipment. This brief, controlled exposure results in higher water flux with no adverse effect on rejection. These membranes are sometime referred to as “high flux” or “high capacity” membranes. Once the salt rejection decreases upon exposure to chlorine, however, the membranes are irreversibly damaged. Hence, this technique should not be attempted in the field.

Chlorination of water containing organics will create trihalomethanes (THMs):

$$CH_4 + 3Cl_2 \Rightarrow CHCl_3 + 3HCl \tag{8.9}$$

where:
CH_4 = Methane
$CHCl_3$ = chloroform

Besides chloroform (the most common THM), the other three trihalomethane compounds are bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$). Trihalomethanes are considered to be carcinogenic at concentrations greater than 100 ppb. Concentration of THMs is a function of pH, temperature, contact time, and concentration of organics that react with chlorine. Concentration of THMs tends to increase with increasing pH, temperature, contact time and concentration of organics.

Control of THMs involves either eliminating the chlorine feed or the organic precursors. In cases where oxidation is required for microbial or organics control, other oxidizers should be considered.

If there is any ammonia present in the water being treated, hydrochlorous acid reacts with it to form chloramines:

$$HOCl + NH_3 \Leftrightarrow NH_2Cl + H_2O \tag{8.10}$$

$$HOCl + NH_2Cl \Leftrightarrow NHCl_2 + H_2O \tag{8.11}$$

$$HOCl + NHCl_2 \Leftrightarrow NCl_3 + H_2O \tag{8.12}$$

where:
NH_2Cl = monochloramine
$NHCl_2$ = dichloramine
NCl_3 = trichloramine

Note that trichloramine is an unstable gas that quickly dissociates into its components. The formation of the specific species of chloramines is dependent on pH and the ratio of chlorine to ammonia. Trichloramine is formed at pH less than 4.4. Dichloramine which is responsible for the "swimming pool" smell, is formed at pH 4.4 to 6.0. Monochloramine is the most prevalent species at pH greater than about 7. The amount of HOCl fed per pound of ammonia also determines the species that is formed. When the ratio of HOCl to NH_3 is less than 6.7:1, monochloramine is formed. Above this ratio, dichloramine is formed, and above 9.5:1, trichloramine is formed. Breakpoint chlorination occurs at ratios greater than 13.5:1, where all mono- and di-chloramines are destroyed.

Chloramines collectively are also known as the "combined" chlorine. The sum of the free and combined chlorine is the "total" chlorine.

Monochloramine is approximately 200 times less effective than free chlorine as a disinfectant.[9] However, it is still used as an alternative to chlorine because chloramines do not react as readily with organic materials to form trihalomethanes (THMs). In theory, due to the less aggressive nature of chloramines, the tolerance of polyamide composite membranes to chloramine is about 300,000 ppm-hrs. However, chloramines are usually in equilibrium with free chlorine, making it difficult to use chloramine in RO pretreatment, as the free chlorine will degrade polyamide composite membranes.

Although chloramines are generally not recommended by membrane manufacturers for use with polyamide composite membranes, there is some anecdotal support for the use of chloramines if the ammonia is naturally occurring in the water to be treated.[9] In such cases, there usually is an excess of ammonia. Difficulties arise when ammonia is added to chlorine to make the chloramines. These systems tend to have more free chlorine present in equilibrium with the chloramines (see Chapter 7.10 for more discussion on this topic).

Since chloramines are created using chlorine and ammonia, there can be some free ammonia present in the chloramine solution. Free ammonia is a gas and as such, is not rejected by a polyamide RO membrane. Additionally, free ammonia in water will swell a polyamide RO membrane, causing it to pass more dissolved solids. The presence of the ammonia is a function of pH, as illustrated below:

$$NH_3+H_2O \xrightleftharpoons{pH} NH_4^+ + OH \tag{8.13}$$

pH	percent free ammonia
6.0	0
8.0	10
9.0	50

where
NH_3 = free ammonia
NH_4^+ = ammonium ion

It is important to keep the pH below 7.0 to assure minimal swelling of the membrane with free ammonia and minimize the impact on product quality. This pH should be maintained in the concentrate stream.

Chloramines can be removed from solution using carbon filtration, as noted in Chapter 8.1.4. However, the contact time for removal is can be up to 4 times that of free chlorine. Chloramines can also be removed using sodium thiosulfate or bisulfite, and the reaction is fairly instantaneous. Note that with the carbon filtration removal method, some ammonia is created, which is toxic and should be considered when using an RO with chloramines for food processing and pharmaceutical applications (see Equation 8.3). However, as free chlorine is removed using sodium bisulfite, the chlorine-chloramine equilibrium can shift back to creating more free chlorine. In this case, complete removal of free chlorine cannot be assured. Carbon filters may be the best method to remove chloramines, but can take anywhere from 5-10 minutes for fresh carbon up to 30 minutes for spent carbon of empty bed contact time for complete reaction with the carbon depending on the age and condition of the carbon. Ultraviolet radiation can also be used to destroy chloramines (see Chapter 8.1.8).

Some jurisdictions, including municipalities that treat make-up water prior to the RO pretreatment systems, have been known to switch disinfection chemicals with little or no warning. In most cases, the switch is from chlorine (or hypochlorite) to chloramines. As discussed in above, if ammonia is added to chlorine to make hypochlorite, chances are that there will be some residual free chlorine in equilibrium with the chloramines that will remain even when the chloramine is "dechlorinated." If free ammonia is present and the RO concentrate pH is greater than 7.0, RO permeate quality can be affected by the switch from free chlorine to chloramine. Any changes in effluent quality for an RO operating on municipal supply should be evaluated for the presence of chlormaine.

Chlorine dioxide is sometimes used for disinfection and organic destruction. Chlorine dioxide is a gas that does not hydrolyze into hydrochlorous acid as does chlorine. Chlorine dioxide reacts with hydroxyl under alkaline conditions to form chlorite (Equation 8.14).

$$ClO_2 + 2OH^- \Rightarrow ClO_3^{2-} + H_2O \tag{8.14}$$

where:
ClO_2 = chlorine dioxide
ClO_3^{2-} = chlorite

Chlorine dioxide is manufactured on site as the gas cannot be stored in compressed form; it is explosive under pressure. Several methods are used to generate chlorine dioxide. The most common method involves the reaction of chlorine gas with sodium chlorite to form chlorine dioxide and sodium chloride:

$$2NaClO_2 + Cl_2 \Rightarrow 2ClO_2 + 2NaCl \tag{8.15}$$

Theoretically, 1 pound of chlorine gas is required for each 2.6 pounds of sodium chlorite. In practice, however, an excess of chlorine is used to lower the pH to about 3.5 and drive the reaction to completion. In reality, the reaction never goes to completion, and there is always free chlorine in equilibrium with the chlorine dioxide. For this reason, membrane manufacturers discourage the use of chlorine dioxide for disinfecting RO systems.[13]

Another method for generating chlorine dioxide involves the acidification of sodium chlorite with hydrochloric acid to from chlorine dioxide, sodium chloride, and water:

$$5NaClO_2 + 4HCl \Rightarrow 4ClO_2 + 5NaCl + 2H_2O \tag{8.16}$$

This method does not form free chlorine and therefore, it may be possible to be use with RO membranes. However membrane manufactures have reservations about using quinine dioxide on a regular basics, including cleaning. Hydranautics recommends futher studies to fully characterize the effect of chlorine dioxide on membrane performance, particularly in the presence of transition metals.[14]

Chlorine dioxide forms a true solution in water; it does not hydrolyze as chlorine does. Therefore, it is very volatile (700 times more volatile than hypochlorous acid) and, therefore, can easily volatize in RO pretreatment systems, leaving the feed water without a disinfectant residual. For this reason and the fact that most chlorine dioxide is generally in equilibrium with free chlorine, makes it unattractive for RO feed water disinfection.

8.2.1.2 Ozone

Ozone is a very powerful disinfectant. Its ORP is greater than that of chlorine. As Table 8.8 shows, the ORP for ozone is nearly twice that for hypochlorite. Ozone is will also destroy a significant amount of organics as TOC.

Although ozone can be generated in a number of different fashions, the most economical method is by dielectric barrier discharge.[12] This method involves the passing of a high-voltage, alternating current (6 to 20kV) through either air or pure oxygen:

$$3O_2 + \text{electric discharge} \Rightarrow 2O_3 \qquad (8.17)$$

When added to water, ozone quickly converts to oxygen, leaving behind no residual ozone. This makes it difficult for ozone to provide residual disinfection of RO feed water. Although no trihalomethanes are produced when using ozone, side reactions have been known to form carcinogenetic compounds such as aldehydes and phthalates.[11]

8.2.1.3 Hydrogen Peroxide

Peroxide or a combination of peroxide and peracetic acid is generally used to treat RO systems that are already contaminated with microbes. Due to its high ORP, however, a solution of only 0.2wt% peroxide is normally used (see Table 8.8). Temperature must be below 25°C and transition metals such as iron must be removed prior to treatment with peroxide to minimize oxidation of the membrane. Further, membrane should be cleaned free of deposits using an alkaline cleaner before peroxide is applied. Finally, a pH of 3–4 should be maintained and exposure limited to about 20 minutes for optimum result and maximum membrane life. Peroxide should not be used for storage of membrane modules.

8.2.2 Non-Oxidizing Biocides

Non-oxidizing biocides are used on membranes to prevent microbial fouling. By definition, these products will not oxidize polyamide composite membranes and can be used directly on the membranes. There two most common, non-oxidizing biocides used with RO membranes: sodium bisulfite and 2,2,-dibromo-3-nitrilo-proprionamide or DBNPA.

8.2.2.1 Sodium Bisulfite

Sodium bisulfite can be used as a biocide on a shock feed basis. Typically, 500 to 1,000 ppm as sodium bisulfite should be fed for 30 minutes. The frequency of use should be dictated by the temperature of the water and the concentration of nutrients for microbes (warmer water and higher concentrations call for more frequent application of the bisulfite).

8.2.2.2 DBNPA

DBNPA (2,2-dibromo-3-nitrilo-propionamide) can be used as a biocide on a shock feed or continuous feed basis. For shock-feed treatment, it is recommended that a concentration of about 100 ppm be fed for 30 to 60 minutes. Frequency of application depends on the degree of microbial fouling or the potential for microbial fouling, but ranges from once every 2 days to once per week. Higher temperatures, pH greater than 8.5, and the presence of residual reducing agents (such as sodium bisulfite) require higher dosages and longer contact time. Continuous treatment calls for about 1 to 2 ppm. Because some of the degradation byproducts (carbon dioxide, ammonia, and bromide ions)[6] and other ingredients in the formulations are not always rejected by the membrane, the shock treatment is preferred, and permeate should be diverted during application as concentration of organics may increase in the system.[11] This is particularly important in ultrapure water applications.

For potable water applications, only off-line treatment with DBNPA is recommended. This is to ensure that the single produce active concentration (SPAC) of 90 ppb of DBNPA in the permeate is not exceeded.[16]

Sodium bisulfite and other reducing agents can decompose the active ingredient in DBNPA formulations. Hence, it is recommended to suspend use of reducing agents during addition of DBNPA to avoid decomposition of the biocide.[16]

Although DBNPA is non-oxidizing, it does give an ORP response of about 400 milliVolts at 0.5 to 3.0 ppm. Chlorine gives a reading of about 700 milliVolts at 1 ppm concentration. It is recommended that the ORP set points be by-passed during addition of DBNPA.

DBNPA can also be used as a cleaner to destroy microbes within the membrane modules. Dosage is about 100 ppm for 30 minutes at pH 6.0 to 7.5. This cleaning may be preceeded by or followed by an alkaline cleaning to help remove any biofilm that may be present (see Chapter 13.2 for more details on membrane cleaning formulations).

Stainless steel injection quills should not be used with DBNPA as they may corrode.

8.2.2.3 Other Non-Oxidizing Biocides

Isothiazolones have also been used as non-oxidizing biocides for RO applications. However, the residence time required is much longer than for DBNPA. For example, a dosage of 50 to 100 ppm requires a 4-hour contact period. Thus, isothiazolones are not recommended for shock feed or continuous feed, but is recommended for cleaning events. Isothiazolone is more effective than DBNPA in high-organic waters.

Quaternary germicides, phenolic compounds and iodine are not recommended as sanitizing against for polyamide membranes as these compounds can cause losses in water flux through the membrane.[18]

8.2.3 Sodium Metabisulfite for Dechlorination

Dechlorination of feed water to polyamide composite membranes is necessary as a polyamide membrane polymer cannot tolerate oxidizers of any kind. The options for dechlorination include activated carbon, sodium metabisulfite chemical feed, and UV radiation. Carbon has its own set of difficulties, as described previously, and UV radiation can be capital intensive.

Sodium metabisulfite is the most commonly used technique to dechlorinate RO influent. In water, the sodium metabisulfite forms sodium bisulfite:

$$Na_2S_2O_5 + H_2O \Rightarrow 2\ NaHSO_3 \tag{8.18}$$

where:
$Na_2S_2O_5$ = sodium metabisulfite
$NaHSO_3$ = sodium bisulfite

The sodium bisulfite then reduces hypochlorous acid as follows:

$$2\ NaHSO_3 + 2HOCl \Rightarrow H_2SO_4 + 2HCl + Na_2SO_4 \tag{8.19}$$

Theoretically, 1.34 mg of sodium metabisulfite is required for every 1 mg of free chlorine. In practice, however, it is recommended that 2 mg

Table 8.9 Shelf life of sodium metabisulfite solutions of various concentrations.

Concentration of Sodium Metabisulfite (wt %)	Life
10	1 week
20	1 month
30	6 month

of sodium metabisulfite be fed per 1 mg of free chlorine. If the sodium metabisulfite solution is 33% active, that means that about 6 mg of product should be fed per 1 mg of free chlorine.

Food-grade sodium metabisulfite that is free of impurities should be used in RO systems. The compound must not be cobalt-activated, as cobalt can catalyze the oxidation of the polyamide composite membrane in a manner similar to iron and manganese (see Chapter 7.6). Further, while the shelf life of solid sodium metabisulfite is 4–6 months, in solution, the shelf life depends on the concentration, as shown in Table 8.9.[11]

Sodium metabisulfite used for dechlorination should be fed down stream of all pretreatment unit operations. In other words, sodium metabisulfite should be fed after the RO cartridge filter, if possible. This allows for protection of the cartridge filters with chlorine.

Dosage of sodium metabisulfite is typically based on Oxidation-reduction potentiometer. To ensure all free chlorine has been removed form RO feed water, the ORP should be controlled to read less than about 175 millivolts.

A note of caution when feeding sodium metabisulfite. If membranes are heavily fouled with heavy metals such as cobalt, iron, or manganese, residual sodium bisulfite actually converts to an oxidant in the presence of excessive oxygen. In this case, the membranes are in danger of being oxidized and destroyed.[11]

8.2.4 Antiscalants

Antiscalants (also known as scale inhibitors or sequestering agents) are used to minimize the potential for forming scale on the surface of an RO membrane. Antiscalants work by one of three methods:

- Threshold inhibition—the ability to keep supersaturated salts in solution

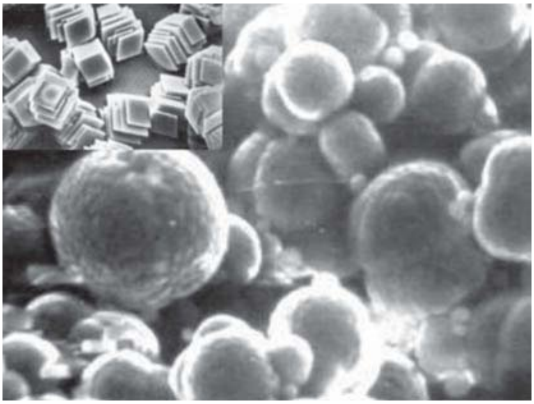

Figure 8.16 Normal crystals (inset) and crystals that have been surface-modified by an antiscalant.

- Crystal modification—the ability to change crystal shapes, resulting in soft, non-adherent scales
- Dispersion—the ability to impart a highly negative charge to the crystal thereby keeping them separated and preventing propagation.

Figure 8.16 shows normal crystals (inset) and crystals that have been modified by an antiscalant to inhibit their growth.

Early antiscalants used sodium hexametaphosphate (SHMP) as a threshold agent to inhibit the growth of calcium carbonate and sulfate-based scales.[7] Most antiscalants on the market today contain sulfonate, phosphate, or carboxylic acid functional groups. Perhaps the most effective antiscalants today contain and blend of polyacrylic acid (PAA) and phosphoric acid or polyacrylate and a hydroyethylidene diphosphonate (HEDP).[15] The polyacrylate HEDP blends also claim to have good dispersion qualities toward silts and clays.[15] Some new inhibitors include a chelant and disperant to keep suspended solids such as iron and manganese oxides in solution. These newer antiscalants are generally more effective than SHMP for a variety of potential scales.[7]

Antiscalants are usually fed alone for most applications. Acid feed is sometime used in conjunction with an antiscalant to control LSI for calcium carbonate scale and to control calcium phosphate and calcium fluoride scales. Antiscalants currently on the market are not generally effective at controlling calcium phosphate scale and have difficulty controlling calcium carbonate scale when the LSI is greater than about +2, depending on the manufacturer. To control calcium carbonate scale, acid is added to drop the LSI down to "acceptable" numbers. "Acceptable" numbers for LSI can range from +1.0 up to greater than +2 (recall that an LSI greater than zero is indicative of calcium carbonate scaling potential), again depending on the manufacturer. Note that membrane manufactures typically require an LSI of the less than +1.8 with antiscalants to meet their warranty; acid will be required when the LSI is greater than +1.8 to keep the LSI at or below +1.8. Antiscalant is then used to provide the balance of scale protection for calcium carbonate scale. In the case of calcium phosphate scale, enough acid should be added to decrease the calcium phosphate scaling potential to 100% or lower. A note of caution when adding acid to lower LSI and calcium carbonate/calcium phosphate scaling potential; the addition of sulfuric acid may significantly increase the potential for forming sulfate-based scales. For this reason, hydrochloric acid is preferred for pH reduction.

Antiscalant feed is typically controlled based on the feed flow rate to the RO. This type of control can lead to inconsistent dosage, as shown in Figure 8.17. Nalco Company offers 3D TRASAR® technology for RO, an alternative dosage control method (3D TRASAR, Nalco, and the logo are trademarks of Nalco, An Ecolab Company, Naperville, IL). The 3D TRASAR® controller relies on a fluorescing molecule that allows a fluorometer to

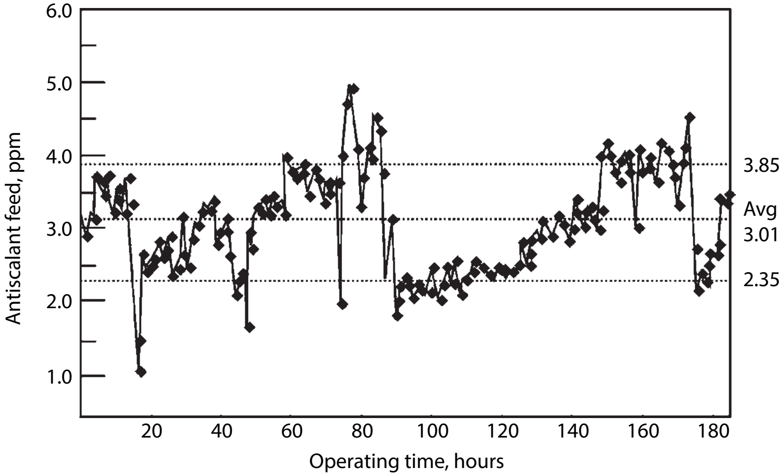

Figure 8.17 Inconsistent dosage of antiscalant based on conventional, flow-proportional control. Note the wide range of antiscalant dosages, resulting in both underfed and overfed of chemical.

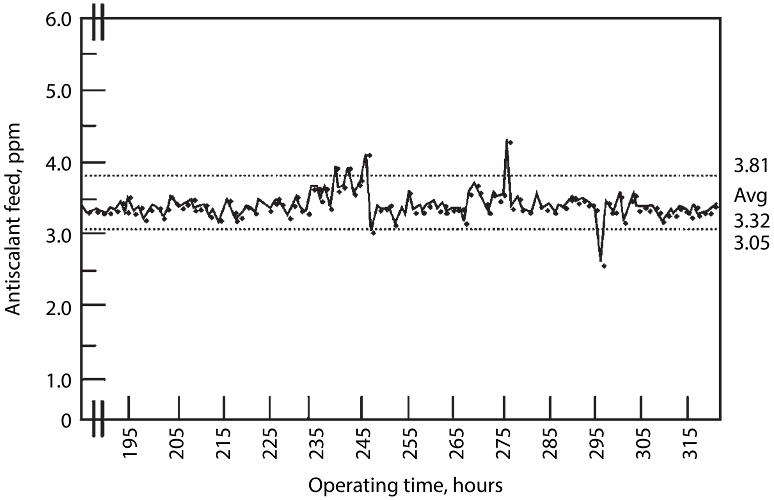

Figure 8.18 Consistent dosage control of antiscalant based on the 3D TRASAR® system. Note the relatively narrow range of antiscalant dosages resulting in few underfed or overfed episodes.

detect exactly how much antiscalant has been fed. Figure 8.18 shows how a 3D TRASAR® system controls the dosage of antiscalant to an RO.

Some antiscalants, such as those containing 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP) are sensitive to chlorine and other oxidizers.[15] They should be fed downstream of the dechlorination point. Most other antiscalants are not affected by chlorine at typical 0.5–1.0 ppm concentrations.[16]

As mentioned in Chapter 8.1.1.4.1, overfeed of cationic coagulants can complex with negatively-charged antiscalants to co-precipitate and foul RO membranes. Care should be exercised to avoid overfeed or carryover of cationic coagulants prior to RO membranes in any case, but particularly when also feeding an antiscalant. Additionally, overdosing of antiscalants containing polyphosphate can result in calcium phosphate scale, as the polyphosphate hydrolyzes to ortho-phosphate.[15] Finally, there is a concern with microbiological contamination of antiscalant solutions. Those antiscalants containing phosphorous can accelerate the growth of microbes, as can some antiscalants in total because they themselves are food for microbes (e.g., SHMP).[15]

Antiscalants are completely rejected by RO membranes and, therefore, are not a concern for product quality.

8.3 Combination Mechanical Plus Chemical Pretreatment—Lime Softening

Lime softening is used to remove the following species from water:

- Calcium
- Iron
- Turbidity
- Organics
- Silica
- Magnesium
- Manganese
- Color
- Oil

Lime softening can be conducted cold (ambient), at warmer temperatures, or hot, where steam is used to heat the process. The differences among the three options are in the removal of hardness, alkalinity, and silica. Table 8.10 lists approximate effluent from cold, warm, and hot lime softeners.[19]

Table 8.10 Effluent from cold, warm, and hot lime softeners.

Species	**Raw Water**	**Cold Lime**	**Cold Lime Soda**	**Warm Lime**	**Hot Lime**	**Hot Lime Soda**
Total Hardness (ppm $CaCO_3$)	250	145	81	70	120	20
Calcium (ppm $CaCO_3$)	150	85	35	30	115	15
Magnesium (ppm $CaCO_3$)	100	60	46	40	5	5
P Alkalinity (ppm $CaCO_3$)	0	27	37	24	18	23
M Alkalinity (ppm $CaCO_3$)	150	44	55	40	28	40
Silica (ppm)	20	19	18	15	1–2*	1–2*
pH	7.5	10.3	10.6	10.4	10.4	10.5

* Silica removal to this concentration may require the additional feed of magnesium oxide with sludge recirculation.

8.3.1 Cold Lime Softening

Cold lime softening is conducted at ambient temperatures and involves feeding calcium as lime ($Ca(OH)_2$) to precipitate out calcium carbonate:

$$Ca(OH)_2 + 2CO_2 \Rightarrow Ca(HCO_3)_2 \tag{8.20}$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \Rightarrow 2CaCO_3 + 2H_2O \tag{8.21}$$

where:
$Ca(OH)_2$ = lime
$Ca(HCO_3)_2$ = calcium bicarbonate
$CaCO_3$ = calcium carbonate precipitate

Calcium can be reduced to about 35–50 ppm in this manner.

The removal of other species requires the addition of sodium aluminate ($Na_2Al_2O_4$). Reduction in the concentration magnesium is only about 10%. The addition of sodium aluminate also helps with the reduction in silica, since the magnesium precipitate, magnesium hydroxide, adsorbs silica. More complete removal requires the addition of soda ash (Na_2CO_3) and warmer temperatures, as shown in Table 8.10.

Cold lime and lime-soda softening is conducted in a solids contact clarifier (see Chapter 8.1.1.). Cold lime softeners are typically followed by filtration and sodium softening to remove suspend solids that carry over from the line softening and the balance of hardness from the water.

The cold lime process is slow, and gets slower as the temperature gets colder. For very cold waters, there is the danger of post-precipitation elsewhere in the facility, as some of the reactions will not be completed in the lime softener, and will continue into the transfer lines.

8.3.2 Warm Lime Softening

Warm lime softening is conducted at 120–140°F, where the solubilities of calcium and magnesium are reduced. Temperature control is critical. A change of as little as 4°F can cause carryover of softener precipitates. Conventional cold lime softening equipment is used for warm lime softening.

8.3.3 Hot Process Softening

Hot lime softening (also known as hot process softening) is conducted at 227–240°F. At these temperatures, the lime softening reactions go to

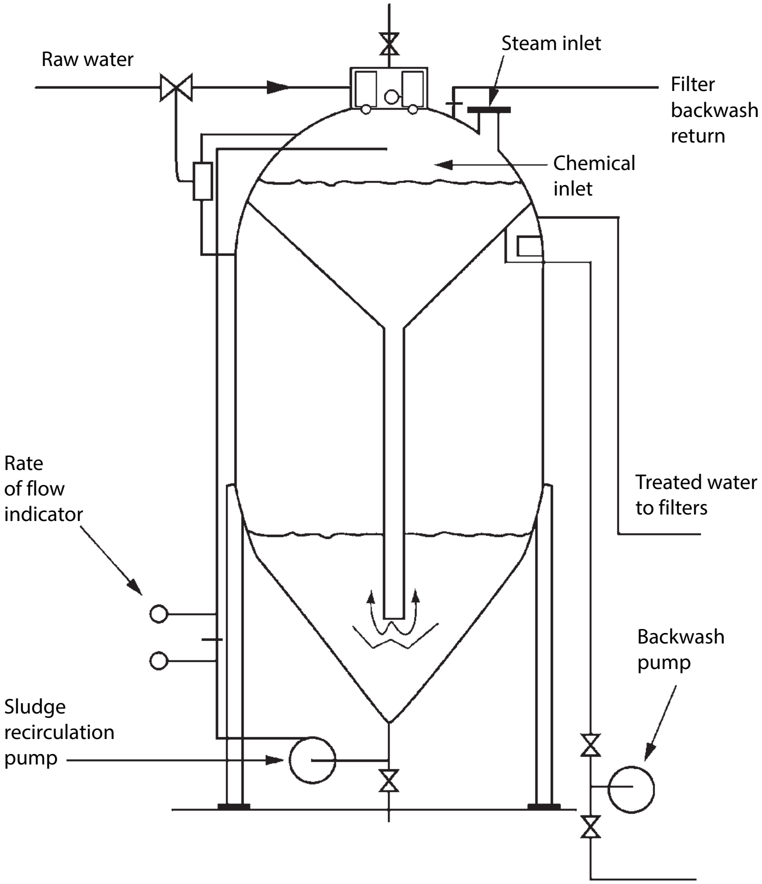

Figure 8.19 Sludge-blanket (upflow) hot process softener. Courtesy of Res-Con, Inc.

completion. Calcium can be reduced to about 8 ppm while magnesium can be reduced to about 2–5 ppm. Furthermore, silica can be reduced to 1–2 ppm.

Steam is used to heat the process. Figure 8.19 shows the cross section of a sludge-blanket (upflow) hot process softener. The operations of the sludge blanket hot process unit is similar to that for sludge-blanket clarifiers (see Chapter 8.1.1.1). Figure 8.20 shows the cross section of a downflow hot process softener. The downflow units rely on recirulation pumps to provide sludge contact.

Silica reduction is accomplished by adsorbing silica on the magnesium hydroxide precipitate. If not enough magnesium is present, magnesium oxide (MgO) can be added to provide the necessary adsorption sites.

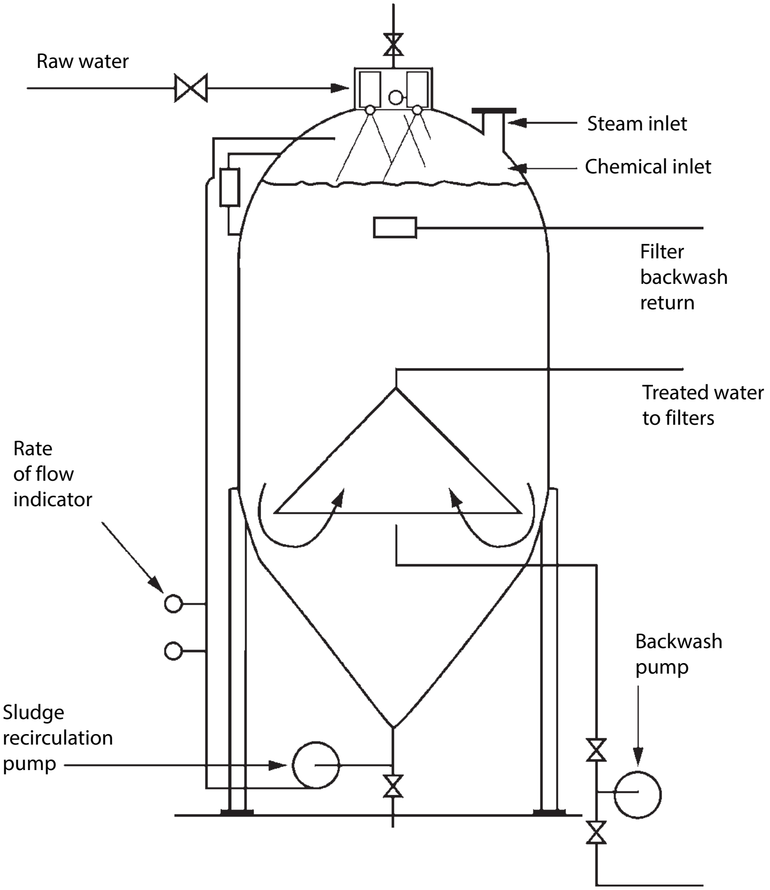

Figure 8.20 Downflow hot process softener. Courtesy of Res-Con, Inc.

8.4 Sequencing of Pretreatment Technologies

Although sequencing of pretreatment technologies is always site specific, there are some generalizations that can be made. Figure 8.21 shows a typical process flow diagram that includes many of the pre- treatment technologies described above. Note that most RO systems will not include all of these unit operations.

- Chemical feed: this includes chlorine, coagulants, and flocculants. The chemical feeds disinfect the water and prepare it for solids and/or hardness removal.

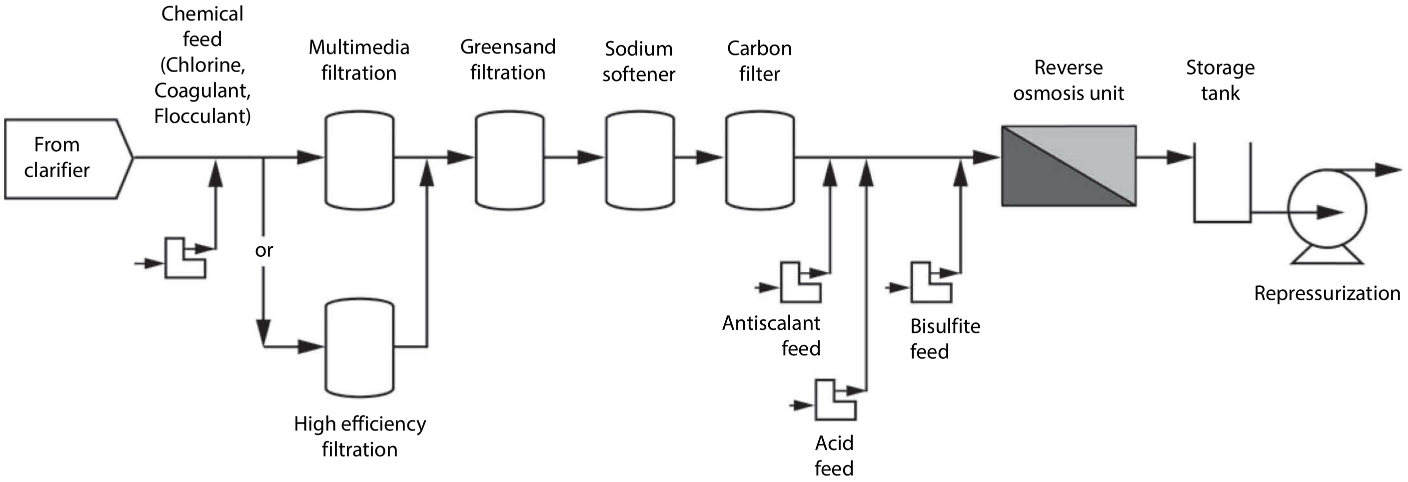

Figure 8.21 Sample reverse osmosis and pretreatment process flow diagram. Not all systems will include all unit operations. Adapted from Anne Aeza, Nalco, an Ecolab Company

- Media filtration: this step includes multimedia filtration or high-efficiency filtration, and reduces the concentrations of suspended solids, turbidity, and SDI.
- Greensand filtration (or pyrolusite filtration): This step removes soluble iron and manganese (and sometime hydrogen sulfide). This type of filtration is typically only used on well water sources. In some cases, media filtration is not required prior to greensand filtration.
- Sodium softener: The softener removes hardness and any residual soluble iron from the RO feed water.
- Carbon filtration: carbon removes chlorine and organics from RO feed water.
- Bisulfite feed: bisulfite is added to eliminate free chlorine, if carbon is not used.
- Acid feed: acid is added to reduce the LSI and calcium carbonate, calcium phosphate or calcuim fluoride scaling potential, if required.
- Antiscalant feed: antiscalant is used to minimize the potential for scaling the membranes.
- Reverse osmosis: the RO unit removes the bulk of the dissolved solids from the feed water. It is typically followed by a storage tank and repressurization for transport on to post-treatment or process.

8.5 Membrane Biofouling and Alternative Disinfectants*

Reverse osmosis (RO) system owners and operators are continuously challenged with minimizing fouling of the RO membranes. The primary foulant affecting virtually all RO systems is bacterial in nature. Traditionally, chlorine gas or bleach has been used for disinfection of the RO feed stream and pretreatment system in an attempt to minimize bio-fouling of the membranes. However, these techniques promote the formation of undesirable species, such as trihalomethanes (THMs) and haloacetic acids (HAAs), which have already faced increasing regulation by the government. Thus, municipalities are turning to alternative means of disinfection of potable

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*Co-authored by Anne Arza of Nalco/an Ecolab Company. Orally presented at the International Water Conference, November 18th, 2014, paper No IWC-14-45. Modified and reproduced with permission.

water to eliminate the formation of THMs and HAAs. Corporations are also looking for alternative disinfection methods as a result of the restriction on these compounds as well as for economical and corporate sustainability reasons. Alternatives to chlorine that are considered frequently include monochloramine, chlorine dioxide, ozone, and nonoxidizing biocides, such as 2,2-dibromo-3-nitrio-proprionamide (DBNPA). This section discusses chemical and physical alternatives to chlorine and their impact on disinfection of an RO feed water and pretreatment system, along with details on application, efficacy, byproducts, and overall advantages and limitations of each alternative. (Note that oxidizing biocides, such as hypochlorite and some of the alternatives to hypochlorite discussed in this section, are not recommended for direct use for cleaning or sanitization of polyamide-type RO membranes due to the destruction of the membrane polymer by the oxidizer.)

8.5.1 Membrane Biofouling

The bane of existence for users of reverse osmosis (RO) and nanofiltration (NF) spiral wound membrane systems is controlling membrane fouling from microorganisms. A study of 150 polyamide membrane autopsies[20] indicated that all membranes examined had some degree of membrane bio-fouling. Forty-nine had colony densities of greater than 10^5 CFU/cm^2; these were determined to be problematic enough to cause membrane failure. Thus, fully one-third of membrane failures were found to be a direct result of biofouling, and the remaining two-thirds had biofouling as a contributing factor.

Biofouling is the irreversible adhesion on a membrane[21,22] of microorganisms and the extracellular polymeric substances (EPS---aka biofilm) that they produce. The process of adhesion involves three steps:

1. Bacterial adhesion, which can become irreversible in just hours, even without nutrients present.[22]
2. Micro-colony formation.
3. Biofilm maturation with formation of EPS, which serves to protect bacteria from biocides, flow shear, and predators.[22]

Factors that favor adhesion and biofilm formation include:

1. Membrane surface roughness. The rougher the surface the more adhesion can occur. (Note that attempts to modify membranes, i.e., change the roughness, or charge, or hydrophilicity, to make adhesion less favorable are not always successful.[23])

2. Membrane surface charge. The more negative the charge, the more repulsion of bacteria occurs.
3. Membrane hydrophilicity. The more hydrophilic the membrane, the less adhesion can occur.
4. Nutrients. The amount of dissolved nutrients in the concentration polarization layer on the membrane[24] can directly affect the tenancy for adhesion and biofilm formation.

Although biofilms are not fully understood, [22,24] it is known that once biofilm has formed, it protects itself and underlying bacteria from disinfecting chemicals and any flow shear forces that try to disrupt the film.

Aerobic bacteria found in seawater, brackish water, and wastewater systems, and anaerobic bacteria found in wells (e.g., iron- and sulfate-reducing bacteria) can all lead to membrane biofouling, although the fouling potential is higher for surface waters.[24] As RO membranes being utilized in recycle/reuse processes, they will have to deal with an even broader range of microbes, which will be aerobic, anoxic, and anaerobic. The effects of these bacteria on a membrane system can include the following:

1. An increase in differential pressure. This effect can be evident within a few days of inoculation.[21]
2. A decrease in membrane flux. This may or may not occur prior to the change in differential pressure.[21]
3. Higher operating pressure to maintain product flow rate.
4. Uneven growth of colonies, which leads to localized areas of lower flow velocity wherein scaling can occur, resulting in an increase in salt passage. This can also occur prior to appreciable increase in differential pressure, particularly for spiral wound (versus hollow fine fiber) membranes.[21]

8.5.2 Techniques to Address Biofouling

The objectives of biofouling treatment techniques are to kill microbes; remove microbes and dead microbial bodies (which can become food for new growth); prevent adhesion, propagation, and biofilm maturation; and remove nutrients that foster microbial growth. Techniques to accomplish these objectives include:

1. Membrane surface modification (as described earlier).
2. Modification of the bacterium or organic nutrient source itself.

3. Disinfection, removal, or killing of the microbes.

The purpose for using bacterium modification and disinfection is to reduce the concentration of *viable* microorganisms in feed water to an RO or NF membrane. Three basic methods of bacterium modification and disinfection are physical, thermal, and chemical. It is vital to recognize that thermal processes are not applicable to standard RO and NF membranes due to their limit of 45°C, which is well below the sterilization temperature for thermal deactivation. "High" temperature membranes are available from a few manufacturers and are intended for food/beverage and pharmaceutical applications (see chapter 4.4.2.6). These membranes tolerate temperature up to 90°C, provided that the Wagner units [temperature (°C) X pressure (bar)] is less than 2000.[25] Hence, as temperature goes up, the feed pressure must go down to minimize damage to the membrane. Also note that as temperature increases, salt rejection decreases.[25] An overview of physical and chemical techniques follows:

Physical Techniques: Physical techniques include ultraviolet radiation (UV), membrane filtration [microfiltration (MF) and ultrafiltration (UF)], and sand filtration. These techniques either modify the bacterium itself to hinder reproduction (UV) or remove bacteria via particle size filtration (MF, UF, and sand filtration). These techniques can be capital intensive and do little to address biofilm once formed.

Other physical techniques include:

1. Electrochemical: This method includes direct electrolyzers that interact directly with the microorganisms, and pulsed electric field that decomposes the DNA or RNA of a cell by suspending the microbe between electrodes and subjection it to high intensity electric field for a short duration.[23] These techniques lead to cell damage, allowing the intra-cellular material to escape the microorganism, leading to death. These systems are not yet commercialized for industrial application.[26]
2. Ultrasound (sonication): This is a chemical-free process to cause cell disruption by inducing cavitation (bubbles) into a solution. The bubbles generate turbulence and pressure differences during both formation and bursting that can lead to rupture of microorganisms.[23] The technique is still under research.
3. Thermosonication: This technique uses temperature (48°C) in addition to sonication to disturb microorganisms. The

technique disrupts and damages cells to where they are unable to adequately generate EPS on an RO membrane; as a result, they form fewer and less aggregated colonies than does untreated water sent to a membrane.[27] Research into this technique for RO membranes is relatively recent and on-going.[27]

Chemical Techniques: Numerous biocides have been used for biocontrol of membranes systems. The efficacy of a biocide depends on several factors, such as:

1. The nature of the biocide.
2. The concentration of the biocide, where higher concentrations typically provide greater efficacy.
3. Side reactions of the biocide that generate inert compounds.
4. Compounds other the microorganisms, such as organics and some metals, that compete for the biocide chemical.
5. pH.
6. Temperature, where higher temperatures typically provide greater efficacy.
7. Residence time of exposure, where longer exposure results in greater efficacy.
8. Type of microorganism.
9. Growth state of the microorganism.
10. Nature of the biofilm.
11. Cost.
12. Disposal.
13. Continuous discharge within the RO reject and any permits required.

Traditionally, biocides can be classified as electrophilic or membrane active.[28] Research over the last 20 years has improved the understanding of biocidal mechanisms to yield additional classifications[28]:

1. Electrophilic Oxidants: Chlorine, bromine, chlorine dioxide, hydrogen peroxide, peracetic acid, ozone.
2. Moderate Electrophiles: Formaldehyde, glutaraldehyde, isothiazolones, carbamates.
3. Membrane Active—Lytic Biocides: Quaternary ammonium compounds, surfactants.

4. Membrane Active—Protonophores*: Weak organics acids, parabens (parahydroxybenzoates and esters of parahydroxybenzoic acid).

Electrophiles attack both the cell wall and the macromolecules within a cell, such as proteins, lipids, carbohydrates, and nucleic acids. The oxidizers exhibit rapid kill, while moderate electrophiles react more slowly to enter into a cell to disrupt the internal macromolecules. (Note the oxidizing biocides can also react with the EPS or slime to create a reaction barrier to limit entry of the biocide into the cell itself.)[29] Membrane active biocides disrupt the structure and function of the cell membrane.[28] This leads to osmotic lysis and leaking of intracellular material. The protonophores are generally not used for water treatment because their rate of kill is slow and they are ineffective against gram-negative bacteria.[28]

Of the oxidizing biocides, chlorine is the most commonly used for membrane pretreatment applications due to its ease of use and availability, and its ability to deactivate most pathogenic microorganisms quickly.[24] However, due to the propensity of chlorine to form trihalomethanes (THMs) and halo-acetic acids (HAAs), other biocides have been considered for use in pretreating RO and NF membranes. These include:

1. Chloramine: lower biocidal activity and slower kinetics than chlorine.
2. Chlorine dioxide: weaker oxidant than chlorine.
3. Ozone: stronger oxidant than chlorine.
4. Bromine: same effects as chlorine, but weaker.
5. Iodine: same effects as chlorine but even weaker than bromine.
6. BCDMH: 1-bromo-3-chloro-5,5-dimethylhydantoin, that produces hydrobromic acid in water.[30]
7. Combination peroxide/peracetic acid: works in hard-to-reach stagnant areas in the pretreatment train; also used to clean, but water and membranes must be free of metals such as iron and manganese, and pH and temperature must be strickly controlled.
8. Potassium permanganate: commonly used in conjunction with greensand filters for iron oxidation and filtration.

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*Protonophores facilitate the transport of protons through the biological cell walls.

9. Copper sulfate: has shown limited algaecidal effect,[21] but copper has environmental impacts.
10. Biochemical: enzymes, bacteriophages, signaling molecules.[31]
11. Sodium bisulfite: 50 ppm continuous feed has shown good efficacy on seawater RO systems.[24]
12. DCC: dichloroisocyanurate, which demonstrated efficacy equivalent to chlorine in testing.[32]
13. DBNPA: 2,2-dibromo-3-nitrilo-propionamide, a non-oxidizing biocide discussed in this section.
14. Isothiazolone: a non-oxidizing biocide discussed in the section.

Table 8.11 lists the reduction potential in volts for various oxidizing compounds that have been used as biocides.[30] Note that higher reduction potential does not necessarily correspond to better disinfection.

The following sections discuss the primary biocide used today, chlorine, and alternative physical and chemical techniques to address membrane biofouling control. The most common alternative techniques examined here include chloramine, chlorine dioxide, ozone, UV, and non-oxidizing biocides such as DBNPA and isothiazolone. Table 8.12 summarizes advantages and limitations of these techniques (adapted from Kim, 2009).[33] It is important to note that some of these biocides/disinfectants can contact the membranes, and others must be removed or destroyed before the water is introduced to the membrane system itself.

Table 8.11 Standard reduction potential for various oxidizing compounds.

Species	E^o, volts	Species	E^o, volts
Hydroxyl Ion, OH^-	+ 2.8	Chlorine gas, Cl_2	+ 1.346
Ozone, O_3	+ 2.076	Dichloramine, NHCl2	+ 1.34
Hydrogen peroxide, H_2O_2	+ 1.776	Oxygen, O_2	+ 1.23
Hypochlorous Acid, HOCl	+ 1.482	Chlorine Dioxide, ClO_2	+ 0.954
Monochloramine, NH_2Cl	+ 1.4	Hypochlorite Ion, OCl^-	+ 0.81

Table 8.12 Comparison of physical and chemical techniques that are used to control microorganisms in reverse osmosis membrane systems.

Method	Technique	Advantages	Limitations	Relative Cost*
Physical	UV	• Easy installation • Effective inactivation • Oxidizes organic matter	• No residual effect • Scaling on lights • High capital investment	$$$$
Chemical	Chlorine	• Effective inactivation • Relatively low cost • Carries residual	• Membrane degradation • THMs, HAAs formation • Toxic gas	$
	Chloramine	• Less destructive to membranes Carries residual	• Relatively low efficacy	$
	Chlorine Dioxide	• Slightly less destructive to membranes	• Must be site generated • Chlorite toxicity • Toxic gas/OSHA exposure limits • May generate some free chlorine also	$$-$$$
	Ozone	• Effective inactivation • Oxidizes organic matter	• Very short half-life • Membrane degradation	$$$$
	Non-oxidizers	• Good membrane compatibility	• Relatively low efficacy • Expensive	$$$-$$$$

*estimated relative costs based on capital and operating costs combined.

8.5.2.1 Chemical Techniques

8.5.2.1.1 Chlorine

Chlorine is an oxidizing biocide used to disinfect the pretreatment system prior to RO or NF membranes. It works by oxidizing cellular material of the microorganism. The most common forms of chlorine used today are

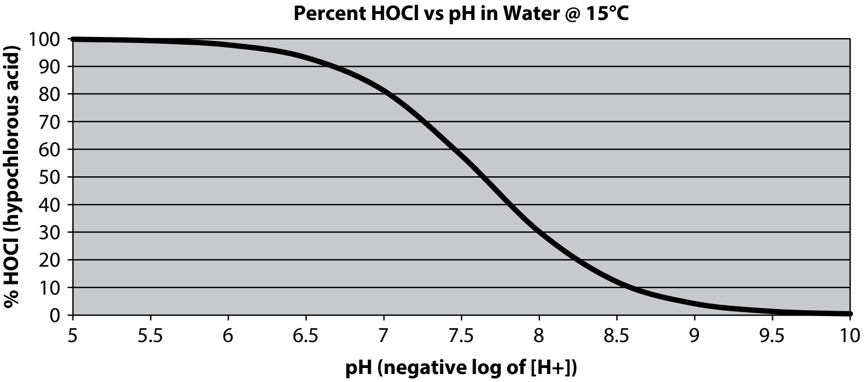

Figure 8.22 Percent hypochlorous acid in water as a function of pH.

the gaseous and liquid sodium hypochlorite forms. Gaseous chlorine is by far the most economical form of chlorine,[34] but it is also the most toxic and requires special storage and handling. Both chlorine gas and sodium hypochlorite immediately hydrolyze in water to form hypochlorous acid, HOCl:

$$Cl_2 + H_2O \leftarrow\rightarrow HOCl + HCl \tag{8.22}$$

$$NaOCl + H_2O \rightarrow HOCl + NaOH \tag{8.23}$$

Note that chlorine gas yields acid, which reduces the pH of the treated water, while sodium hypochlorite yields caustic, which raises the pH of the treated water. Hypochlorous acid is unstable and decomposes to form hypochlorite ion, OCl:

$$HOCl \leftarrow\rightarrow H^+ + OCl^- \tag{8.24}$$

The stability of hypochlorous acid is a function of pH, temperature, and salinity. Figure 8.22 shows the percentage of hypochlorous acid on the left and hypochlorite ion on the right of the curve as a function of pH. Hypochlorite is a weaker disinfectant that hypochlorous acid because it has a negative charge, making it difficult to penetrate the negatively charged microorganisms.[23]

The efficacy of treatment with chlorine prior to a membrane system is a function of pH, exposure time, and method of application. As discussed above, the stronger hypochlorous acid form is present in greater amounts as the pH drops, making lower pH desirable for treatment. An exposure time of 20 to 30 minutes is recommended at the head of the pretreatment train to ensure that maximum kill is achieved.[24]

Following the exposure time, a residual of 0.5–1.0 ppm should be maintained throughout the pretreatment system for residual disinfection.[24,35] (The optimum dosage for chlorine to achieve this residual can be determined by using the ASTM method D 1291, "Standard Practice for Determining Chlorine Requirement of Water.") Finally, continuous feed of chlorine has shown to be more effective at hindering development of biofilm than shock treatment alone.[35] It has been reported that no biofilm was formed on a seawater RO system carrying 0.04–0.05 ppm residual free chlorine.[36] Continuous feed plus shock treatments during warm weather has also been effective at controlling bio growth and preventing biofilm development.[21]

While chlorination is easy to employ and is relatively inexpensive, there are limitations to using this technique.

1. Chlorination is ineffective at controlling some pathogens, including *Cryptosporidium parvum* and *Mycobacterium avium. Mycobacterium* is ubiquitous in biofilms within water systems and has excellent resistance to chlorine.[37] Chlorination is also poor at deactivating protozoa and endospores.[38]
2. Chlorine oxidizes organic molecules into smaller organic pieces. While this may help minimize fouling of the RO with larger chain organics, such as humic acids, the smaller particles are converted into assimilable organic carbon (AOC) which microbes can assimilate for growth.[21,24]
3. Perhaps the biggest issue with chlorination is the formation of carcinogenic species such as trihalomethanes (THM) and haloacetic acids (HAA).
4. Finally, chlorine will oxidize the membrane polymer and, in effect, destroy the integrity of the membranes. Specifically, the chlorine attacks the amide functional group that destroys the hydrogen-bond linkages in the polymer.[39,40]

Due to chlorine's deleterious effects on polyamide membranes, it [and more specifically, free chlorine (i.e., hypcochlorite, + hypochlorous acid + chlorine gas + trichloride ion)] must be removed to prevent contact with the membranes. Dechlorination is relatively simple, typically using either sodium bisulfite to chemically remove free chlorine or carbon filtration to catalytically remove chlorine (see chapter 8.2.3. and 8.1.4, respectively).

8.5.2.1.2. Chloramine

Chloramine, like chlorine, is an oxidizing biocide used for disinfection. Three species collectively make up chloramines, also known as "combined chlorine": monochloramine, NH_2Cl; dichloramine, $NHCl_2$; and nitrogen trichloride (trichloramine), NCl_3. Of these, monochloramine has the highest standard reduction potential; furthermore, it is less prone to impart chlorinous taste and odor to water like other forms of chloramine. As a result, monochloramine is preferred for disinfection applications.

Chloramines are generated by reacting hypochlorous acid with free ammonia, NH_3:

$$\mathrm{HOCl + NH_3 \leftarrow\rightarrow NH2CL + H_2O} \tag{8.25}$$

$$\mathrm{2HOCl + NH_3 \leftarrow\rightarrow NHCl_2 + 2H_2O} \tag{8.26}$$

$$\mathrm{3HOCl + NH_3 \leftarrow\rightarrow NCl_3 + 3H_2O} \tag{8.27}$$

Figure 8.23 shows the distribution of mono-, di-, and tri-chloramine as a function of pH.

The intentional action of combining chlorine with ammonia is called chloramination. The reactions strongly depend on pH, the relative concentration of the reactants, and temperature.[41] At 25°C, the reaction time for monochloramine to form is minimized at pH 8.4.[30] Stoichiometrically,

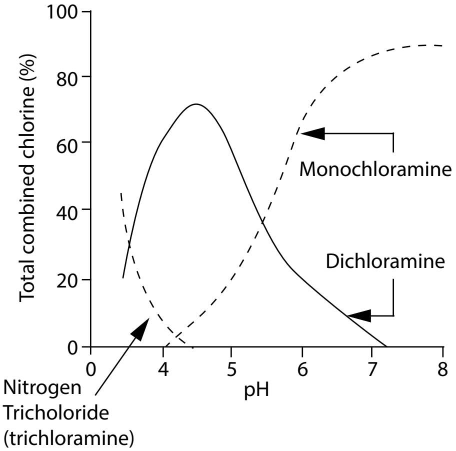

Figure 8.23 Combined chlorine species as a function of pH. Trichloramine (nitrogen trichloride) predominates at low pH, 1- 3; dichloramine exists at pH ranging from 4–7; and monochloramine predominates at pH greater than 7.

Equation 8.25 shows that one mole of hypochlorous acid reacts with one mole of ammonia to form one mole of monochloramine. On a weight basis, this corresponds to a chlorine to nitrogen (Cl_2:N) ratio of about 5:1. Higher ratios slow the reaction;[30] lower ratios result in more di- and tri-chloramines being formed. At the same time, lower temperature slows the reaction.

Another feature to note from Equation 8.25 is that it is a reversible reaction, so that chlorine will always be in equilibrium with monochloramine.[30,42] This can be a source of concern when using monochloramine with RO membranes.

Monochloramine potentially is as effective at penetrating and disrupting metabolism of microorganisms as chlorine, as shown in Table 1, and is equally effective at oxidizing compounds, such as disulfides. But in reality, monochloramine has only 0.4% of the biocidal capability as hypochlorous acid.[43] Also, its kinetics are slower.[44] The slow kinetics of monochloramine results in longer existence of residuals in distributions systems than chlorine provides, making monochloramine more desirable for municipal water distribution systems. However, the slower kinetics means that it might take days or weeks to accomplish acceptable kill of microorganisms,[43] which may be acceptable for water distribution systems but not for immediate disinfection prior to an RO.

The concentration of monochloramine to treat water requires an understanding of breakpoint chlorination. Figure 8.24 illustrates breakpoint chlorination (adapted from Lenntech, 1998).[42]

Chloramination occurs in Section I of the figure where chlorine added to ammonia naturally is present (or added) to form monochloramine. The maximum concentration of monochloramine occurs when all of the

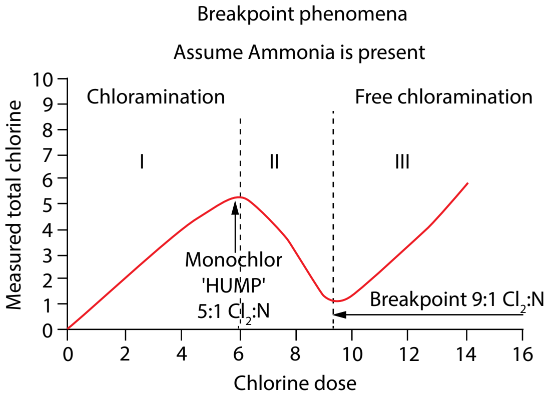

Figure 8.24 Breakpoint chlorination.

ammonia present has reacted with the added chlorine. This is the "monochloramine hump." Any chlorine added after this point results in the formation of trichloramine and the continued "breaking down" of nitrogen species. This continues until "breakpoint" is achieved, and any chlorine added after this point yields only free chlorine.

The advantages of using chloramination for disinfection rest primarily on the diminished capability of chloramine to form hazardous disinfection by-products (DBP) relative to chlorination. Limitations to chloramination include the following:

1. When the total organic carbon (TOC) concentration exceeds approximately 3 ppm, organic chloramines form,[42] and they have little or no disinfectant capabilities.
2. The reaction rate is slow, as discussed above.
3. Chloramines are not as effective as chlorine on pathogenic microorganisms.
4. The ammonia added to generate chloramine also provides nutrients for nitrifying bacteria, which may cause nitrate concentrations to rise in water treated with chloramination.

Due to the fact that free chlorine is in equilibrium with monochloramine, water treated by chloramination should be treated for removal prior to RO membranes. Although most membrane manufacturers allow for a chloramine exposure of about 300,000 ppm-hrs, this exposure is calculated based on PURE chloramine. There are several methods to remove chloramine (e.g., sodium thiosulfate, UV, ascorbic acid): the most common methods are carbon filtration and sodium bisulfite. Empty bed contact time (EBCT) for fresh carbon can be as short as 10 minutes, while used carbon can require up to 30 minutes of EBCT for removal. The reaction for sodium bisulfite is as follows and has rapid kinetics.[45]

$$NH_2Cl + NaHSO_3 + H_2O \rightarrow NaHSO_4 + NH_4Cl \qquad (8.28)$$

8.5.2.1.3 Chlorine Dioxide

Chlorine dioxide is also an oxidizing biocide. Over the last 20 to 30 years, its use has increased significantly for disinfection, color reduction, and taste and odor control.[30,44] While it minimizes the production of THMs by oxidizing the THM precursors, it does form chlorite and chlorate, both of which are considered disinfection by-products (DBPs). Note that the EPA has established a maximum contaminant level goal (MCLG) for chlorite of 0.8 ppm; because 75% of chlorine dioxide that is applied to water forms chlorite, the maximum chlorine dioxide concentration allowable is

1.3 ppm unless a chlorate removal process is employed.[30] While chlorate does not have a MCLG established, studies indicate that it is a potential health hazard.[47]

Chlorine dioxide is a highly volatile compound and is not stable in concentrated solutions: the gas detonates upon compression. Thus, chlorine dioxide must be generated on site. The conventional method for generating chlorine dioxide involves the mixing of sodium chlorite with chlorine gas (Equation 8.29) or hypochlorous acid (Equation 8.30):

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \tag{8.29}$$

$$2NaClO_2 + HOCl + HCl \rightarrow 2ClO_2 + H_2O + 2NaCl \tag{8.30}$$

These methods have the potential for leaving behind unreacted chlorine gas or hypochlorite that will damage RO membranes:

> "The recommendation is to not use chlorine dioxide with FILMTEC membranes. FILMTEC membranes have shown some compatibility with pure chlorine dioxide. Chlorine dioxide that is generated on-site from chlorine and sodium chlorate, however, is always contaminated with free chlorine that attacks the membrane."[48]

Thus, other methods of forming chlorine dioxide must be used with RO membranes:

$$2NaClO_2 + H_2O_2 + H_2SO_4 \rightarrow 2ClO_2 + NaSO_4 + O_2 + 2H_2O \tag{8.31}$$

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \tag{8.32}$$

Despite the lack of free chlorine shown in Equations 8.30 and 8.31, chlorine dioxide is not 100% compatible with RO membranes. Compatibility depends on dosage, exposure time, and pH. Adams (1990) did an extensive study on the effects of chlorine dioxide on RO membranes.[48] His work and others[50] discovered decreases in rejection at almost any pH; however, the higher the pH, the worse the damage.

Representative results include a drop in rejection for Filmtec FT-30 membranes to 98% over 152 days at a exposure of 1 ppm (see Figure 8.25), and a drop to 96% in 24 days at an exposure of 5 ppm (see Figure 8.26) (both tests were conducted at a pH of 7.0). Work by Glater (1981) shows severe damage at 1200 ppm-hrs exposure at pH 8.6, and relatively little damage under the same conditions at pH 5.8. [50] Little if any studies have been recently reported which is hydranautics recommends are studies are (see chapter 8.2.1.1).[14]

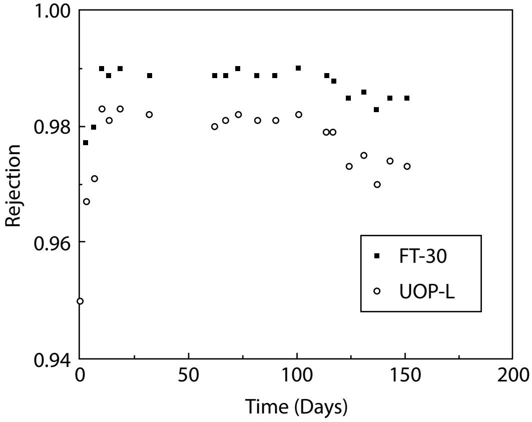

Figure 8.25 Rejection vs. time for FT-30 and UOP-L membranes at 2.17 MPa (390 psi) with 1 ppm chlorine dioxide, pH 7.0, conductivity 6000 µS/cm. *Courtesy of Elsevier Limited.*

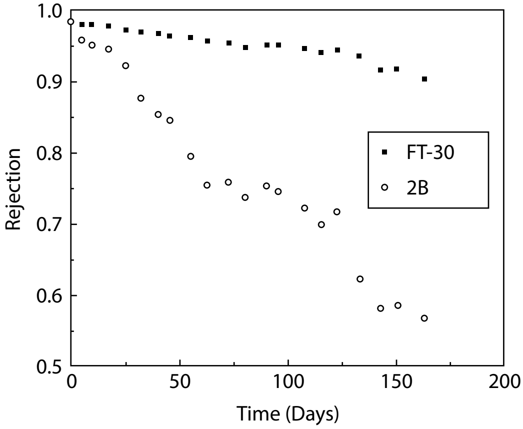

Figure 8.26 Rejection vs. time for FT-30 and Desalination Systems 2B membranes at 2.17 MPa (390 psi) with 5 ppm chlorine dioxide, pH 7.0, conductivity 6000 µS/cm. *Courtesy of Elsevier Limited.*

Despite the membrane issues, chlorine dioxide is a very effective biocide, hence its attraction. Work has shown that less than 0.1 ppm of chlorine dioxide can successfully inactivate common water pathogens (e.g., *Salmonella paratyphi B, Eberthella Typhosa*, and *Shigells Dysenterias*) in five minutes of exposure.[51] Malpas (1965) demonstrated that chlorine dioxide was at least as effective and in some cases more effective than chlorine on *Escherichia coli, Salmonella typhosa*, and *Salmonella paratyhi*.[52]

Chlorine dioxide works best on relatively clean surface waters when the concentration of oxidant-demanding species such as iron, manganese, and organics are low.[30] Dosing is best located after clarification and even filtration to lower the oxidant demand. These may not be the best locations to disinfect RO pretreatment systems but are desirable to keep the dosages and concentrations of the product low.

The advantages of chlorine dioxide are that it does not yield THMs and HAAs and that it is a more effective disinfectant than chlorine. Its limitations include:

1. Potential damage to RO membranes.
2. Formation of chlorite and chlorate.
3. High volatility and explosive nature.
4. Difficulty in dosing the product when other oxidant-demanding species are present.

8.5.2.1.4 Ozone

Ozone (O_3) or trioxygen is an allotropic form of oxygen. It is a strong oxidizing biocide used to disinfect pretreatment systems prior to RO or NF membranes. Ozone was first used for disinfection in water in 1886. It is a colorless gas at room temperature and condenses to a blue liquid. It is extremely unstable.[30] It works by oxidizing cellular material of the microorganism, either directly or through decomposition, that forms other radical species that react with organic matter.[53] Ozone is a 50% stronger oxidizer than chlorine and acts over 3000 times faster. It is one of the strongest oxidizers available (see Table 1).[54] Ozone is effective at deactivating bacteria, viruses, protozoa, and endospores. [27]

Ozone decomposes rapidly in water to form hydroxyl free radicals OH- that effectively destroy microorganisms.[27] Direct reactions with O_3 are also possible. The typical reactions are:

$$O_3 + OH^- \rightarrow O_2^- + HO_2 \tag{8.33}$$

or

$$O_3 + \text{Organic} \rightarrow \text{Organic}_{ox} \tag{8.34}$$

Ozone and its related radicals weaken the biofilm matrix and allows for removal of biomass by sheer forces.[36] The free radicals can also form H_2O_2 that penetrates the cell walls of a microorganism and disrupts cell physiology.

Ozone is extremely corrosive; therefore, the materials of construction for both generation equipment and distribution equipment should be carefully considered. Ozone will attack all metals except 316SS, gold, and platinum. Many plastics are not compatible. Only select fluoropolymers should be considered. [30]

The overall efficiency of ozone is difficult to predict due to the complex nature of natural organic materials, water characteristics, temperature, and pH.[53] Ozone dosage is based on two factors: first, the amount of ozone needed (mg) to stoichiometrically consume the contaminants present, and second, the amount needed for disinfection in mg/l based on a concentration over time. Both steps require correct injection and mixing time. Ozone must physically come into contact with the contaminants to be effective. Filtration is almost always required to remove particulates. Any excess ozone will create off gas, which must be destroyed.[54] Most water system conditions are variable in nature. In practice, dosage is based on the creation of a barely measurable residual.[30]

In nature ozone occurs mainly by electrical and radiation generation. Ozone can be commercially generated by several methods: electrical discharge (corona discharge), electrolysis of acid, photochemically (UV), radiochemically, and other less commonly used chemical methods. Electrical discharge generation is by far the most common, safest, and most economical method for ozone generation.[54]

Electrical generation of ozone occurs when extremely dry air or pure oxygen is exposed to a uniform high voltage electrical discharge. The generated gas is then transferred to water to be treated via eduction, pressure injection, diffusion, or packed towers. Because ozone degrades quickly, it must be generated in a plug flow manner rather than in a mixed fashion.[52,55] Ozone generation costs are approximately four times that of chlorine.[36]

Due to its highly oxidative nature, ozone must be removed before the membrane as it has been known to breakdown the membrane surface.[36] Ozone can be removed by adsorption, catalysis, chemical reaction, UV, timed decay, or thermally. Ozone can be removed catalytically with metal oxides.[54] This method and thermal destruction require elevated temperatures of 85F-160F, which are not compatible with most membranes. The most viable methods for ozone removal prior to a membrane are carbon adsorption or ultraviolet light. Ozone can be removed by adsorption on carbon.[56] This method can potentially produce heat and a possible safety hazard if ozone is generated with pure oxygen. Ultraviolet light is commonly used prior to membrane systems to remove ozone.[24] A 254nm light is used to add energy to ozone converting it into water and O_2 (see Figure 8.27).

To maximize the sanitation benefits, both the carbon or ultraviolet destruct should be located as close as possible to the membrane to allow the ozone to remain in the system as long as possible.[56]

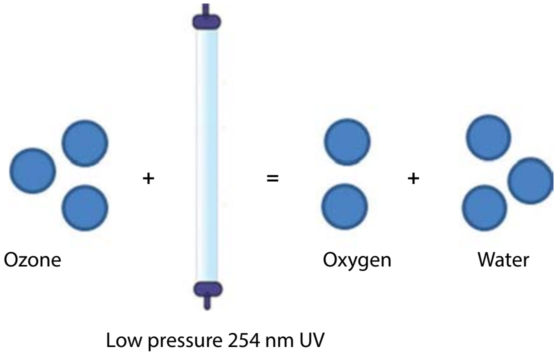

Figure 8.27 Deactivation of ozone with UV light.

As a strong oxidizer, ozone is especially effective at preventing biofouling. However, low doses of ozone may not effectively deactivate some viruses, spores, and cysts. The correct dosage is difficult to predict based on changing water characteristics and monitoring dosages. Ozone must be generated onsite, which reduces shipping and handling hazards, but it does require a more complex technology for creation, contact, and destruction. Filtration is required in most cases. Overall, ozone does have a higher cost than other forms of control. The materials of construction must be carefully considered with ozone due to its reactive and corrosive nature.[55] Any residual ozone must be removed before the membranes to prevent damage.[24] Under specific conditions ozone can create bromates or bromine compounds that have been found to be carcinogenic. Ozone can also cause larger organics to break down into smaller organics, which favors microorganism growth.[36]

8.5.2.2 Chemical Techniques—Non-Oxidizing Biocides

8.5.2.2.1 2,2-Dibromo-nitrilo-Propionamide (DBNPA)

DBNPA is a non-oxidizing, moderate electrophile biocide that is compatible with membranes. Its mode of action is similar to oxidizers, but is not as aggressive; it acts on the cell wall as well as with the cell cytoplasm, but it does not interact with the slime (EPS). Application for membranes can either involve shock treatment, such as 6–12 ppm as active for 60 minutes, every two to three days, or continuous treatment at 2–3 ppm as 20% product. Due to the expensive nature of the treatment, continuous treatment is typically not economical. Work by Schook *et al.* has shown the use of 8.5 ppm as active DBNPA for three hours once per week can be more effective that 20 ppm (as active) exposure for one hour once per week (see figure 8.28).[60]

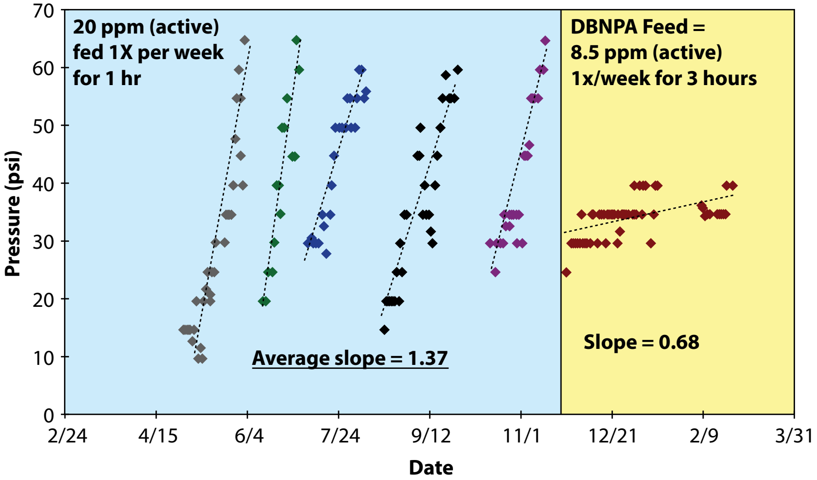

Figure 8.28 Differential pressure as a function of time for an RO system operating on the Weisse Elster River in Germany while being treated with DBNPA using two different scenarios. Orally presented at the International Water Conference, November, 2012.

DBNPA is well rejected by RO membranes, up to 99.98%[60], so on-line treatment is acceptable for most industrial applications. DBNPA can be used for potable applications if the treatment occurs offline (due to the limited passage of the biocide)[60], and the system is rinsed and monitored properly. The key factor for DBNPA effectiveness is to eliminate the active biological slime from the system via a cleaning process before using DBNPA, since DBNPA is a moderate electrophile, that does not attack the ESP.[59] Thus, DBNPA is most effective on membranes that are relatively free of mature biological colonies and slime. At a pH above 8, the product tends to hydrolyze, so application at neutral pH is recommended;[61] The half life of DBNPA is 24 hours at pH 7, 2 hours at pH 8, and 15 minutes at pH 9.

8.5.2.2.2 Isothiazolones

Isothiazolone biocides are commonly used in water treatment for controlling microbial growth and biofouling. The most common isothiazolone biocide used is a 3:1 ratio of 5-chloro-2-methyl-4-isothizolin-3-one (CMIT) and 2 methyl-4-isothiazolin-3-one (MIT).[62] The mechanism of action of isothiazolones is complex. It involves a rapid inhibition of growth followed by a slower cell death.[62]Cell physiological activities that are rapidly inhibited by isothiazolones include respiration and energy generation [adenosine triphosphate (ATP) synthesis]. Killing of the cells is a function of the production of free radicals (among other pathways) within the cell.[62]

Cell death can take several hours, [61] but it is enhanced by higher concentrations of the biocide or via the addition of other actives, such as surfactants.[62] Although resistance to many biocides (including halogens) has been exhibited by microorganisms, resistance to isothiazolones has been infrequently reported and can be easily remedied by rotating biocides or adding surfactants to enhance efficacy.[62] Isothiazolones are effective against aerobic and spore-forming bacteria at pH 6.5–9.0, and act as an effective algaecides and fungicides, at acid to slightly alkaline pH.[61] Dosage rates are typically 50–120 ppm of a 1.5% active product for five to six hours of exposure.[61] Due to the relatively high dosage and long contact time required for isothiazolones to work, they are generally used for cleaning and layup of RO membranes rather than for on-line or intermittent treatments. Note that isothiazolones have high aquatic toxicity, so their use may be limited for some applications. Additionally, the products are expensive, further limiting their use for on-line or shock treatments.

8.5.2.2.3 Sodium Bisulfite

Sodium bisulfite is a reducing agent/antioxidant with good efficacy on aerobic bacteria.[24] It is generally used as an inhibitor of biogrowth during membrane storage.[63,64] Prior to storage, the membranes should be cleaned to remove as much biogrowth as possible before the membranes are laid up in the non-cobalt-catalyzed bisulfite solution. Most membrane manufacturers recommend a storage solution of 1% sodium bisulfite for storage up to six months. The bisulfite solution decomposes to acid when consumed by biologicals:

$$HCO_3^- \rightarrow H^+ + SO_3^{2-} \tag{8.35}$$

This effect is naturally exacerbated at higher storage temperatures when microorganisms tend to proliferate at a faster rate. The pH of the membrane storage solution should be frequently monitored, and the bisulfite solution replace when the pH drops to about 3.

LG NanoH$_2$O also recommends shock treatment of on-line membrane systems using sodium bisulfite.[64] The recommendation is 500 ppm for 30 to 60 minutes of exposure time.

Sodium bisulfite has also been used as a biostatic pretreatment technique for seawater RO systems.[24] Dosages up to 50 ppm have been used. However, this treatment is only effective on low-to-medium fouling potential feed waters.[24] Open seawater intakes or intakes in the vicinity of harbors and municipal discharge are not good candidates for microbial control with sodium bisulfite.[24]

8.5.2.3 Physical Techniques Ultraviolet radiation (UV)

Ultraviolet (UV) is a form of electromagnetic radiation located between X-Ray and visible light on the electromagnetic spectrum. Ultraviolet light is located in the 100-400nm wavelength range. Ultraviolet radiation is broken into four sub categories: UV-A 400-315nm, UV-B 315-280nm, UV-C 280-200nm, and Vacuum UV (VUV) 200-100nm. Primary disinfection by UV happens in the 200-300nm wavelength range (see Figure 8.29).[30] Vacuum UV is not effective due to rapid dissipation and due to the degradation of organics providing an easily consumable food source for biologicals.[27]

Ultraviolet disinfection is a physical process that transfers electromagnetic energy either to an organism's genetic material (DNA and RNA) to destroy its ability to reproduce,[57] or by direct organism inactivation that begins with the adsorption of photons by the proteins and nucleotides in the cell. Ultraviolet light adsorption by the proteins in the outer wall of the cell leads to the disruption of the cell membrane, resulting in protoplasm leakage and cell death.[58] In order for cell disruption to occur the organism's DNA must adsorb energy at the correct wavelength and light must be available in sufficient energy. The optimal wavelength for cell disruption is 250-270nm. Low pressure lamps emit a wavelength of 254nm. Under specific circumstances, photobiochemical repair may occur in the organism.[30] Increasing the time of exposure and the amount of radiation will reduce this reversal potential and increase the effectiveness of UV.

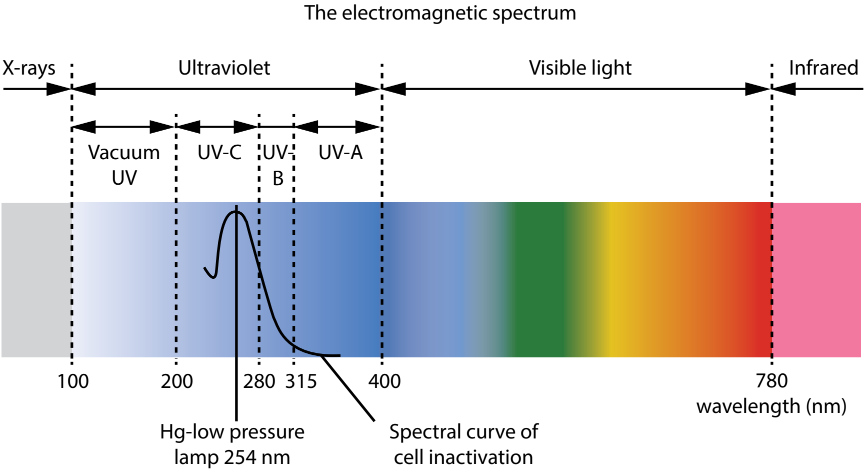

Figure 8.29 Electromagnetic spectrum showing UV range and optimum wavelength for disinfection.

Ultraviolet radiation is excellent on protozoa. It is less effective on bacteria, viruses, and endospores, particularly at low dosages.[54] This technique typically performs best in conjunction with hypochlorite, H_2O_2, or other chemical methods.[34]

Factors affecting efficacy include wavelength, dosage, exposure time, and the manner of distribution of light in the water. Ultraviolet light is adversely impacted by higher levels of turbidity, total suspended solids, iron, and humic acids.[26,56] Equipment maintenance is key in a well operated system. A good preventative maintenance program is required to prevent fouling of the system.

The generation of UV light is typically achieved by placing a voltage across a gas mixture contained in lamp tubes. The gas is temporarily excited by the voltage and emits photons as it returns to a lower energy state. The gas mixture determines the wavelength emitted. Common lamp types are mercury vapor, metal halide, pulsed UV, and excimer or LED. The most common water treatment lamp is the mercury vapor. A typical system consists of the UV lamps, reactor, ballasts, lamp sleeves, and sensors.[30]

Ultraviolet light has no residual effects in the system and therefore no need for removal before a membrane system. The UV irradiation should be placed as close as possible to the membrane system to minimize the time between irradiation and filtration.[57]

Ultraviolet technology is effective for the destruction of specific biological species in bulk water. It is easy to install and maintain. It has no harmful byproducts and no residual effects that adversely affect membranes. Its effectiveness is not affected by pH, and it requires no chemical handling.

Ultraviolet light generation is costlier than chlorine but can be competitive after considering chlorine removal expenses. the operational costs include power consumption, cleaning chemicals/supplies, equipment repairs, and replacement of lamps and sleeves.[58] Furthermore, the initial equipment investment can be substantial.

The major limitation is that up is not as effective on some species of biologics as a standalone treatment. (Studies indicate it can be more effective in conjunction with chemicals.) It can have low performance in light scattering waters. Filtration is usually required to ensure effectiveness because sediment and other particles can shade microorganisms from the light.[59] If the wavelength is not carefully controlled, it can break down larger organics, thereby creating a food source for other biologics. There is no residual kill effect so placement of the unit close to the membrane system is critical. The units are prone to scaling and fouling, particularly in high hardness waters.

8.5.2.4 Other Biocides and Techniques

Many other less common chemical, operational, and mechanical methods are available for biological control in membrane systems.

Non-oxidizing biocides can be used in continuous or batch feed to treat many membrane systems depending on local regulations.[60] While there are many non-oxidizing chemicals commercially available, such as quaternary amines (Quats), Glutaraldehyde, and dithiocarbamates, not all non-oxidizers are compatible with membranes. Dibromonitrilopropionamide (DBNPA) and Isothiazolones are the only viable choices for use with membrane systems.[28] Quats are membrane-active biocides, but are not recommended for polyamide membrane applications as they cause irreversible flux loss.[66] Aldehydes, such as glutaraldehyde and formaldehyde, are moderate electrophiles that cause irreversible damage to new membranes; their use is recommended only for "used" polyamide membranes. Furthermore, formaldehyde is a carcinogen and has strict handling regulations. Carbamates are also moderate electrophiles that require dosages of 100–200 ppm for exposure times of four to six hours, making them unsuitable for on-line or shock treatment of RO membranes. They are not recommended for use with polyamide membranes.

Bromine, iodine and BCDMH (1-Bromo-3-Chloro-5, 5-dimethylhydantoin) are oxidizing biocides similar in action to chlorine, but they are weaker and removal of residual is more complex. They are significantly more expensive than hypochlorite, but BCDMH comes in a solid form, which may provide advantages for certain systems.[30]

Other oxidizing compounds like potassium permanganate (KMnO4), hydrogen peroxide (H_2O_2), and H_2O_2 combined with peracetic acid can be used as oxidizers similar to chlorine, but they are less effective overall, pose safety and handling issues, and have higher costs. Hydrogen peroxide and peracetic acid are effective in penetrating stagnant areas in a pretreatment system;[21] they must be used in the absense of metals at pH 7 and of temperatures below 25°C.

Advanced oxidation processes (AOPs) rely on the generation of highly reactive radical intermediates, specifically the hydroxyl (OH^-) radical.[30] Hydroxyl radicals are formed via the decomposition of ozone, but the concentration of hydroxyl radical is too low for this to be considered a viable AOP.[30] The most common AOPs using the following combinations of compounds/techniques to generate more of the hydroxyl radical are:[30]

- Ozone/UV.
- Ozone/Peroxide.
- Peroxide/UV.

Because no research data is available on the disinfection potency of hydroxyl radical, it is not a recognized disinfectant.[30] Thus, any disinfection must be achieved with the companion oxidant, such as ozone, prior to the formation of the hydroxyl radical. The hydroxyl radical is used primarily for removal of volatile organic chemicals, pesticides, and taste and odor compounds that are not effectively removed by conventional clarification/filtration processes rather than for disinfection. Therefore, AOPs are generally not used for disinfection of RO pretreatment systems.

The chloramine compound Dichloroisocyanurate (DCC) is under study and shows promising initial results for effectiveness and minimal membrane damage.[33]

Copper Sulfate has been used in large systems. It is limited to an algaecide, and due to copper discharge restrictions has limited use.[21]

The addition of caustic for pH adjustment creates a negative charge repulsing organics including biocides, but is not generally used for this purpose. Additional costs will be incurred for neutralization.[27]

Biochemical methods such as enzymes, bacteriophages, and signaling molecules can be used to change how a film forms or to inhibit formation. These methods have a high cost and may only be effective or stable under specific conditions. Their low toxicity and biodegradability make them attractive.[25]

In medium risk systems, regular preventative cleanings may take the place of or be done in addition to biocide addition. Single attached bacteria are easier to remove than full biofilm.[22] This approach requires a cleaning system and unit downtime. It has a moderate chemical cost but is more labor intensive. Depending on the frequency required and the chemicals used for cleaning, membranes may degrade faster.[67]

Sieving and repulsion of charge via ultrafiltration (UF), microfiltration (MF), multimedia, or other physical barriers may to have high capital costs (UF and MF) and are not 100% effective (see Chapter 16.1 for discussions on UF and MF technologies). Membrane filtration typically requires an oxidant to be used concurrently with the membrane system to maximize the biocidal effect.

There are two electrical methods used for treating biologicals in water: electrochemical and pulsed electric field. Both techniques require generating an electrical field that either directly affects the microorganisms or indirectly creates oxidizing species that affect the microorganisms. They can create mutagenic compounds in the water, have cathodes that tend to foul, and lack any residual effects. Neither has been extensively studied for applications with membranes.[27]

Ultrasound and thermosonication (ultrasound plus heat) are techniques under study for biological control in membranes. Both are non-chemical methods and have no residual effect. They are expensive to operate and their effectiveness is influenced by the medium, the presence of dissolved gasses, and the type of microorganism. Initial studies indicate the need for further research.[27]

Membrane surface modification is also used to reduce biofouling by minimizing bacterial adhesion. This is done with smoother surfaces, more hydrophilic membranes preferring to interact with water and creating a more negatively charged surface to repel microorganisms. New generation of membrane module feed spacers have improved mixing at the membrane surface loading to claimer lower potential for biofouling.[68] Anti-microbial nano particles like silver, titanium dioxide, and carbon nanotubes have also been incorporated into membranes. Not all changes have resulted in positive results; improving biofouling results can increase the risk of other types of fouling.[26]

8.5.3 Summary

This section discussed hypochlorite and some of the common alternatives to hypochlorite and their impact on disinfection of an RO feed water and pretreatment system; as well as details on application, efficacy, byproducts, and overall advantages and limitations of each alternative. The best way to determine which technique or chemical is the most effective on biologicals in any system is to pilot test. This is often not practical.[21] Hence, this section provides information for evaluating which option may be appropriate for any specific application, short of (or in preparation for) a pilot study.

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3

SYSTEM DESIGN

9

Design Considerations

Operating conditions affect the performance of an RO system. These conditions include:

- Feed water quality and source
- Temperature
- Pressure
- Feed water flow
- Concentrate flow
- Beta
- Recovery
- pH
- Flux

The effects of these conditions on the performance of an RO system are discussed in this chapter.

9.1 Feed Water Quality

Feed water quality and its tendency to foul has a significant impact on the design of an RO system. Selection of the design flux, feed water and reject flows (and hence, the array), and salt rejection is influenced by the feed water quality.

9.1.1 Feed Water Source

The feed water source has a great impact on the potential of the water to foul an RO membrane. High-quality source water, such as well water with SDI less than 3, has a lower chance of fouling an RO membrane than a lower-quality source water, such as surface water with an SDI of 5. An RO system designed to operate on higher-quality source water can be designed with a higher flux than one operating on a lower-quality source water. This is because a higher the flux rate brings contaminants (suspended solids, hardness) to the surface of the membrane faster than would a lower flow rate. These contaminants then collect in the concentration polarization boundary layer at the membrane surface, which leads to accelerated fouling or scaling of the membrane (See Chapter 3.5). Hence, the higher the concentration of suspended solids and hardness in the feed water, the lower the flux should be to reduce the potential for fouling and scaling the membranes.

Table 9.1 lists the recommended average and conservative flux rates for various feed water source qualities.[1,2] As the table shows, an RO system operating on well water could be designed with a flux as high as 14–16 gfd, while a surface water with SDI less than 5 should only have a flux of 10–12 gfd. In other words, for a given product flow rate, a well water-based RO system can have a 14% smaller RO system than the surface water RO due to the higher allowable flux. This not only reduces capital and operating costs, but also results in additional operating cost savings due to reduced membrane cleaning and replacement frequencies because of the higher quality feed water.

Feed water source also influences the design array of the RO unit. This is because the feed water flow and concentrate flow rates are also determined based on feed water quality. Higher feed water quality allows for higher feed flows and lower concentrate flows to be employed. Higher feed water flows and lower concentrate flows reduce the number of membrane modules required in the RO system.

Tables 9.2 and 9.3 list the recommended feed water and concentrate flow rates, respectively, as functions of feed water source quality.[1] Higher feed water flow rates result in water and its contaminants being sent to the membrane

Table 9.1 Recommended flux rates as a function of feed water source, as adapted from Dow Water and Process Solutions and Hydranautics.[1,2]

Feed Water Source	Silt Density Index	Average Flux, gfd*	Conservative Flux, gfd*
RO Permeate	<1	21–25	22
Well Water	<3	14–16	14
Surface Supply	<3	12–14	12
Surface Supply	<5	10–12	10
Secondary Municipal Effluent—Microfiltration Pretreatment**	<3	10–14	10
Secondary Municipal Effluent—Conventional Pretreatment	<5	7–12	7

* For 8-inch diameter, brackish water membrane modules

** Microfiltration pore size <0.5 microns.

Table 9.2 Recommended feed water flow rate as a function of feed water source for brackish water membranes, as adapted from Dow Water and Process Solutions.[1]

Feed Water Source	Maximum Feed Flow Rate for 365 ft^2 Modules gpm	Maximum Feed Flow Rate for 400 and 440 ft^2 Modules, gpm
RO Permeate	65	75
Well Water	65	75
Surface Supply	63	73
Surface Supply	58	67
Secondary Municipal Effluent—Microfiltration Pretreatment*	52	61
Secondary Municipal Effluent—Conventional Pretreatment	52	61

* Microfiltration pore size <0.5 microns

Table 9.3 Recommended concentrate flow rates as a function of feed water source for brackish water membranes, as adapted from Dow Water and Process Solutions.[1]

Feed Water Source	Minimum Concentrate Flow Rate for 365 ft^2 Modules, gpm	Minimum Concentrate Flow Rate for 400 and 440 ft^2 Modules, gpm
RO Permeate	10	10
Well Water	13	13
Surface Supply	13	13
Surface Supply	15	15
Secondary Municipal Effluent—Microfiltration Pretreatment*	16	18
Secondary Municipal Effluent—Conventional Pretreatment	18	20

* Microfiltration pore size <0.5 microns

more rapidly, leading to faster rates of fouling and scaling. As Table 9.2 shows, an RO operating on a well water source can have a feed flow rate as higher as 65 to 75 gpm per pressure vessel, while a surface water source RO should not exceed 58 to 67 gpm per pressure vessel. The well water RO would require 12% fewer pressure vessels than the surface water RO.

The opposite is true for the concentrate flow rate. Here, the slower the flow rate, the thicker the concentration polarization boundary layer, and the greater the chance for fouling or scaling the membranes. Table 9.3 shows that an RO operating on relatively clean well water should have a concentrate flow rate of not less than 13 gpm per pressure vessel, while an RO operating on high-solids surface water should have a concentrate flow rate of not less than 15 gpm per pressure vessel.

9.1.2 Total Dissolved Solids

The total dissolved solids (TDS) concentration affects both the system flux and the salt rejection of an RO system. Figures 9.1 and 9.2 shows the effect of TDS on flux and rejection, respectively, under conditions of constant

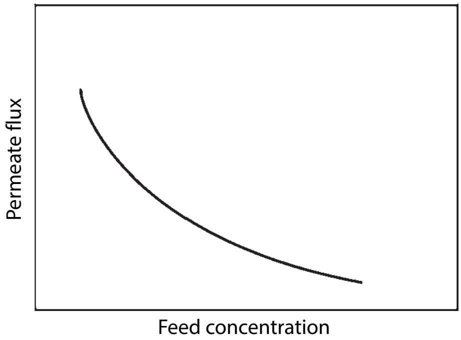

Figure 9.1 Reverse osmosis membrane flux as a function of feed water total dissolved solids. Assumes constant applied feed pressure.

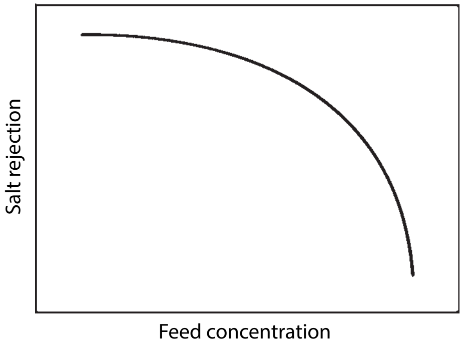

Figure 9.2 Reverse osmosis membrane rejection as a function of feed water total dissolved solids. Assumes constant applied feed pressure.

pressure.[1] As feed TDS increases, the driving force for water decreases (under constant applied pressure), due to the increase in osmotic pressure of the feed. This results in a decrease in system flux. As the driving force for water decreases, the amount of water passing through the membrane relative to the amount of salt passing through the membrane decreases, resulting in a higher TDS concentration in the permeate. Thus as shown in Figure 9.2, the rejection is lower (and salt passage is higher) at higher feed water TDS.

9.1.3 Calcium and Natural Organic Matter

Divalent cations, particularly calcium, have been shown to enhance fouling of membranes with natural organic matter (NOM) including humic, fulvic, and tanic acids.[3] Because is it's acidic nature, NOM can form complexes with dissolved metal ions. The strongest bonds occur with calcium.

Complex formation is a function of the size of the metal ion, it's electronic charge, and the energy it takes to break the shell of water molecules that typically hydrate metal ions in water. When the hydration shell breaks away from calcium, several negatively-charged NOM molecules can simultaneously attached to the same calcium ion, creating a much larger particle. These type of particles are responsible for forming the biofouling layers on membrane surfaces by providing nutrients for microbes.[4]

Factors that affect fouling with NOM-calcium complexes include permeate flux and cross flow rate. At higher flux though the membrane, the concentration of calcium increases in the concentration polarization boundary layer at the membrane surface, as described above. Lower cross flow rates also increase the concentration of calcium in the boundary layer. The increases concentration of calcium at the membrane surface enhances the fouling of the membranes by the NOM-calcium aggregates.[5]

9.1.4 Chemical Damage

Chemical damage occurs when a contaminant in the feed water is incompatible with the polymer comprising the membrane, the microporous support, or the fabric support. Besides oxidizers that degrade the cross-linking of a thin-film membrane, there are a variety of chemicals that swell or dissolve the polysulfone microporous support, including the following compounds:

- Ketones
- Aldehydes
- Esters
- Strong ethers
- Aromatic hydrocarbons such as benzene, toluene, xylene, and diesel fuel and gasoline.
- Solvents such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acedimide (DMAc) to name a few.

Low-molecular weight solvents such as methanol, propanol, and isopropanol are considered acceptable.

9.2 Temperature

Temperature influences system flux and rejection performance. Figures 9.3 and 9.4 shows the effect of temperature on water flux and salt rejection,

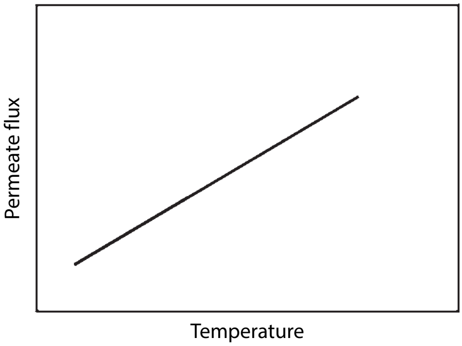

Figure 9.3 Reverse osmosis membrane water flux as a function of temperature. Assumes constant applied feed pressure and less than 45°C temperature.

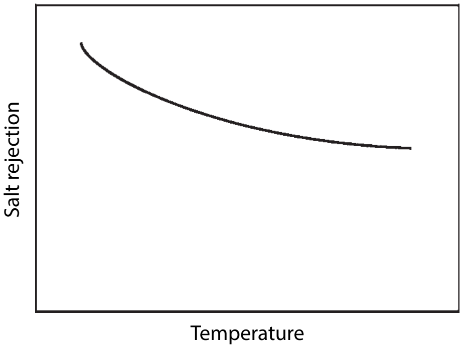

Figure 9.4 Reverse osmosis membrane salt rejection as a function of temperature. Assumes constant applied feed pressure and less than 45°C temperature.

respectively, under conditions of constant pressure and at temperatures less than 45°C. As shown in Figure 9.3, water flux is linearly proportional to the water temperature. For every 1°C change in temperature, there is a 3% change in water flux. This occurs because the lower viscosity of warmer water allows the water to flow more readily through the membranes.[6] On the other hand, salt rejection decreases slightly with increasing temperature. Salt diffusion through the membrane is higher at higher water temperature (the salt transport coefficient shown in Equation 4.2 is a function of temperature).

In practice, temperature changes are dealt with by adjusting the operating pressure: lower pressure in the warmer summer months and higher pressure in the colder winter months in surface waters. If there are significant variations in temperature between summer and winter, a 2000 ppm TDS at pH 7.6 feed water, 75% recovery, 3:2:1 array with 3 membranes per pressure vessel, FilmTec BW30-400/34 membranes. variable frequency drive

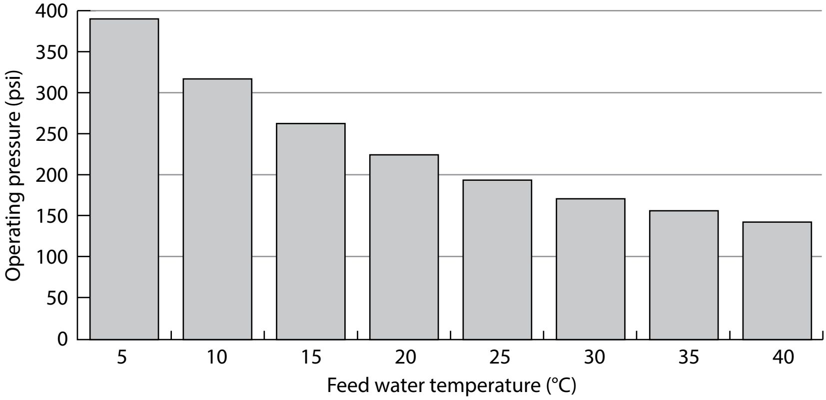

Figure 9.5 Operating pressure as a function of feed water temperature. Assumes 2000 ppm TDS at pH 7.6 feed water, 75% recovery, 3:2:1 array with 3 membranes per pressure vessel, FilmTec BW30-400/34 membranes.

(VFD) can be used to adjust the speed of the feed pump motor to run according to the water temperature (see Chapter 6.2). A VFD can save considerable energy in the summer months. Figure 9.5 shows how the operating pressure changes with changing feed water temperature for a brackish water system at constant product flow rate.

At temperatures greater then 45°C, the structure of the membrane itself changes. The membrane anneals, meaning it gets denser. As a result, it becomes more difficult to force water through the membrane.[7] At temperatures greater than 45°C, flux goes down and rejection goes up, assuming constant driving pressure (see discussion in Chapter 4.4.2.6).

9.3 Pressure

Operating pressure directly affects water flux and indirectly affects salt rejection. Figures 9.6 and 9.7 show the effect of pressure on flux and rejection, respectively. Because operating pressure directly affects the driving force for water across the membrane, higher pressure will result in higher flux (see Equation 4.1). Salt transport, however, is un-affected by pressure (see Equation 4.2). So, the same amount of salt passes through the membrane at low or at high feed water pressure. However, because more water has passed through the membrane at higher pressure, the absolute salt concentration in the permeate is lower, so it appears as if the salt passage decreases and the salt rejection increases as pressure increases, as shown in Figure 9.7.

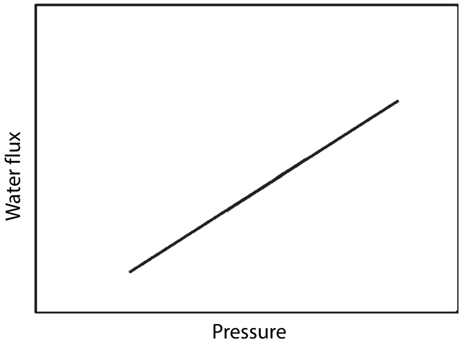

Figure 9.6 Reverse osmosis membrane water flux as a function of pressure.

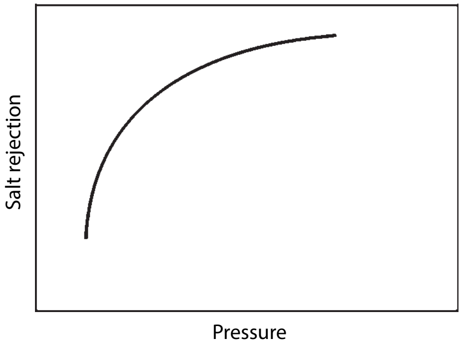

Figure 9.7 Reverse osmosis membrane salt rejection as a function of pressure.

9.4 Feed Water Flow

The feed water flow through an RO system should be dictated by the water source, as described in Chapter 9.1. The "cleaner" the water source, the higher the feed water flow may be, resulting in smaller systems and lower overall cost of operation.

Table 9.2 listed the recommended feed flow rates as a function of water source.[1] At higher feed water flow rates, contaminants such as colloids and bacteria that may be present in the source water, are sent to the membrane more rapidly, resulting in faster fouling of the membrane. This is why lower flow rates are recommended for water sources that contain high concentrations of contaminants.

9.5 Concentrate Flow

The recommended concentrate flow rate is a function of feed water source, as described in Chapter 9.1. The "cleaner" the water source, the lower the concentrate flow may be, resulting in smaller systems and lower overall cost of operation.

Table 9.3 listed the recommended concentrate flow rates as a function of water source.[1] At lower concentrate flow rates, good cross-flow velocity is not maintained, and contaminants, such as colloids and scale-formers, have a much greater chance of fouling or scaling a membrane. This is because the concentration polarization boundary layer is thicker at lower cross-flow velocities than it would be at higher concentrate flow rates. Since the bulk concentration of contaminants toward the concentrate end of the pressure vessel can be 3, 4, or even 5 times the concentration as found in the feed water, and since the concentration of contamination is even higher in the boundary layer, the potential for fouling or scaling a membrane can be very high at low concentrate flow rates.

9.6 Beta

Beta is the ratio of the concentration of a species at the membrane surface to that in the bulk solution, as described in Chapter 3.6. Beta is not a property of the membrane, nor does the designer of the RO system directly select it. It is a function of how quickly the influent stream is dewatered through the RO system. Hence, Beta is a consequence of the system design that is selected.

Beta affects both the flux through an RO membrane and the salt rejection. The increase in Beta due to concentration polarization at the membrane surface results in increased osmotic pressure and decrease is water flux, as shown in Equation 9.1 (modified Equation 4.1). Salt passage also increases, as shown in Equation 9.2 (modified Equation 4.2).

$$J_w = A\,(\Delta P - \beta\,\Delta\pi) \tag{9.1}$$

$$J_s = K\,(\beta\,C_{A2} - C_{A3}) \tag{9.2}$$

where:

J_w = water flux

A = water permeability coefficient

ΔP = applied pressure driving force

β = beta
Δ^{π} = osmotic pressure of feed – concentrate solution
J^{s} = salt flux
K = salt permeability coefficient
C_{A2} = molar concentration of solute in boundary layer
C_{A3} = molar concentration of solute in permeate

Figures 9.8 and 9.9 shows how Beta affects flux and salt passage (rejection), respectively, for two different brackish water concentrations (assumes membrane will deliver 20 gfd at 400 psi with a rejection of 99% at Beta equal to one (no concentration polarization)).[8] From the Figures, it is shown that at Beta values greater than about 1.1, the water flux and salt passage (rejection) are significantly affected by Beta. Also shown is that the effect of Beta on performance is more pronounced at higher TDS feed water than with lower TDS feed water.

In reality, Beta for RO systems is always greater than 1.0, and hence, concentration polarization always exists. While concentration polarization cannot be eliminated, it can be minimized by judicial RO system design:

- Beta can be changed by adjusting the permeate backpressure on each individual stage. This can be accomplished by adding flow restrictors into the permeate pipeline. Increasing the backpressure decreases water flux (the rate at which

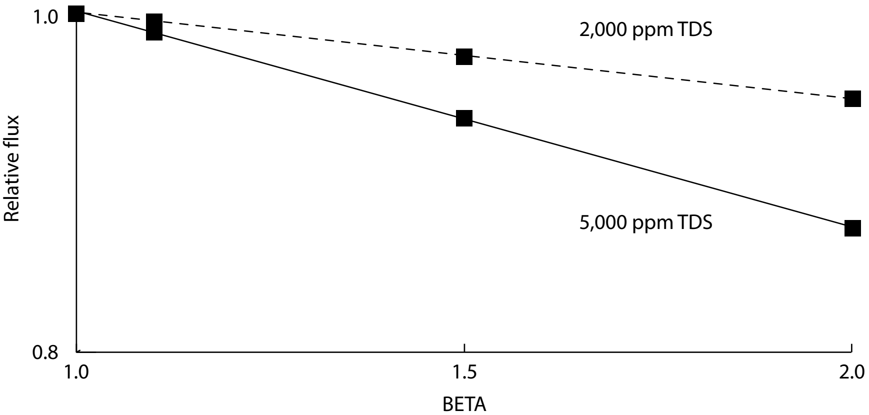

Figure 9.8 Beta's effect on membrane water flux for two different brackish water concentrations.

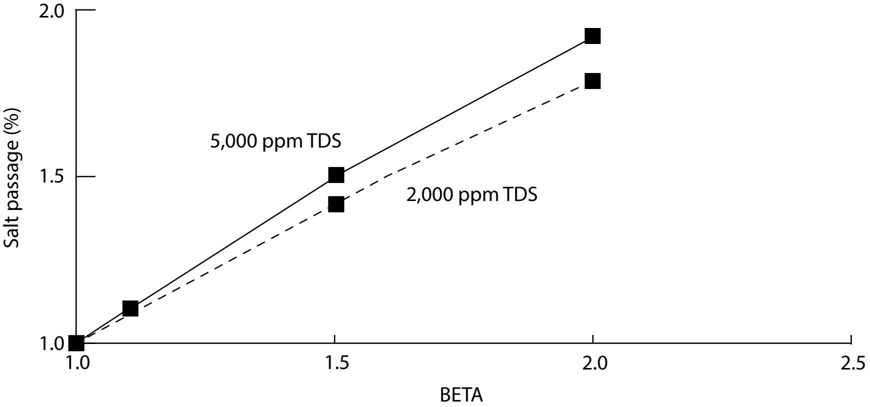

Figure 9.9 Beta's effect on salt passage for two different brackish water concentrations.

Table 9.4 Hydranautics' recommendation for beta values as a function of feed water quality.[2]

Beta (Individual Module)	RO Permeate	Brackish Well Water	Brackish Surface Water	Tertiary Waste Water
Conservative	1.30	1.18	1.18	1.18
Maximum	1.70*	1.2	1.2	1.2

* aggressive design, 1.40 is typical.

water is removed from the influent stream) which, in turn, decreases Beta.

- Adjusting the array of the RO system can also change Beta. Increasing the number of pressure vessels in a subsequent stage will decrease the back pressure due to the prior stage and, therefore the applied pressure required by the prior stage, thereby decreasing the flux and Beta for that prior stage.
- Adherence to recommended concentrate flow rates and membrane module recovery can also minimize Beta and the effects of concentration polarization.

Conventional wisdom calls for Beta values less than 1.2 in an RO design to minimize membrane fouling and scaling.[9] Table 9.4 lists Hydranautics' recommended beta values as a function of feed water quality.[2]

9.7 Recovery

Reverse Osmosis recovery affects the overall water flux and salt rejection as shown in Figures 9.10 and 9.11 respectively. As the recovery increases, the water flux decreases slowly due to the increase in feed-side osmotic pressure until the recovery is so high that the osmotic pressure of the feed water is as high as the applied pressure, in which case, the driving force for water through the membrane is lost and the flux ceases.

The drop in water flux affects the apparent salt rejection. As the osmotic pressure of the feed/concentrate stream approaches the applied pressure, the driving force for water is decreased, but the driving force for salt is unaffected (see Equation 4.2, which shows that the solute flux is not a

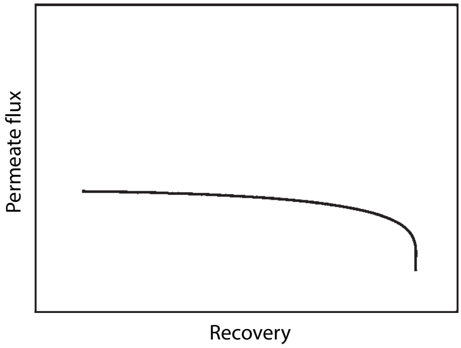

Figure 9.10 Reverse osmosis membrane water flux as a function of recovery. Assumes constant applied feed pressure.

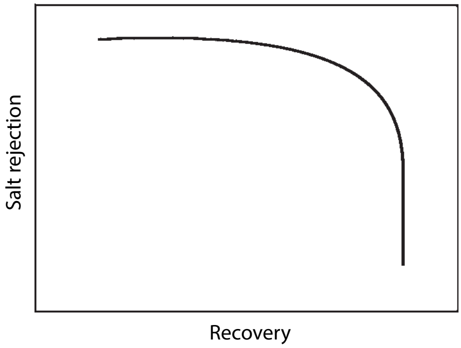

Figure 9.11 Reverse osmosis membrane salt rejection as a function of recovery. Assumes constant applied feed pressure.

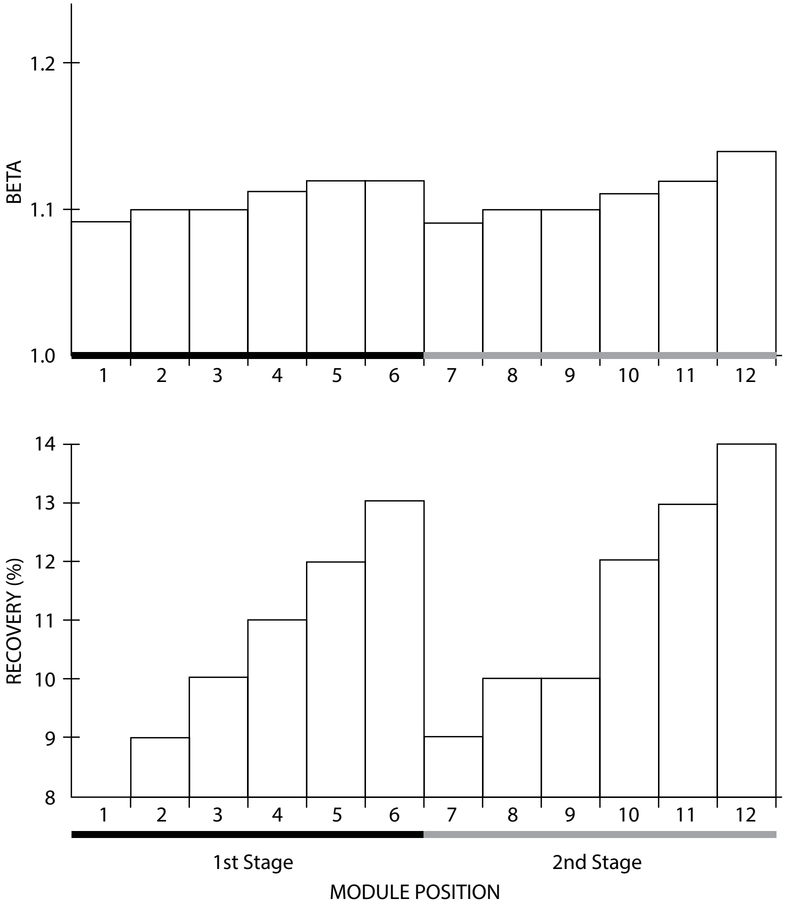

Figure 9.12 Individual membrane module recovery and rejection as a function of position in a 2-stage RO system with 6 modules per pressure vessel.

function of pressure driving force). Hence, less water passes through the membrane relative to the amount of salt passing through the membrane. Thus, it appears as if the salt passage increases and salt rejection decreases with increasing recovery. Salt rejection becomes 0% at about the same time that the flux ceases.

Recovery through individual membrane modules changes, based on the position of the module in the pressure vessel. Most spiral wound membrane modules operate with individual module recoveries ranging from 10% to 15%, with an average of 11% to achieve 50% recovery in a single, 6-module pressure vessel stage. The module at the feed end of the pressure vessel typically exhibits the lowest recovery of all modules in the pressure vessel. The module at the concentrate end of the pressure vessel operates at the highest recovery in the vessel. This is because as more water is recovered through the pressure vessel, the percent of the total feed to a given module recovered by that module gets larger. Figure 9.12 shows this effect. Also shown in the figure is how Beta for individual modules changes through the pressure vessel. High recovery conditions leads to increased rates of fouling and/or scaling due to a higher concentration of species in the boundary layer, hence the higher Beta.

The designer of an RO system has at their discretion, the ability to manipulate the recovery of the system to minimize the potential for scaling of the membrane, both on the system and individual module level. As system recovery increases, the concentration of salts in the feed/concentrate stream increases to the point of saturation for some species near the outlet end of the pressure vessel. If acid and antiscalants are not effective (or cannot be used), recovery is typically decreased to minimize the scaling potential. Higher recovery can also result in too much water being removed in the lead modules in the pressure vessel, making them more prone to fouling and scaling (increasing Beta). Adjusting the recovery down will increase both the flux and rejection as described in Chapter 9.6. Adjusting the recovery so that it is higher (to minimize concentrate waste) is only recommended when the feed water is relatively free of suspended solids and scale formers.

9.8 pH

pH affects the stability of both polyamide composite and cellulose acetate membranes. Cellulose acetate membranes are stable over a pH range of 4 to 6, due to hydrolysis at higher and lower pH – see Figure 4.6. (Hydrolysis is a chemical reaction where a compound is broken down by reaction with water.) Polyamide composite membranes also react with water, but the pH range of nominal application is much broader, ranging from as low as 2 to as high 11, depending on the specific membrane and manufacturer. Acceptable operating pH is a function of temperature, with higher temperatures requiring narrower pH ranges of operation.

pH also affects the rejection capabilities of polyamide composite membranes. Rejection of most species is highest at about pH 7.0–7.5, as shown in Figure 9.13.[10] Rejection drops off at higher and at lower pH, but the drop off is very gradual at lower pH. The reason for this phenomenon is not clearly defined in the literature, but most likely stems from the ionic state of the ions being rejected, as well as some changes on the molecular

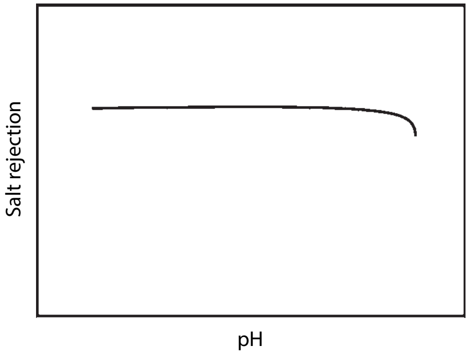

Figure 9.13 Reverse osmosis membrane salt rejection as a function of pH. Assumes constant applied feed pressure.

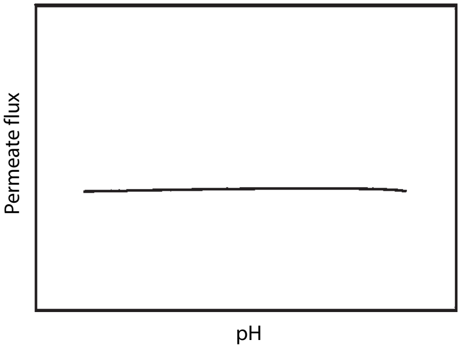

Figure 9.14 Reverse osmosis membrane water flux as a function of pH. Assumes constant applied feed pressure.

level with the membrane itself. The flux through a polyamide composite RO membrane is relatively constant over the range of pH, as shown in Figure 9.14.[10]

Because of the carbon dioxide present in most waters, the pH of RO product water is generally lower than the pH of feed water, unless the carbon dioxide is completely removed from the feed water. If carbon dioxide is present in feed water, it will be present in permeate, as gases are not rejected by RO membranes (see Chapter 3.3). However, the membrane rejects carbonate and bicarbonate. Passage of carbon dioxide upsets the equilibrium among these compounds in the permeate. Carbon dioxide readily passes through the membrane while bicarbonate does not. Hence, the permeate will be relatively high in carbon dioxide and low in bicarbonate. Hence a new equilibrium occurs in the permeate, hence lowering its pH:

$$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+ \tag{9.3}$$

9.9 Flux

Flux determines the overall size of the RO system in terms of membrane area required to achieve the desired separation. As discussed in Chapter 9.1.1, the water flux for a given application should be based on the feed water source. "Cleaner" source water allows for higher flux, which, in turn, means less membrane area is required to achieve the desired separation.

Water flux is affected by several operating variables, as discussed in this chapter. In summary:

- Water flux is directly proportional to operating pressure.
- Water flux is directly proportional to water temperature.
- Water flux decreases slightly as recovery increase until the osmotic pressure of the feed water equals the driving pressure, at which point productivity ceases.
- Water flux decreases with increasing feed concentration of dissolved solids.
- Water flux is relatively constant over a range of pH, although for some newer polyamide membranes, flux is also a function of pH.[8]

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10

RO Design and Design Software

Sound RO system design incorporates all issues discussed in Chapters 1–9. Perhaps the most important considerations when developing a new design are the following:

- Water flux (see Chapter 3.4)
- Feed flow rate per pressure vessel (see Chapter 9.4)
- Concentrate flow rate per pressure vessel (see Chapter 9.5)
- Beta (see Chapter 9.6)
- Scaling indexes (see Chapter 3.8)

Adherence to the recommended guidelines for these variables can determine the success of a design. This chapter covers the basics of designing an RO system, including the use of design software available from various membrane manufacturers.

The starting point in any RO design is the water flux. The desired water flux should be selected by the designer based on the feed water source and quality (see Chapter 3.4 and Table 3.3).

Once the flux has been selected, the other variable that the designer needs to determine is which membrane to use and how much membrane area per module is suitable for the particular application. As discussed in Chapter 4.3.3, 8-inch diameter spiral wound modules are available with various membrane areas. For example, the Dow Water and Process Solutions FilmTec FT-30 membrane is available with 365 ft^2 or 400 ft^2 of membrane area. The BW30-365 membrane carries a 34-mil feed spacer while the BW30-400 carries a 28-mil spacer. The BW30-365 is recommended for more fouling-prone feed waters because of the thicker feed spacer. Dow Water and Process Solutions also offers the BW30-400/34i, a 400 ft^2 module with 34-mil spacer and the *iLEC* end caps. This module would be used as a replacement for the BW30-365 when a lower flux is required on fouling-prone feed waters, or in a new system to reduce the size of the system versus using the BW30-365 and still get the resistance to fouling offered by the thicker feed spacer.

Having selected the appropriate water flux and membrane type, the designer can use equation 10.1 to back calculate how many membrane modules are required to meet the desired productivity.

$$J_w = F_p * 1/MA * 1/N \tag{10.1}$$

where:

J_w = water flux, gfd
F_p = product flow rate, gallons/day
MA = membrane area per module
N = number of modules

Solving equation 10.1 for the number of modules, N, can give the designer an idea of what the array might look like. For a two-stage, 75% recovery system with a tapered design, 2/3 of the total number of modules would be in the first stage and the remaining 1/3 would be in the second stage. Once the array has been estimated, the design can be optimized with respect to other design variables including flow rates, scaling indexes, recovery, and Beta.

At this point continuing to create a design by hand calculation is very tedious considering all the variables that must be addressed by the designer. Thus, design software has been developed to aid the designer in developing a design of an RO system. Some membrane manufacturers have made available to the public, design software that is specific for their membranes. Each software package, while different in presentation, delivers the same result: design of the RO unit, including array, operating pressure, scaling indices, and product and concentrate water qualities.

The software is based on stabilized, nominal performance of the membrane selected under design conditions. Actual performance may vary up to + /−15% of nominal, according to the Dow Water and Process Solutions-FilmTec Technical Manual. The differential holds in systems with at least 36 membranes. Smaller systems may exhibit 1.5 times the salt passage verses the projection.[1] The software will give warnings when the basic element operating parameters are exceeded, such as high element recovery or low concentrate flow. However, the software will not give warnings when the overall design is not practical. In fact, the Dow Water and Process Solutions FilmTec Technical Manual states:

> "ROSA [Reverse Osmosis System Analysis] 6 only projects reverse osmosis and nanofiltration system performance from a User-controlled set of data input and design decisions. *The program does not judge whether a system design is realistic* [emphasis added] or optimized for a given set of conditions. It is the User's responsibility to review and judge the system design based on the anticipated or existing pretreatment, reasonable design guidelines, and experience."[1]

Hence, experience and common sense are necessary to ensure the design selected using the any design software package is realistic, particularly for feed streams other than relatively clean sources, such as well water with SDI < 3.

Table 10.1 lists six U.S. membrane manufacturers and their respective design programs that are available to the public. Some of these design program are discussed in detail below. Most of these programs can be downloaded from the manufacturers' respective websites. Some of the newer programs are web-based. Applied Membranes®, Inc., (Vista, California), another U.S. manufacturer, does not offer a design program to the public; their in-house membranes cover in-home and small commercial installations using 2.5" and 4" membrane elements. They also supply Dow, Koch, Hydranautics, and other membranes.

Author's Note: Design detail is not offered here on GE's WinFlow and TriSep's TROI due to the nature of all design programs that regularly issue updates at least yearly, if not more often; by the time this 2nd edition is printed, the program versions will be obsolete. However, they both deserve mention here as their products are either common or serve important niche applications, and their projections programs can now be downloaded from their respective websites.

Table 10.1 Six U.S. suppliers of RO membranes and their design programs. Some are available to the public via download from their respective websites.

Membrane Manufacturer	Design Software Package
Dow Water Solutions—FilmTec (Minneapolis, MN) www.dow.com	Water Application Value Engine (WAVE)
Toray Membrane, USA (Poway, CA) www.toraywater.com	Toray Design System (TorayDS)
Hydranautics (Oceanside, CA) www.membranes.com	Integrated Membrane Solutions™ (IMSDesign)
Koch Membrane Systems (Wilmington, MA) www.kochmembrane.com	ROPRO®*
TriSep corporation (Goleta, CA) www.trisep.com	TROI
Gewater & Process Technologies (Trevose PA) www.gewater.com	WinFlows

* No longer available to the public in download.[2]

The selection of whose software program to use depends entirely on which membrane manufacturer is specified by the customer. Each RO system designer may have a favorite program that they use to provide projection information should the membranes of choice not be specified. In most cases, it makes sense to run several programs and compare/contrast the differences among them to find which membrane performance meets the requirements of the specific application. While each program is unique to its particular manufacturer's membranes, there are similarities among the programs. Updates in four design programs listed in Table 10.1, are discussed below.

10.1 Dow WAVE – Water Application Value Engine

Contirbuted by Leaelaf Hailemariam, Dow Water & Process Solutions

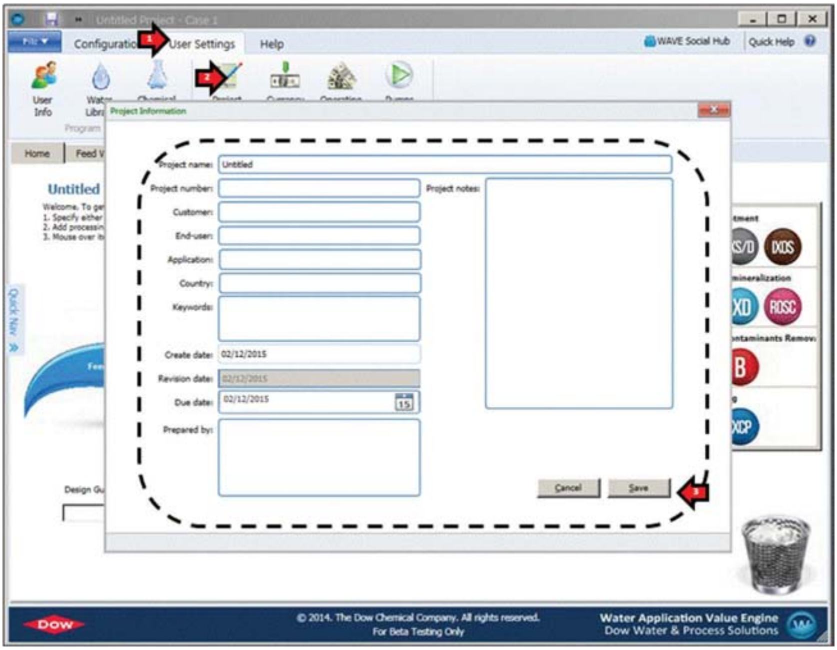
The Water Application Value Engine (WAVE) program from Dow Water & Process Solutions, currently in Beta testing, was developed as an integrated program that offers the possibility of modeling reverse osmosis (RO), ultrafiltration (UF) and ion exchange (IX) separately or in combination. The description in this section would concentrate on the reverse osmosis modeling component of WAVE. Further information on the modeling of the other treatment processes is described elsewhere.

The RO Component of WAVE has the following major sections:

- Project information Input
- Feed Water Specification
- RO System Configuration
- Chemical Adjustment
- Report Generation & Review
- Batch Operation and Case Management

The Project Information Input Window (shown in Figure 10.1) allows the designer to input information about the project including the project name, the customer name, date and other relevant information. The numbered arrows indicate the access and information path.

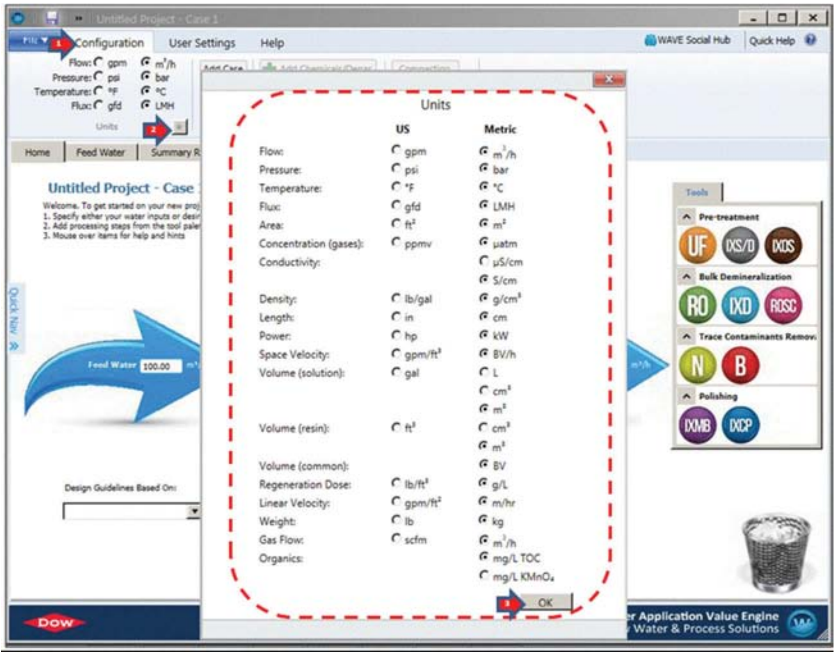
Another key set of inputs used in WAVE are the units of measure for the modeling. These are specified as shown in Figure 10.2. Others include the list of chemicals available for pH adjustment, chemical, electrical and wastewater disposal costs as well as pump efficiencies (see Figures 10.3 – 10.7).



Project Information

Project name: Untitled
Project number:
Customer:
End-user:
Application:
Country:
Keywords:
Create date: 02/12/2015
Revision date: 02/12/2015
Due date: 02/12/2015
Prepared by:
Project notes:

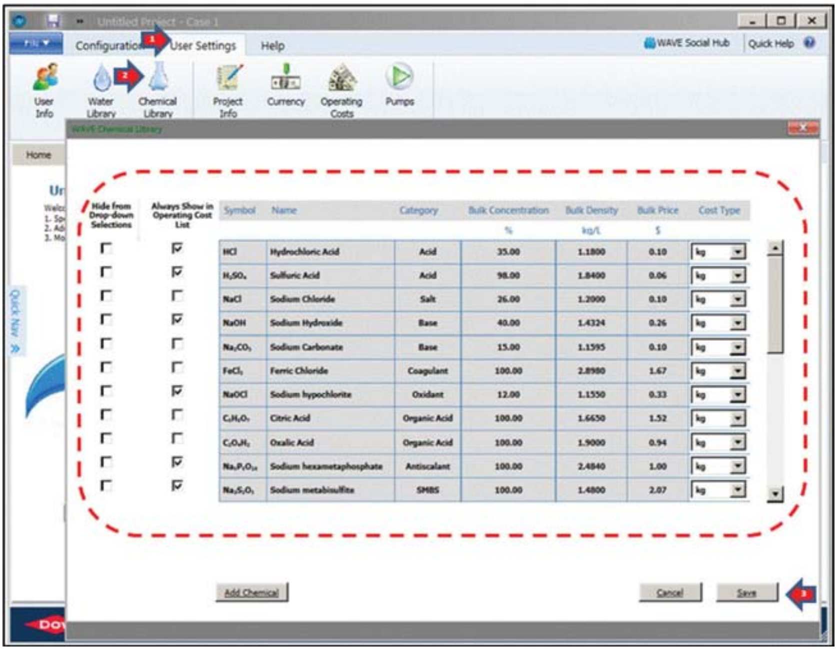
Figure 10.1 Project Information specification in WAVE



Units

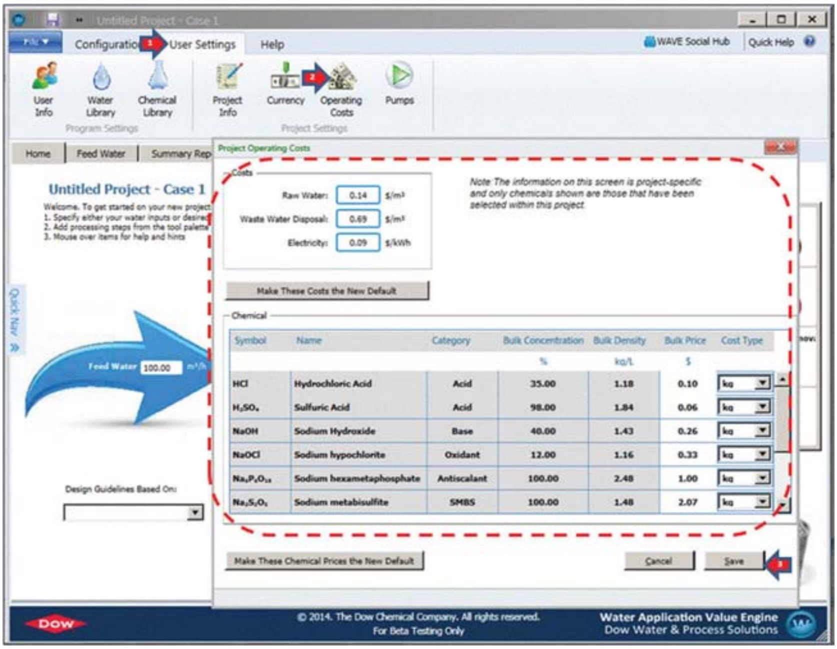
	US	Metric
Flow:	○ gpm	● m³/h
Pressure:	○ psi	● bar
Temperature:	○ °F	● °C
Flux:	○ gfd	● LMH
Area:	○ ft²	● m²
Concentration (gases):	○ ppmv	● µatm
Conductivity:		○ µS/cm ● S/cm
Density:	○ lb/gal	● g/cm³
Length:	○ in	● cm
Power:	○ hp	● kW
Space Velocity:	○ gpm/ft³	● BV/h
Volume (solution):	○ gal	○ L ○ cm³ ● m³
Volume (resin):	○ ft³	○ cm³ ● m³
Volume (common):		● BV
Regeneration Dose:	○ lb/ft³	● g/L
Linear Velocity:	○ gpm/ft²	● m/hr
Weight:	○ lb	● kg
Gas Flow:	○ scfm	● m³/h
Organics:		● mg/L TOC ○ mg/L $KMnO_4$

Figure 10.2 Unit of Measure specification in WAVE



Hide from Drop-down Selections	Always Show in Operating Cost List	Symbol	Name	Category	Bulk Concentration %	Bulk Density kg/L	Bulk Price $	Cost Type
☐	☑	HCl	Hydrochloric Acid	Acid	35.00	1.1800	0.10	kg
☐	☑	H_2SO_4	Sulfuric Acid	Acid	98.00	1.8400	0.06	kg
☐	☐	NaCl	Sodium Chloride	Salt	26.00	1.2000	0.10	kg
☐	☑	NaOH	Sodium Hydroxide	Base	40.00	1.4324	0.26	kg
☐	☐	Na_2CO_3	Sodium Carbonate	Base	15.00	1.1595	0.10	kg
☐	☐	$FeCl_3$	Ferric Chloride	Coagulant	100.00	2.8980	1.67	kg
☐	☑	NaOCl	Sodium hypochlorite	Oxidant	12.00	1.1550	0.33	kg
☐	☐	$C_6H_8O_7$	Citric Acid	Organic Acid	100.00	1.6650	1.52	kg
☐	☐	$C_2O_4H_2$	Oxalic Acid	Organic Acid	100.00	1.9000	0.94	kg
☐	☑	$Na_6P_6O_{18}$	Sodium hexametaphosphate	Antiscalant	100.00	2.4840	1.00	kg
☐	☑	$Na_2S_2O_5$	Sodium metabisulfite	SMBS	100.00	1.4800	2.07	kg

Figure 10.3 Specification of the list of chemicals available for use in WAVE



Untitled Project - Case 1

Welcome. To get started on your new project:
1. Specify either your water inputs or desired
2. Add processing steps from the tool palette
3. Mouse over items for help and hints

Project Operating Costs

Costs

Raw Water: 0.14 $/m³

Waste Water Disposal: 0.69 $/m³

Electricity: 0.09 $/kWh

Note: The information on this screen is project-specific and only chemicals shown are those that have been selected within this project

Make These Costs the New Default

Chemical

Symbol	Name	Category	Bulk Concentration	Bulk Density	Bulk Price	Cost Type
			%	kg/L	$	
HCl	Hydrochloric Acid	Acid	35.00	1.18	0.10	kg
H_2SO_4	Sulfuric Acid	Acid	98.00	1.84	0.06	kg
NaOH	Sodium Hydroxide	Base	40.00	1.43	0.26	kg
NaOCl	Sodium hypochlorite	Oxidant	12.00	1.16	0.33	kg
$Na_6P_6O_{18}$	Sodium hexametaphosphate	Antiscalant	100.00	2.48	1.00	kg
$Na_2S_2O_5$	Sodium metabisulfite	SMBS	100.00	1.48	2.07	kg

Make These Chemical Prices the New Default

Cancel

Save

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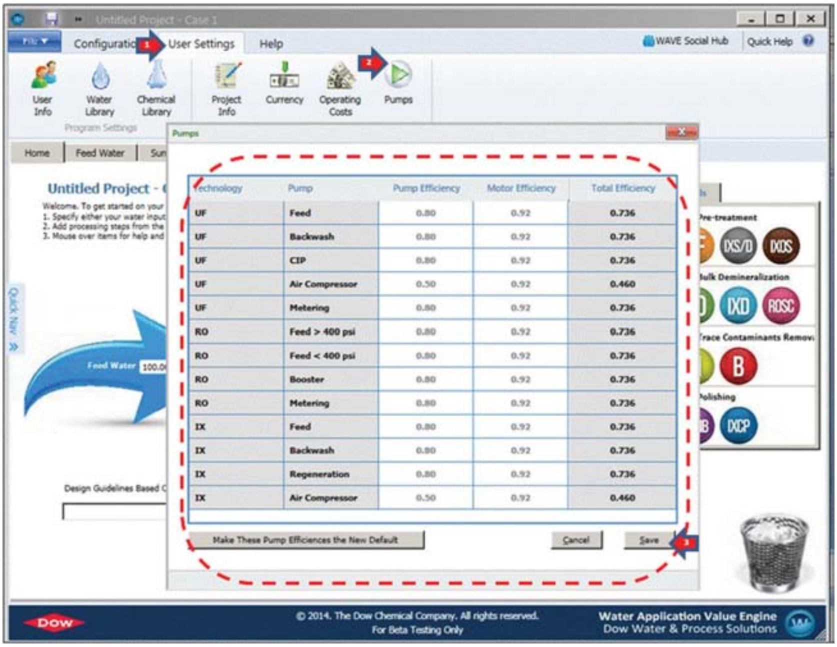
Figure 10.4 Specification of the chemical, electrical, feed water and wastewater disposal costs in WAVE



Pumps

Technology	Pump	Pump Efficiency	Motor Efficiency	Total Efficiency
UF	Feed	0.80	0.92	0.736
UF	Backwash	0.80	0.92	0.736
UF	CIP	0.80	0.92	0.736
UF	Air Compressor	0.50	0.92	0.460
UF	Metering	0.80	0.92	0.736
RO	Feed > 400 psi	0.80	0.92	0.736
RO	Feed < 400 psi	0.80	0.92	0.736
RO	Booster	0.80	0.92	0.736
RO	Metering	0.80	0.92	0.736
IX	Feed	0.80	0.92	0.736
IX	Backwash	0.80	0.92	0.736
IX	Regeneration	0.80	0.92	0.736
IX	Air Compressor	0.50	0.92	0.460

Make These Pump Efficiences the New Default

Cancel

Save

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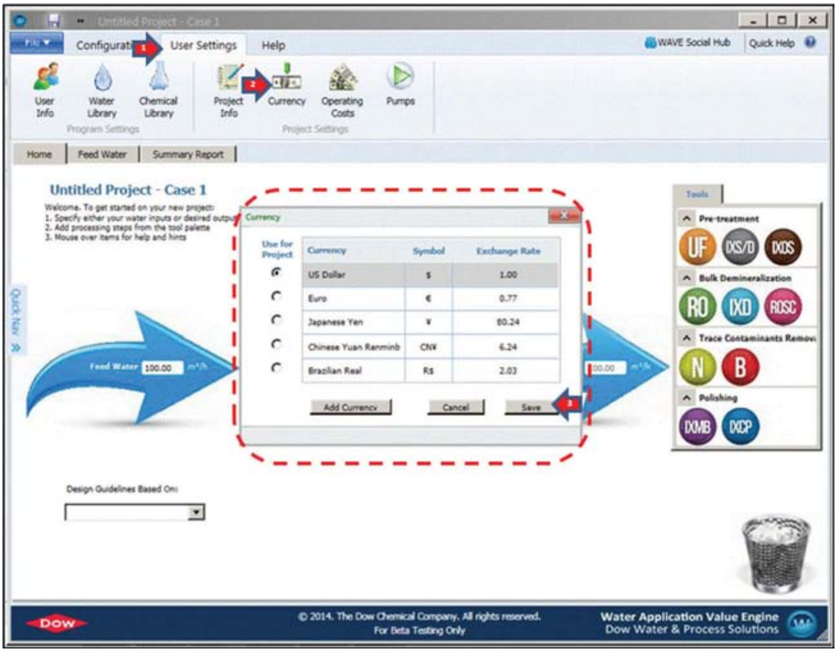
Figure 10.5 Specification of pump efficiencies in WAVE



Untitled Project - Case 1

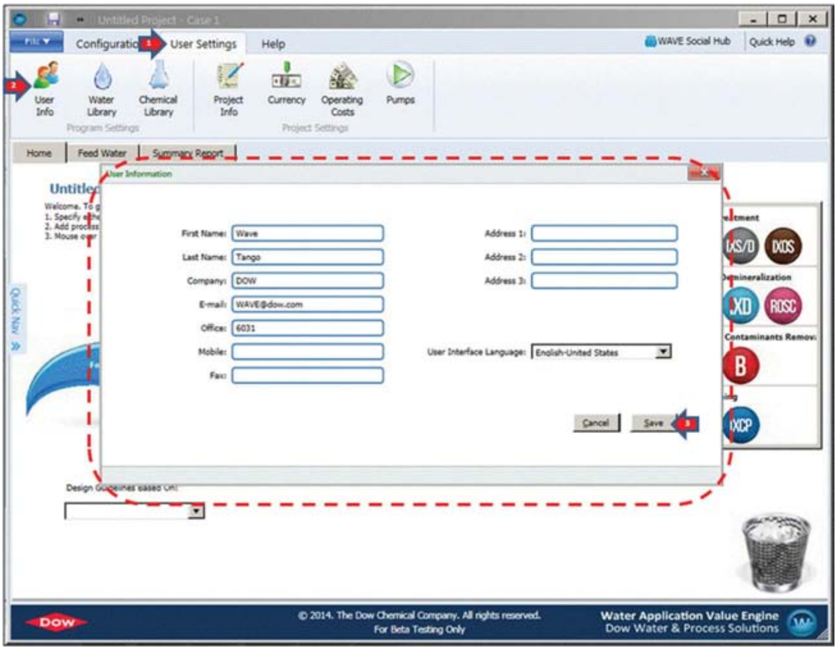
Welcome. To get started on your new project:
1. Specify either your water inputs or desired outputs
2. Add processing steps from the tool palette
3. Mouse over items for help and hints

Currency

Use for Project	Currency	Symbol	Exchange Rate
●	US Dollar	$	1.00
○	Euro	€	0.77
○	Japanese Yen	¥	80.24
○	Chinese Yuan Renminb	CN¥	6.24
○	Brazilian Real	R$	2.03

Add Currency Cancel Save

Figure 10.6 Specification of currencies in WAVE

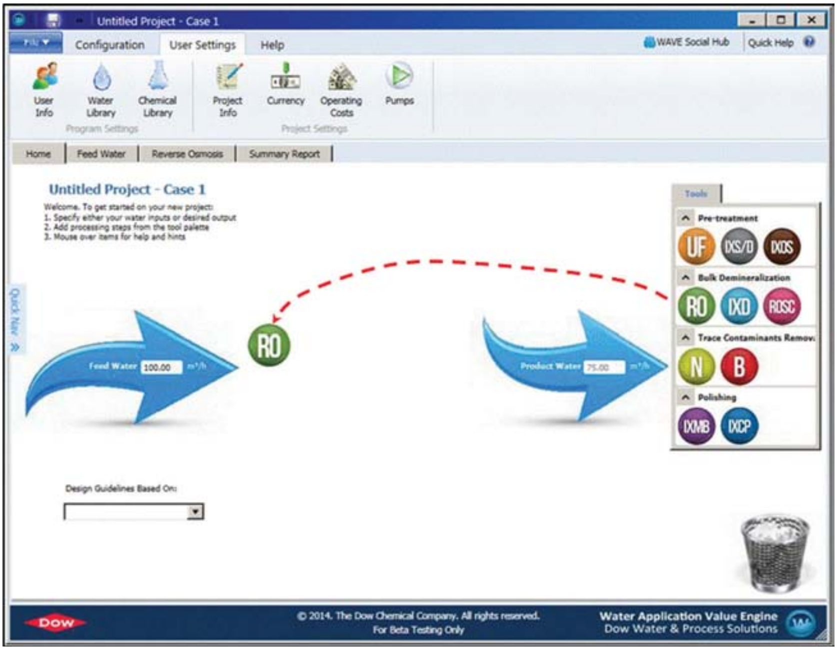


User Information

First Name: Wave
Last Name: Tango
Company: DOW
E-mail: WAVE@dow.com
Office: 6031
Mobile:
Fax:
Address 1:
Address 2:
Address 3:
User Interface Language: English-United States

Cancel Save

Figure 10.7 Specification of user information (including language) in WAVE



Untitled Project - Case 1

Welcome. To get started on your new project:
1. Specify either your water inputs or desired output
2. Add processing steps from the tool palette
3. Mouse over items for help and hints

Feed Water 100.00 m³/h

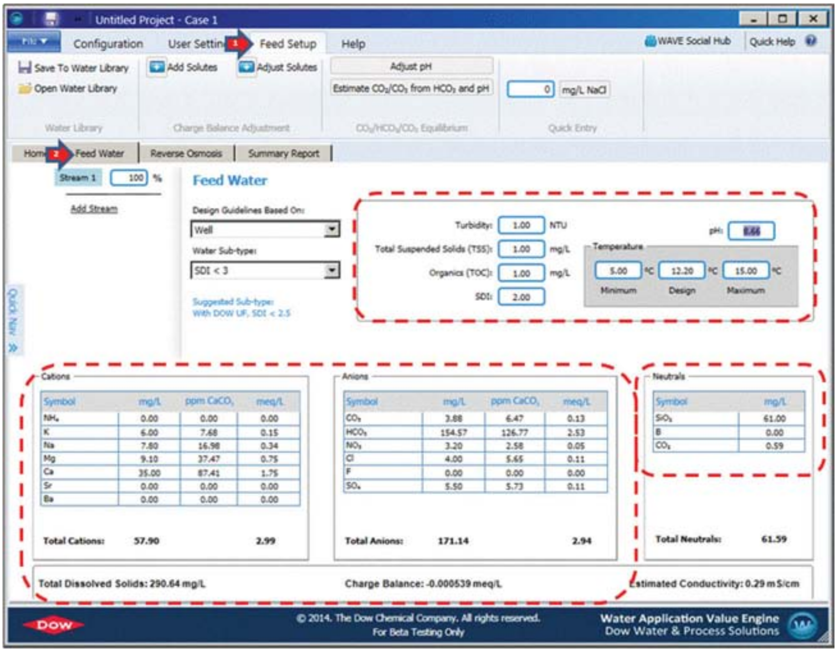
Product Water 75.00 m³/h

Figure 10.8 RO Icon drag-and-drop in WAVE to start RO modeling

In WAVE, an RO design starts with selecting an RO process icon from menu shown in Figure 10.8. The icon must be dragged and dropped between the two large blue arrows. WAVE has icon placement rules that would always place UF upstream of an RO icon. The current version of WAVE uses a separate icon for standard RO modeling and small commercial RO modeling.

10.1.1 Feed Water Specification

The feed water characteristics are filled into the Feed Water section as shown in Figure 10.9. The cations, anions and inerts are specified in different panels. WAVE also has a Quick-entry option to enter a desired NaCl concentration. In addition to ionic composition, the WAVE user is encouraged to input information on water solid content including NTU (Nephelometric Turbidity Unit), SDI (Silt Density Index) and TSS (Total Suspended Solids) as well as the organic content (in TOC or Total Organic Content). These are used to identify appropriate design guidelines for the user.



Stream 1 100 %

Feed Water

Design Guidelines Based On: Well

Water Sub-type: SDI < 3

Suggested Sub-type:
With DOW UF, SDI < 2.5

Quick Entry: 0 mg/L NaCl

Turbidity: 1.00 NTU
Total Suspended Solids (TSS): 1.00 mg/L
Organics (TOC): 1.00 mg/L
SDI: 2.00
pH: 8.66

Temperature

Minimum	Design	Maximum
5.00 °C	12.20 °C	15.00 °C

Cations

Symbol	mg/L	ppm $CaCO_3$	meq/L
NH_4	0.00	0.00	0.00
K	6.00	7.68	0.15
Na	7.80	16.98	0.34
Mg	9.10	37.47	0.75
Ca	35.00	87.41	1.75
Sr	0.00	0.00	0.00
Ba	0.00	0.00	0.00
Total Cations:	**57.90**		**2.99**

Anions

Symbol	mg/L	ppm $CaCO_3$	meq/L
CO_3	3.88	6.47	0.13
HCO_3	154.57	126.77	2.53
NO_3	3.20	2.58	0.05
Cl	4.00	5.65	0.11
F	0.00	0.00	0.00
SO_4	5.50	5.73	0.11
Total Anions:	**171.14**		**2.94**

Neutrals

Symbol	mg/L
SiO_2	61.00
B	0.00
CO_2	0.59
Total Neutrals:	**61.59**

Total Dissolved Solids: 290.64 mg/L **Charge Balance: -0.000539 meq/L** **Estimated Conductivity: 0.29 mS/cm**

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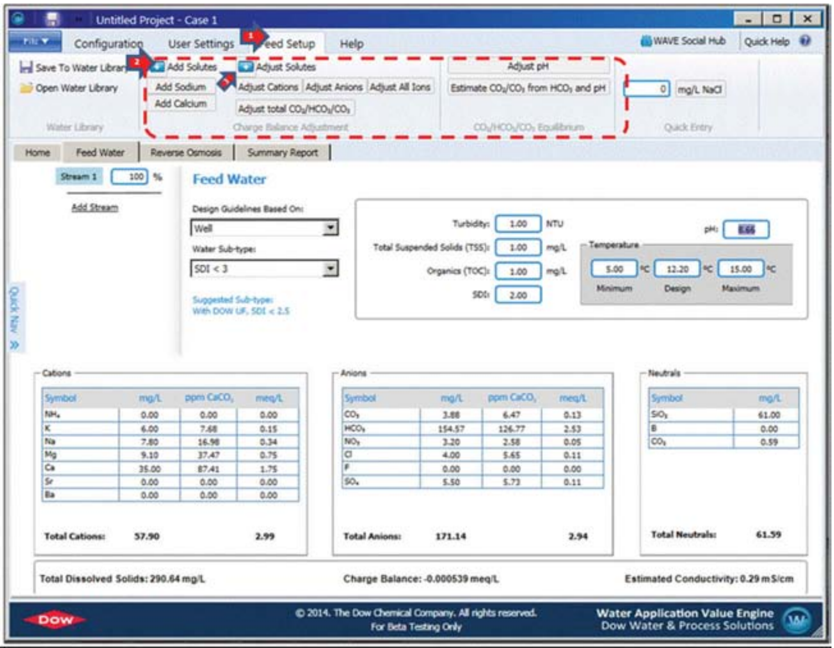
Figure 10.9 Specification of the ionic composition in WAVE



Stream 1 100 %

Feed Water

Design Guidelines Based On: Well

Water Sub-type: SDI < 3

Suggested Sub-type:
With DOW UF, SDI < 2.5

Quick Entry: 0 mg/L NaCl

Turbidity: 1.00 NTU
Total Suspended Solids (TSS): 1.00 mg/L
Organics (TOC): 1.00 mg/L
SDI: 2.00
pH: 8.66

Temperature: Minimum 5.00 °C, Design 12.20 °C, Maximum 15.00 °C

Cations

Symbol	mg/L	ppm $CaCO_3$	meq/L
NH_4	0.00	0.00	0.00
K	6.00	7.68	0.15
Na	7.80	16.98	0.34
Mg	9.10	37.47	0.75
Ca	35.00	87.41	1.75
Sr	0.00	0.00	0.00
Ba	0.00	0.00	0.00
Total Cations:	**57.90**		**2.99**

Anions

Symbol	mg/L	ppm $CaCO_3$	meq/L
CO_3	3.88	6.47	0.13
HCO_3	154.57	126.77	2.53
NO_3	3.20	2.58	0.05
Cl	4.00	5.65	0.11
F	0.00	0.00	0.00
SO_4	5.50	5.73	0.11
Total Anions:	**171.14**		**2.94**

Neutrals

Symbol	mg/L
SiO_2	61.00
B	0.00
CO_2	0.59
Total Neutrals:	**61.59**

Total Dissolved Solids: 290.64 mg/L **Charge Balance: -0.000539 meq/L** **Estimated Conductivity: 0.29 mS/cm**

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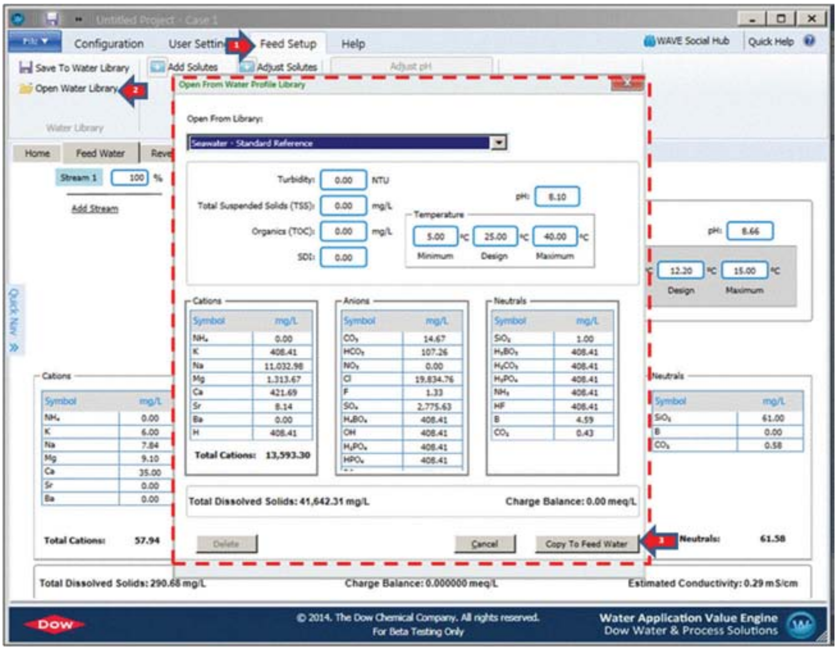
Figure 10.10 Charge-balancing options in WAVE



Open From Water Profile Library

Open From Library: Seawater - Standard Reference

Turbidity: 0.00 NTU

Total Suspended Solids (TSS): 0.00 mg/L

Organics (TOC): 0.00 mg/L

SDI: 0.00

pH: 8.10

Temperature: 5.00 °C Minimum, 25.00 °C Design, 40.00 °C Maximum

Cations

Symbol	mg/L
NH_4	0.00
K	408.41
Na	11,032.98
Mg	1,313.67
Ca	421.69
Sr	8.14
Ba	0.00
H	408.41

Total Cations: 13,593.30

Anions

Symbol	mg/L
CO_3	14.67
HCO_3	107.26
NO_3	0.00
Cl	19,834.76
F	1.33
SO_4	2,775.63
H_4BO_4	408.41
OH	408.41
H_2PO_4	408.41
HPO_4	408.41

Neutrals

Symbol	mg/L
SiO_2	1.00
H_3BO_3	408.41
H_2CO_3	408.41
H_3PO_4	408.41
NH_3	408.41
HF	408.41
B	4.59
CO_2	0.43

Total Dissolved Solids: 41,642.31 mg/L

Charge Balance: 0.00 meq/L

Stream 1 100 %

Add Stream

pH: 8.66

12.20 °C Design, 15.00 °C Maximum

Cations

Symbol	mg/L
NH_4	0.00
K	6.00
Na	7.84
Mg	9.10
Ca	35.00
Sr	0.00
Ba	0.00

Total Cations: 57.94

Neutrals

Symbol	mg/L
SiO_2	61.00
B	0.00
CO_2	0.58

Neutrals: 61.58

Total Dissolved Solids: 290.68 mg/L

Charge Balance: 0.000000 meq/L

Estimated Conductivity: 0.29 mS/cm

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Figure 10.11 The WAVE Water Library

WAVE enforces charge balancing for RO applications. Charge balancing can be performed by adding cations or anions, or both or by varying pH (which affects $HCO_3/CO_3/CO_2$ equilibrium) as shown in Figure 10.10. Depending on the pH and temperature, WAVE automatically calculates the equilibrium HCO_3, CO_3 and CO_2 equilibrium composition.

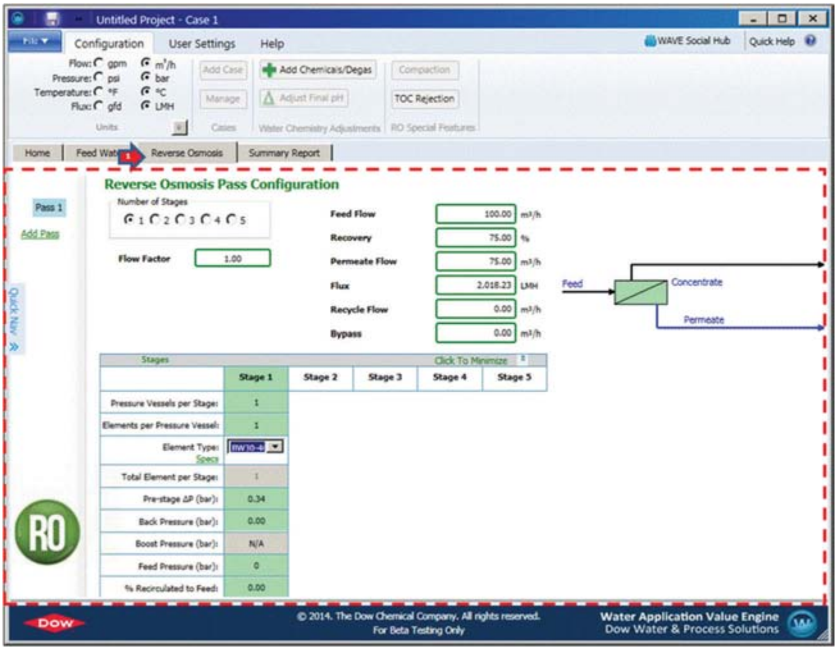
Several water profiles are provided in WAVE by default in the Water Library as shown in Figure 10.11. The user can save the water they have just specified. In addition, WAVE allows the user to blend several feed water streams

10.1.2 RO System Configuration

WAVE takes the system feed flow rate or system permeate flow rate (whichever one is specified) in the RO Configuration section as shown in Figure 10.12. The following inputs are used to specify an RO system:

- Number of passes: WAVE currently allows for a maximum of 2 passes
- Number of stages: WAVE currently allows for a maximum of 5 stages

- The Flow Factor – this is used to simulate worst case scenarios in terms of rejection and energy demand. The number of pressure vessels for each stage
- The number of elements per pressure vessel: WAVE restricts this number to between 1 and 8.
- The elements of interest. Standard Filmtec® elements can be selected here. The specifications for each element are displayed by clicking on the 'Specs' link.
- Internally Staged Design (ISD): Simulates performance of different element types in one pressure vessel, as shown in Figure 10.13. The following website gives more information about the ISD: http://dowwater.custhelp.com/app/answers/detail/a_id/13895/kw/isd
- Permeate backpressure for each stage
- Boost pressure between stages
- Feed pressure: specifying the feed pressure would require WAVE to calculate the recovery based on feed pressure: thus the user-specified recovery may be over-written
- Stage Recycle: WAVE allows the user to model recirculation of the concentrate from the end of a given stage to the feed



Flow: ○ gpm ● m³/h
Pressure: ○ psi ● bar
Temperature: ○ °F ● °C
Flux: ○ gfd ● LMH

Reverse Osmosis Pass Configuration

Number of Stages: ● 1 ○ 2 ○ 3 ○ 4 ○ 5

Flow Factor: 1.00

Feed Flow: 100.00 m³/h
Recovery: 75.00 %
Permeate Flow: 75.00 m³/h
Flux: 2,018.23 LMH
Recycle Flow: 0.00 m³/h
Bypass: 0.00 m³/h

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Pressure Vessels per Stage:	1				
Elements per Pressure Vessel:	1				
Element Type:	[illegible]				
Total Element per Stage:	1				
Pre-stage ΔP (bar):	0.34				
Back Pressure (bar):	0.00				
Boost Pressure (bar):	N/A				
Feed Pressure (bar):	0				
% Recirculated to Feed:	0.00				

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Figure 10.12 RO System Specification in WAVE

Element Configuration - Internally Staged Design

	Element 1	Element 2	Element 3	Element 4	Element 5	Element 6	Element 7
Product:	BW30-400	BW30-400	LE-400	LE-400	LE-400	LE-400	LE-400
Active Area:	400 (37)	400 (37)	400 (37.2)	400 (37.2)	400 (37.2)	400 (37.2)	400 (37.2)
Max. Pressure:	225 (15.5)	225 (15.5)	150 (10.3)	150 (10.3)	150 (10.3)	150 (10.3)	150 (10.3)
Flow:	10.500 (40)	10.500 (40)	11.500 (43.5)	11.500 (43.5)	11.500 (43.5)	11.500 (43.5)	11.500 (43.5)
Salt Rejection:	99.5	99.5	99.3	99.3	99.3	99.3	99.3
oron Rejection:							
Salt:	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl	NaCl
Test Pressure:	225 (15.5)	225 (15.5)	150 (10.3)	150 (10.3)	150 (10.3)	150 (10.3)	150 (10.3)
Concentration:	2000	2000	2000	2000	2000	2000	2000
Recovery:	15	15	15	15	15	15	15
Diameter:	8	8	8	8	8	8	8

Element Type: Specs	ISD Edit ISD
Total Element per Stage:	7
Pre-stage ΔP (bar):	0.34
Back Pressure (bar):	0.00
Boost Pressure (bar):	N/A
Feed Pressure (bar):	0
% Recirculated to Feed:	0.00

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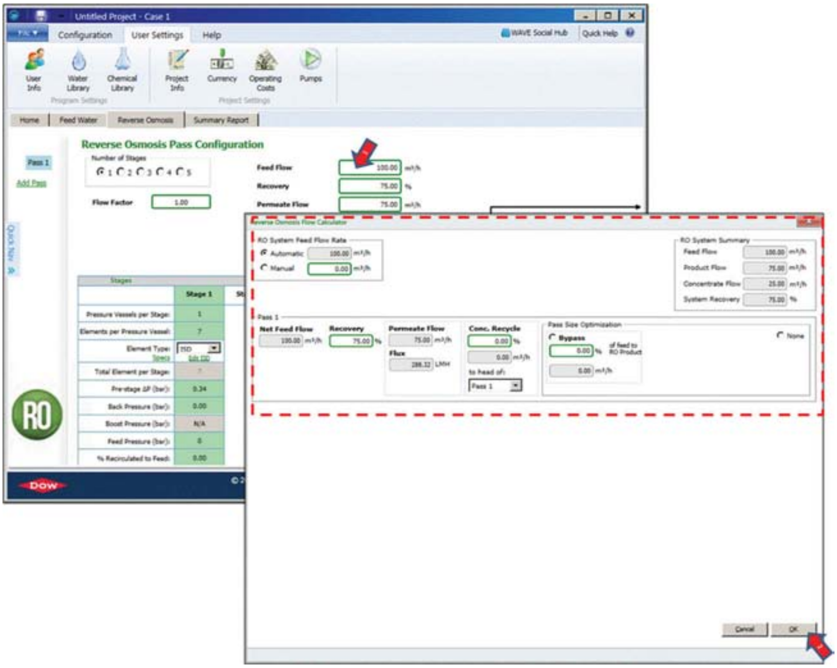
Figure 10.13 Internally Staged Design Specification in WAVE

WAVE assumes by default that the system recovery is 75% for RO and that there are no recycles, bypasses or splits in the permeate stream. These details are specified in the Flow Calculator window as shown in Figure 10.14, where the user can specify:

Concentrate recycle rate: WAVE allows for concentrate recycle from either pass to itself or an upstream pass (e.g. from the concentrate of Pass 2 to the feed of Pass 2 or the feed of Pass 1)

Split Permeate: WAVE allows the user to take permeate from intermediate points along the pressure vessel containing the RO elements. These intermediate points might be in between elements or sometimes partway through an element. The Permeate upstream of each intermediate point would be 'split off' and set directly to product (from that Pass) instead of being mixed with the Permeate streams coming from elements further downstream. The Split Permeate amount can be specified in WAVE

Bypass: To meet permeate quality requirements, it might be necessary to bypass a given Pass and mix the bypassing portion of the Feed with the Permeate from that Pass.



Reverse Osmosis Pass Configuration

Number of Stages: ● 1 ○ 2 ○ 3 ○ 4 ○ 5

Flow Factor: 1.00

Feed Flow: 100.00 m³/h

Recovery: 75.00 %

Permeate Flow: 75.00 m³/h

Stages	Stage 1
Pressure Vessels per Stage:	1
Elements per Pressure Vessel:	7
Element Type:	ISD
Total Element per Stage:	7
Pre-stage ΔP (bar):	0.34
Back Pressure (bar):	0.00
Boost Pressure (bar):	N/A
Feed Pressure (bar):	0
% Recirculated to Feed:	0.00

Reverse Osmosis Flow Calculator

RO System Feed Flow Rate
● Automatic 100.00 m³/h
○ Manual 0.00 m³/h

RO System Summary
Feed Flow 100.00 m³/h
Product Flow 75.00 m³/h
Concentrate Flow 25.00 m³/h
System Recovery 75.00 %

Pass 1
Net Feed Flow 100.00 m³/h
Recovery 75.00 %
Permeate Flow 75.00 m³/h
Flux 288.32 LMH
Conc. Recycle 0.00 %
0.00 m³/h
to head of: Pass 1

Pass Size Optimization
○ Bypass 0.00 % of feed to RO Product
0.00 m³/h
○ None

Figure 10.14 The Flow Calculator window in WAVE

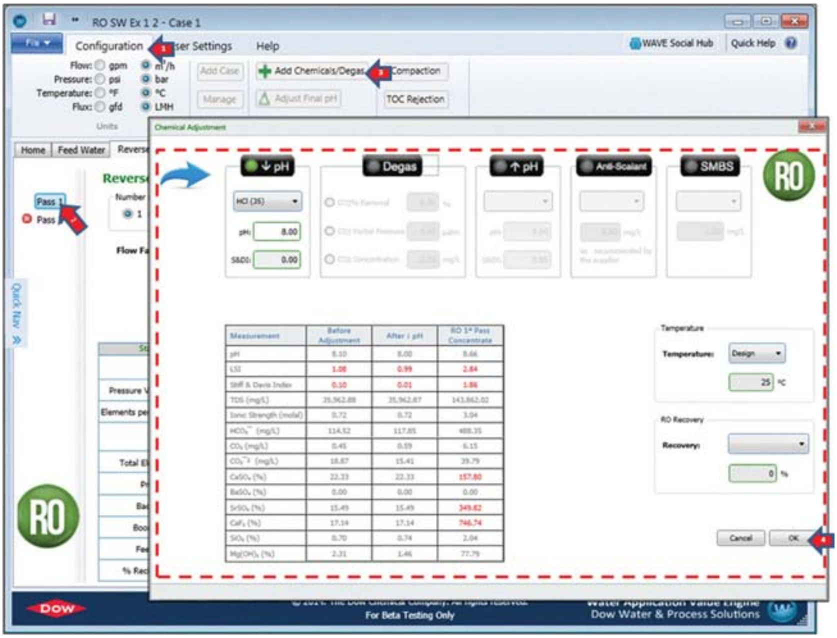
10.1.3 Chemical Adjustment

WAVE makes possible adjustment of the water chemistry ahead of the first pass, between the two passes as well as in the permeate. As shown in Figure 10.15, the user can specify pH targets, extent of degasification (CO_2 removal) as well as antiscalant and SMBS addition for the first pass. For the second pass, the pH adjustment can be specified in terms of target pH or S&DI (Stiff & Davis Index) values and extent of degasification (CO_2 removal). Based on the pH target, temperature, pass recovery and extent of degasification, WAVE would estimate the concentrate concentration and the risk of scaling (as in terms of LSI (Langlier Saturation Index), S&DI and extent of saturation.

Adjustment of the Permeate pH is handled in a similar manner by clicking on the “Adjust Final pH” button shown in Figure 10.16.

10.1.4 Special Features

WAVE currently provides two special features as shown in Figure 10.16 and 10.17.



Flow: ○ gpm ● m³/h
Pressure: ○ psi ● bar
Temperature: ○ °F ● °C
Flux: ○ gfd ● LMH

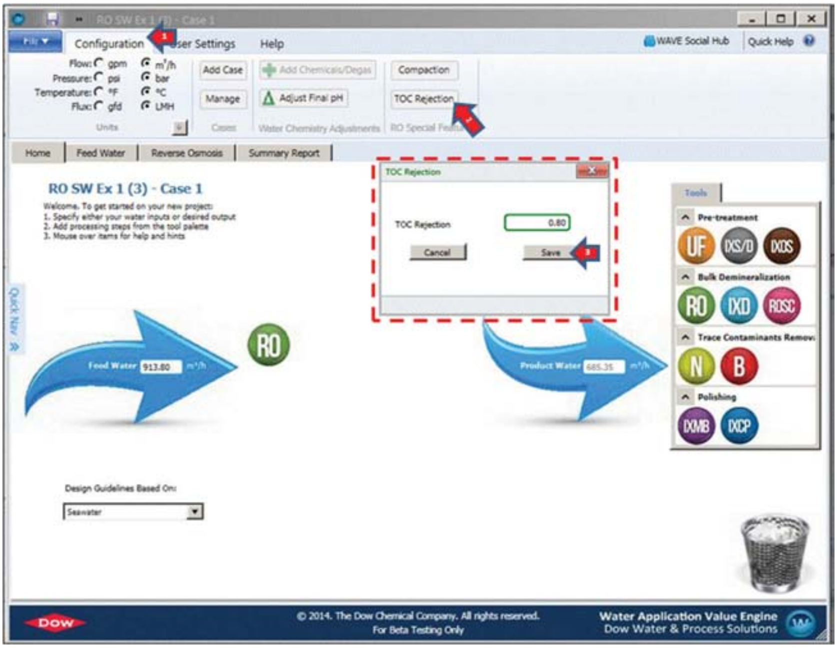
HCl (35)
pH: 8.00
SBDI: 0.00

Measurement	Before Adjustment	After ↓ pH	RO 1st Pass Concentrate
pH	8.10	8.00	8.66
LSI	1.08	0.99	2.84
Stiff & Davis Index	0.10	0.01	1.86
TDS (mg/L)	35,962.88	35,962.87	143,862.02
Ionic Strength (molal)	0.72	0.72	3.04
HCO_3^- (mg/L)	114.52	117.85	488.35
CO_2 (mg/L)	0.45	0.59	6.15
CO_3^{-2} (mg/L)	18.87	15.41	39.79
$CaSO_4$ (%)	22.33	22.33	157.80
$BaSO_4$ (%)	0.00	0.00	0.00
$SrSO_4$ (%)	15.49	15.49	349.82
CaF_2 (%)	17.14	17.14	746.74
SiO_2 (%)	0.70	0.74	2.04
$Mg(OH)_2$ (%)	2.31	1.46	77.79

Temperature
Temperature: Design
25 °C

RO Recovery
Recovery:
0 %

Figure 10.15 Chemical Adjustment in WAVE for RO



Flow: ○ gpm ● m³/h
Pressure: ○ psi ● bar
Temperature: ○ °F ● °C
Flux: ○ gfd ● LMH

RO SW Ex 1 (3) - Case 1

Welcome. To get started on your new project:
1. Specify either your water inputs or desired output
2. Add processing steps from the tool palette
3. Mouse over items for help and hints

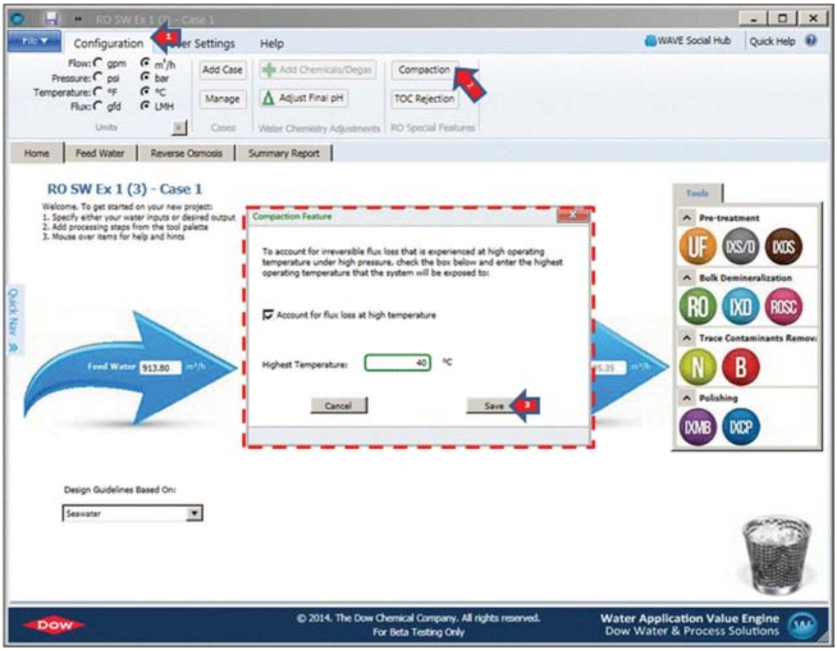
TOC Rejection
TOC Rejection 0.80

Feed Water 913.80 m³/h

Product Water 685.35 m³/h

Design Guidelines Based On: Seawater

Figure 10.16 TOC Rejection specification in WAVE



RO SW Ex 1 (3) - Case 1

Welcome. To get started on your new project:
1. Specify either your water inputs or desired output
2. Add processing steps from the tool palette
3. Mouse over items for help and hints

Compaction Feature

To account for irreversible flux loss that is experienced at high operating temperature under high pressure, check the box below and enter the highest operating temperature that the system will be exposed to:

☑ Account for flux loss at high temperature

Highest Temperature: 40 °C

Feed Water 913.80 m³/h

Design Guidelines Based On: Seawater

Figure 10.17 Compaction specification in WAVE

TOC Reduction: It is well known that several organic compounds are rejected by RO membranes. The extent of this rejection is set by default for 80% in WAVE but can be modified by the user.

Compaction: RO membranes can compact when subjected to a combination of high pressure and moderate to high temperatures. Compaction can cause reduction of flow which might lead to higher feed pressures to compensate, WAVE allows users to opt to consider compaction in their modeling.

10.1.5 Report Generation & Review

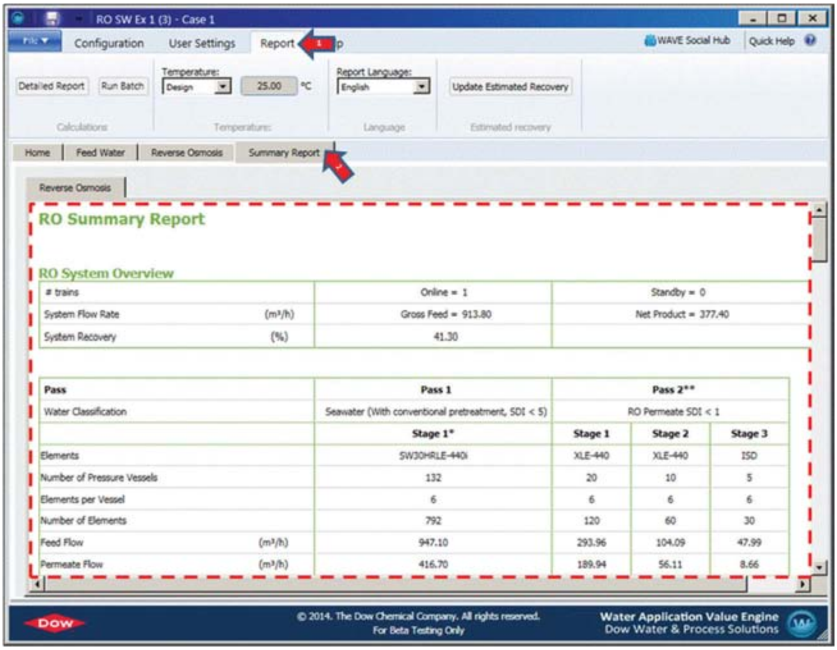
Once the necessary inputs are included in WAVE, the user would need to click on the "Summary Report" tab to generate an overview report (shown in Figure 10.18) which includes the following:

- The summary of the RO system configuration, flow and TDS at the system, pass and stage level
- The Permeate Quality table

- Design warnings and a solution guide
- The results of the scaling calculations
- A pass level diagram of the RO system

The overview report is expected to provide sufficient output to support iterative design. Once the user is satisfied with the design, a detailed report can be generated by clicking on the "Detailed Report" button. The Detailed Report (shown in Figure 10.19) includes the following additional information:

- Detailed flow at the pass level, including recycles and bypasses
- Flow table at the stage level including flows, TDS and pressure drops in each stage for each pass
- Flow table at the element level including flows, TDS and pressure drops in each element in each stage for each pass
- Solute concentrations in the feed, permeate and concentrate streams for each stage in each pass
- RO Utility and Chemical Costs – including wastewater disposal, unrecovered water cost, chemical cost and electrical cost



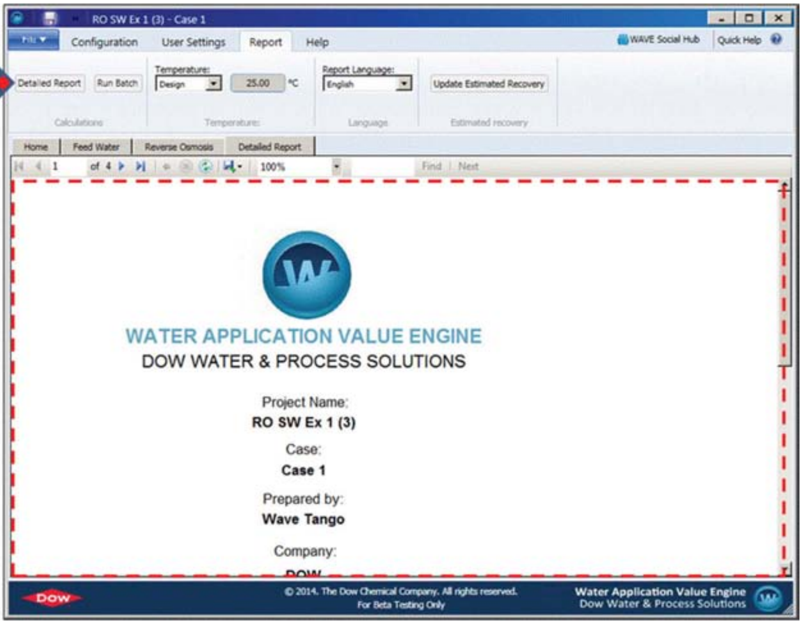
RO Summary Report

RO System Overview

# trains		Online = 1	Standby = 0
System Flow Rate	(m³/h)	Gross Feed = 913.80	Net Product = 377.40
System Recovery	(%)	41.30	

Pass		Pass 1	Pass 2**		
Water Classification		Seawater (With conventional pretreatment, SDI < 5)	RO Permeate SDI < 1		
		Stage 1*	Stage 1	Stage 2	Stage 3
Elements		SW30HRLE-440i	XLE-440	XLE-440	ISD
Number of Pressure Vessels		132	20	10	5
Elements per Vessel		6	6	6	6
Number of Elements		792	120	60	30
Feed Flow	(m³/h)	947.10	293.96	104.09	47.99
Permeate Flow	(m³/h)	416.70	189.94	56.11	8.66

Figure 10.18 The WAVE Overview Report



WATER APPLICATION VALUE ENGINE
DOW WATER & PROCESS SOLUTIONS

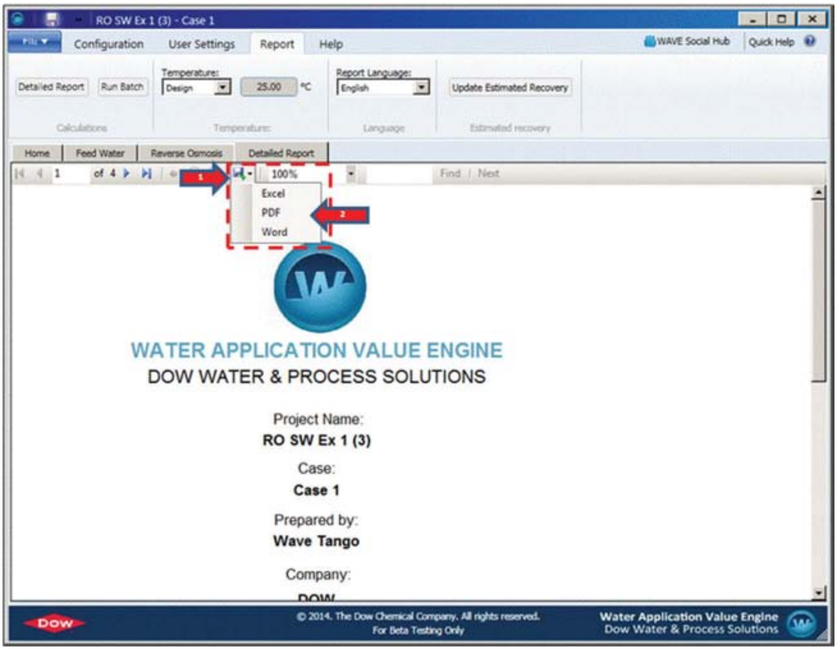
Project Name:
RO SW Ex 1 (3)

Case:
Case 1

Prepared by:
Wave Tango

Company:
DOW

Figure 10.19 The WAVE Detailed Report



WATER APPLICATION VALUE ENGINE
DOW WATER & PROCESS SOLUTIONS

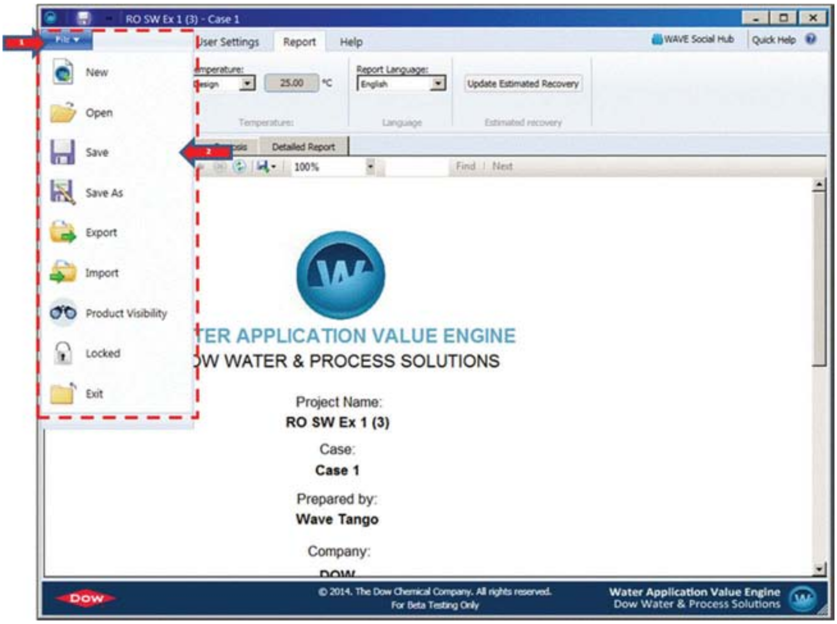
Project Name:
RO SW Ex 1 (3)

Case:
Case 1

Prepared by:
Wave Tango

Company:
DOW

Figure 10.20 Exporting a Detailed WAVE report in WAVE



TER APPLICATION VALUE ENGINE
)W WATER & PROCESS SOLUTIONS

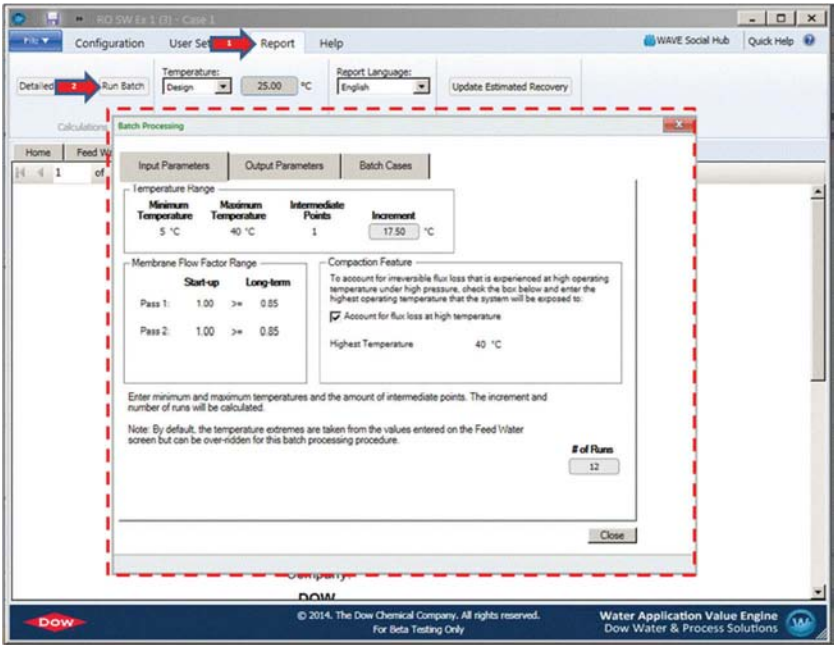
Project Name:
RO SW Ex 1 (3)

Case:
Case 1

Prepared by:
Wave Tango

Company:
DOW

Figure 10.21 Saving or Exporting a WAVE project in WAVE



Temperature Range

Minimum Temperature	Maximum Temperature	Intermediate Points	Increment
5 °C	40 °C	1	17.50 °C

Membrane Flow Factor Range

	Start-up		Long-term
Pass 1:	1.00	>=	0.85
Pass 2:	1.00	>=	0.85

Compaction Feature

To account for irreversible flux loss that is experienced at high operating temperature under high pressure, check the box below and enter the highest operating temperature that the system will be exposed to:

☑ Account for flux loss at high temperature

Highest Temperature 40 °C

Enter minimum and maximum temperatures and the amount of intermediate points. The increment and number of runs will be calculated.

Note: By default, the temperature extremes are taken from the values entered on the Feed Water screen but can be over-ridden for this batch processing procedure.

# of Runs 12

Figure 10.22 The Batch Feature in WAVE

The user can export the Detailed Report as a PDF, Excel or Word document as shown in Figure 10.20. Once the user is satisfied with the design, it can be saved as a project in a database or exported as DWPX file (as shown in Figure 10.21) which can be e-mailed to others. Conversely, the WAVE user can either directly open a project from their database or import a DWPX file from a colleague to open as a project.

10.1.6 Batch Operation and Case Management

During RO system design, it is frequently helpful to be able to investigate the effect of multiple combinations of a few factors. For instance, it is instructive to model the RO system at high temperature and a low flow factor to simulate challenging operating conditions. Instead of defining

Table 10.2 Key differences between ROSA and WAVE

ROSA	**WAVE**
1-2 Passes, 1-9 stages/pass, 1-8 elements/PV	1-2 Passes, 1-5 stages/pass, 1-8 elements/PV
Volume-balance based	Mass balance based (considers compressibility of water)
Recycle Flows specified in gpm (m^3/hr)	Recycle Flows specified in %
≥ 2 stages required for ISD, individual elements (in a PV) cannot be specified	Each element in an ISD design (for ≥ 1 stage) can be individually specified
Internal ROSA charge balance of feed water	Enforced charge balance of feed water
Stage level concentrate recycle not enabled	Stage level concentrate recycle enabled
Chemical, wastewater disposal costs not estimated	Chemical, wastewater disposal costs estimated
Case creation from Batch Run not possible	Case creation from Batch Run possible
RO for small commercial elements handled through a checkbox	RO for small commercial elements handled through a separate icon
Not possible to integrate the RO permeate or concentrate with UF (ultrafiltration) modeling	Can integrate the RO permeate or concentrate with UF (ultrafiltration) modeling

several individual cases, WAVE allows the user to define a potentially large number of Flow Factor and Temperature combinations and generate key performance metrics (e.g. feed pressure, permeate TDS) in one batch as shown in Figure 10.22. WAVE also allows the user to create cases from this design feature.

10.1.7 Comparison between WAVE and ROSA

WAVE is based on the legacy DW&PS software called ROSA (which was described in the first edition of this book) but there are several key differences as described in Table 10.2. Some of the key differences reflect the multi-technology nature of WAVE. For instance, users can simulate the use of RO permeate or concentrate for backwash, front flush or CIP (Clean-In-Place) purposes using WAVE.

10.2 Toray DS2 Version 2.0.1.93

Contributed by John Buonassisi, Toray Membrane USA.

The Toray DS2 RO system design software has all the features of the earlier version plus many new innovative and useful features for basic and more sophisticated RO designs such as: two pass designs incorporating energy recovery devices, recycle options, partial and split permeate collection, flux balancing using permeate back pressure, interbank boost devices, etc.

The main input screens are accessed from the upper left menu tabs, as follows:

- Start Screen: Here is where the designer can select to use the “Template” design option; or “Create a New Project.” In addition there is a “Quick Start” option to use as a reference document. This narrative will follow the “Create a New Project” route to construct an RO design projection. Click on “Design a New Project” to advance to the next screen.
- Project Screen: This screen allows the user to enter unique project information. Minimum data required is project identification and engineer’s name (or designer’s name/initials). Next, click on “Create Project” to proceed to the next screen.
- Feed Data Screen: *At this point it is useful to select the engineering units desired. Click on the “Unit” tab to select*

appropriate engineering units for the design. The Feed Data Screen is where raw feed water information is entered.

- Select the raw water source from the drop down list. DS2 will automatically review your calculated design and compare it to Toray Guidelines for the selected water source. Warnings or errors will relate to Toray Guideline infractions such as: excessive lead element flow, flux, too low brine flow, etc. *Toray Design Guidelines are available for viewing by clicking on the "help" tab located at the top of this screen*. DS2 can accommodate up to three raw feed water sources at desire percentages.
- Other data inputs to enter on this screen are: pH, temperature, and individual ion concentrations for each feed source (if multiple sources are entered, the combined feed source analysis can be viewed by clicking on the "Show Combined" button).
- An alternate option to entering individual ion concentrations is to select "Set TDS as NaCl." DS2 can also help the designer "balance" the feed source with any ion entered. This can only *add* ions to achieve a charge balance. Right click on the ion to be used for balancing and a pop-up will indicate the new ion concentration to achieve a balance. Alternatively one can balance ion concentrations with NaCl or MgSO4.
- Another feature in Toray DS2 is the capability to access any water analysis residing in the designers DS2 database. This data can be accessed by clicking the "Load/Review Analysis" button.
- The designer has the option to activate the automatic ion charge balance function by checking the box to the left of "auto balance." To proceed to the next screen, click on the "RO Design" tab at the top of the Feed Data screen.

- RO Design Screen:
  The RO design screen is divided into four areas.

1. **Center Upper Panel.** This panel contains the main flow schematic, flow and recovery inputs, and membrane array icon.
2. **Left Side Panel**. The display is selected by using the tabs at the bottom left hand side of the panel:

   a) **Flow Diagram**: Allows user to add/remove design choices: feed bleed/recycle/ split takeoff options/ two pass designs.
   b) **Configuration:** Allows user to select screen displayed: Pass (flow schematic)/ Stage/Vessel or Element (element selection screen) or input/change data for specific operations (dosing chemical addition)/Degassing (CO2 removal)/ Pressure (permeate back pressure)/ Pump (selection of efficiency + suction pressure details for pump energy calculations, including system feed pump, main HP pump and Permeate pump options)/ ERD (choose to add an Energy Recovery Device to the design – options include turbochargers/Pelton wheel turbines/ work exchangers and isobaric devices). Also available are additional buttons to allow the user to input/ change Permeate back pressure/interstage boost and interstage pressure losses/replacement rates and pumps
   c) **Select Elements:** Allows user to choose element type and enter the membrane array details. NOTE: This screen can also be accessed by clicking the blue membrane array icon on the flow schematic.
3. **Right Hand Side Panel**. The display is user selected by tabs along the bottom right hand side of the panel:
   a) System Overview: Calculation result information (pressures/TDS and flux). NOTE: mMore data can be seen by opening the separate Stage Details Diagram window (click Project Configuration>Show Stage Details Diagram from main menu bar).
   b) Chemical Dosing – select location of dosing points on the flow schematic NOTE: To input chemical choice and pH targets, click in the “barrel” icon on the flow schematic after location is selected.
   c) Degassing – select location of any degasser unit operations for CO2 removal.
   d) Pressure – select location for permeate back pressure/ interstage boost.
4. **Center Lower Panel**. Displays results and design warnings (user selectable from tabs below the panel).

a) Results: The flow schematic includes stream identifiers (number in small blue boxes). Drag and drop the blue box into any column in the results and (after calculation) to display the listed results. NOTE: Left click in the "items" column to select which three ions/values to be displayed.

b) Errors/warnings: Shows errors and warnings generated by the design.

Entering Recovery and Flow Information:

- In the center of this screen above the membrane array icon is a gold colored star. Click on the star and select your design priority (Recovery or Permeate Flow). Typically permeate flow is selected. Enter the permeate flow using the previously selected engineering units. Enter desired recovery rate in the center membrane element array icon or use the up/down arrows to increment the recovery value.
- The next step is to construct the RO array. Click on the lower left tab labeled "Select" to advance to the next screen. On this new screen the designer can input the following:
  - Number of passes, stages (up to ten total) within each individual pass, pressure vessel (PV) element capacity (up to ten total).
  - Selection of membrane element type (SW, BW, LPRO, etc.), element age, associated fouling factor (if not using DS2 default values), annual salt passage increases (as a%), etc.
  - DS2 allows different membrane models in different stages as well as different membrane models in the same PV of any stage.
  - Typical data entry for a two stage RO system design: Stage 1 – Select "Pass" 1, "Total Stages" 2, "Current stage" 1, Vessels per Stage (enter as required), "elements in Vessel." Enter the membrane element performance "year." *If the user has selected the DS2 fouling and salt passage default values, they will automatically change with the year selection.* Select the membrane model type by clicking on the arrow to the right of "element type." If the model numbers are unfamiliar, click on any model and the element performance characteristics will be displayed.
  - Stage 2 – Locate "current stage" and enter "2." Next enter, as before, the number of stage 2 PV and number of elements per PV for stage 2. All other conditions will remain the same. Finally click on "View flow Diag." This will take

  you back to the screen used to enter the recovery and permeate flow.
  - To apply or "calculate" the design input selections, the designer needs to click the "calculate" button located at the upper right of this screen. If no pop-up notifications are displayed, the design calculated performance is close enough to be successfully calculated.
  - To view design warnings, click on the tab labeled "Errors/ Warnings" located at the bottom left of the screen. If any projected performance parameters violate the Toray Design guidelines (based on the raw water type selected earlier), a warning will appear and corrective action is warranted.
  - By clicking on the upper menu tab labeled "Project Configuration" then "Show Stage Details Diagram," one can view, in detail, stage by stage performance parameters. Values listed in RED indicate a deviation from Toray Design guidelines and need to be addressed by referencing the guideline values and making needed changes to the current design. One can also click on "Errors/ Warnings" to view the infraction and magnitude of the indicated design error.
- By clicking on the lower tab labeled "Config," other design options are made available, such as:
  - Permeate back pressure for flux balancing.
  - Interbank boost pump discharge pressure for flux balancing.
  - Membrane Element Replacement calculator.
  - Selection of pre and/or post treatment chemical addition for pH, LSI, or Hardness adjustments.
  - Select "degasification" if desired to view estimate pH/TH changes, etc.
- To the left of the "Config" tab is the "Flow Diag" tab. Clicking on this tab will make the following options available for 1 Pass and 2 Pass RO design selections: Pass 1 Feed water by-pass blend to permeate.
  - Pass 1 Concentrate recycle to feed stream. This is helpful to increase brine flow in smaller RO designs.
  - Split permeate take off.
  - Pass 2 Inter pass boost pump pressure selection.
  - Pass 2 recycle second pass concentrate to first pass feed stream.

  - Partial and split permeate take off options for single and two pass designs.
- Saving the project design is accomplished by clicking on the upper left "Project" tab then clicking on the upper menu tab labeled "Save Now as a New Revision." This action saves the design in the DS2 database and makes all entered data available for various output options: PDF file, MS Excel, or .tds file.
- Multiple cases can be constructed by clicking on the "New Case" button, entering the desired design change on the appropriate screen, then recalculating the design and returning to the "Project" screen and clicking on "Save Now as a New Revision." Cases can be deleted or modified should a data entry error be discovered.
- To access the output "REPORT" file, "open" the desired Project *and* case and click on "Report." Reports are presented in a short and long format. Select the desired output format from the upper "Project Configuration" tab. The reports list process stream water qualities, flow rates, lead element and system flux rates, pressures, specific compound concentrate saturation values, power consumption, and design warnings and errors. The long format calculates various performance parameters stage by stage as well as element by element within a particular stage and pressure vessel.
- A process flow diagram is available for viewing at the end of each report.

Project reports can be printed or saved as a PDF file. Projects can also be saved as a. tds file and exported to a computer HD. This is useful if another DS2 user wishes to share and be able to edit the design without the need to renter the design inputs. The DS2. tds file can be emailed and then imported into the recipients DS2 Project files.

Other features unique to DS2:

- Located within the "Project Configuration" tab are two options for sea water osmotic pressure calculation methods. The designer can select either the TEOS 10 method or the more accurate Pitzer method.
- In the "tools" tab one can export the current design or total Project (with all cases) to an MS Excel file.

- Multiple design runs. In the "tools' tab, it is possible to set up the program to do multiple design runs and automatically export the results to Excel
  a) For a user selectable temperature range and interval.
  b) For a user selectable membrane age and interval.
- Element replacement rate studies.
  - In the Tools tab it is possible to make the program do multiple design runs automatically, exporting the results to Excel for program defined replacement strategies with user defined rates of replacement.
  - The program also allows each individual element in each stage of the membrane array to have its own values for membrane age, fouling factor, and salt passage increase. It is therefore possible to simulate highly defined partial replacement scenarios with user defined mixes of new and older elements with different levels of fouling and salt passage increase.

10.3 Hydranautics IMS Design

Contributed by Wayne Bates, Hydranautics

Author's Note: Hydranautics will be releasing IMSD-2015 in the spring of 2015. This program will be significantly updated from the 2008 program described in the first edition of this book. The new program will be more user friendly with have advanced features, including:[4]

- An improved flow diagram will show all design flows no matter how complex the design.
- By default, the flow diagram will be attached to the printed projections.
- The estimated energy use in kw-hr per 1000 gallons or per cubic meter will be on the first page of the printout, no matter how complex the design.
- A blend of multiple feed waters analyses can be used to run projections.
- The feed water analysis will accommodate the use of custom ions.

  Custom cations will include:
    - Copper
    - Chromium

    - Manganese
    - Iron
    - Cobalt
    - Nickel
    - Molybdenum
    - Silver
    - Aluminum
    - Lead
    - Zinc
    - Radium
    - Uranium

  Custom anions will include:

    - Bromide
    - Iodide
    - Sulfide

- A "floating" flow diagram will automatically be developed as one designs the RO/NF and adds options.
- After a user selects an RO or NF element from the draw down menu, the program will automatically display all pertinent element information, including square feed and feed spacer thickness. It also will run a quick calculation for the given design and let the designer know what the permeate TDS and feed pressure will be without going back to the design page.

References

1. Dow Water and Process Solutions Form 609-02058-1004, http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0035/0901b80380035b70.pdf?filepath = liquidseps/pdfs/noreg/609-02058.pdf&fromPage = GetDoc, accessed July 11, 2014.
2. Yacoubowiz, Henia, *Koch Membrane Systems*, personal communication, July 7, 2014.
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4. Bates, Wayne, *Hydranautics*, personal communication, July 2, 2014.

4

OPERATIONS

11

On-Line Operations*

The keys to understanding how well an RO system is operating operate are to take the proper data, to use the appropriate analytical techniques to interpret these data, and to perform maintenance to keep the RO and pretreatment systems operating as designed. This chapter covers both data that should be collected and how to interpret them, as well as a preventive maintenance schedule to help keep the RO and pretreatment systems performing well.

11.1 Reverse Osmosis Performance Monitoring

Performance of "conventional" deionization technologies, such as ion exchange, is well known and understood. In the case of RO, however, operator and engineers do not have a long history with this technology,

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*Adapted from "Reverse Osmosis Performance: Data Collection and Interpretation," originally presented at the 28th Annual Electric Utility Chemistry Work-shop, Champaign, IL, May 2008, and published in "UltraPure Water® Journal, www.ultrapurewater.com, April, 2009.

and many lack the understanding of performance that comes with experience. Furthermore, monitoring of an RO system is not straightforward; observed performance is not always indicative of what is actually happening at, on, or in the membrane.

11.2 Data Collection

Table 11.1 lists primary data points that should be monitored to determine how an RO system is basically functioning.[1] The parameters listed in Table 11.1 all affect the product flow rate and/or product quality, as described in Chapter 9. Of all the data points identified in Table 11.1, feed, product, and reject data are most commonly measured, and most RO skids are constructed with required instrumentation for measuring these variables.

However, many RO skids are not equipped with interstage-measuring capabilities. Interstage data are necessary to obtain when considering performance, as these data can assist with determining what is occurring within each stage of the RO system. Without interstage data, any degradation in performance cannot be identified as occurring in the first stage of the RO (and thus, most likely related to fouling of the membrane) or occurring in the final stage of the RO (most commonly related to scaling of the membrane). Interstage pressure instrumentation is commonly provided interstage conductivity and flow are not commonly provided but are very useful to have.

In addition to the data in Table 11.1, it is necessary to gather other information so that a complete analysis of performance can be conducted.[2]

Table 11.1 Typical input data required by normalization software programs.

Input Data	**Raw water**	**Feed**	**Permeate**	**Reject**
Date and time		X		
Flow			X	X
Pressure			X	X
Conductivity		X	X	X*
Turbidity	X	X		
ORP		X		
SDI	X	X		

*Desirable

- Permeate backpressure: Are there valves on the permeate line or unit operations (including tanks) that may exert backpressure on the membranes? Has this backpressure been taken into account in the performance projections?
- pH: What chemicals and concentrations are being added, what is the dosing set point, and how is dosage being controlled?
- Oxidizing biocide: Which one(s) is being used and how is its dosage controlled? Also, how is it being removed and how is that being controlled?
- Reducing agent (Anti-oxidant): Which one(s) is being used and what is the feed protocol? How is the dosage being controlled?
- Non-Oxidizing biocide: Which one(s) is being used and how is the dosage controlled? On-line or off-line usage?
- Antiscalant: What product is being used, what is the dosage, and how is the dosage controlled? Is flow proportional control being used?
- Other pretreatment chemical feeds: These include coagulants and flocculants. What is the nature of the chemical(s) being fed, the dosage, and how is the dosage controlled?
- Particle monitors: Particle monitors can be used to follow changes in the nature of the suspended solids in the feed water and throughout the pretreatment system. Do the monitors indicate a change in the number of particles of a given size? This could indicate a change in source water quality or in the efficiency of the pretreatment.

11.3 Data Analysis and Normalization

Parameters listed in Table 11.1 directly affect the observed product flow rate and observed salt passage through an RO membrane. Additional factors that affect membrane performance include the degree of membrane fouling, scaling, and degradation that has occurred. These three factors directly affect the observed product flow rate and observed salt passage, just as temperature, concentration, and pressure do. Because these operating conditions are constantly changing, it is not possible to compare the observed performance, such as product flow rate, at one time with the observed performance at another time.

11.3.1 Data Normalization

Data normalization was developed to allow for the direct comparison of performance at one time with that at another time by “neutralizing” via normalization the effects of temperature, pressure, and concentration on the performance parameter of interest. Normalization converts data collected at a given time and conditions to those at a designated baseline time, typically at start up of the RO system (or following installation of new membranes). In this manner, effects of temperature, pressure, and concentration are eliminated so that the only changes in normalized performance are due to membrane fouling, scaling, and/or degradation.

11.3.1.1 Normalized Product Flow

Equation 11.1 is shows how temperature, in terms of the temperature correction factor, TCF; pressure, P; and concentration, as osmotic pressure, Π, are used to normalize product flow rate.[3]

$$\text{Normalized flow} = \frac{[(\text{AAP}_s - \Delta\Pi_s)]\text{TCF}_s}{[(\text{AAP}_a - \Delta\Pi_a)]\text{TCF}_a} \bullet \text{Actual flow} \tag{11.1}$$

where AAP = the average applied transmembrane pressure

$$= \text{P}_{\text{feed}} - \frac{\Delta \text{P}}{2} - \text{P}_{\text{perm}} \tag{11.2}$$

where

P_{feed} = applied feed pressure
ΔP = pressure *drop* from feed inlet to concentrate effluent
P_{perm} = permeate pressure
$\Delta\Pi$ n = difference between the osmotic pressure on the membrane feed and permeate sides
TFC = temperature correction factor (membrane and manufacturer dependent)
“s” = subscript for “standard” conditions
“a” = subscript for “actual” conditions

In practice, data normalization is calculated using a spreadsheet or other of computer program. The best programs are integrated into a package that includes the hardware to actually capture the raw data. This eliminates the need to manually enter data. In general, systems that require manual data entry do not stand up to the test of time; operators will usually cease manually entering data within the first couple of months after start-up, and they are left with only observed data with which to analyze performance. As

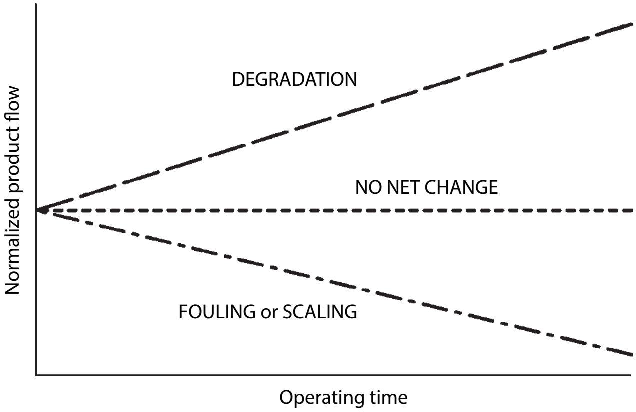

Figure 11.1 Trends in normalized product flow.

discussed previously, observed data are unreliable due to the effects of pressure, temperature, and concentration on product flow and salt rejection.

Once the normalized permeate flow (NPF) is calculated, it is best graphed to observe trends. Figure 11.1 shows various trends in the NPF. Curves with a positive slope are indicative of membrane degradation, as more water is passing through the membrane at time T > 0 than at the initial operating conditions (T = 0). A negative slope is indicative of membrane fouling or scaling, as less water is passing through the membrane then would be at the initial operating conditions. A flat slope is indicative of no change in performance (this can mean no changes have occurred or that both degradation and fouling or scaling are occurring and, in effect, canceling each other out).

Case Study

Figure 11.2 shows the actual raw data from a facility operating on Delaware River Water.[4] As the graph shows, the operators did an excellent job of keeping the productivity of the system steady at 340 gpm the design flow rate. Based on these raw data, one would believe that the RO system was operating well.

Figure 11.3 shows the normalized data for the same system.[4] The normalized product flow exhibited an initial negative slope with time. Based on the information given in Figure 11.1, it appears as if the RO system was fouling or scaling, leading to a decrease in normalized permeate flow. Upon investigation, the operators were constantly increasing the operating pressure of the membrane system to force water through the increasingly

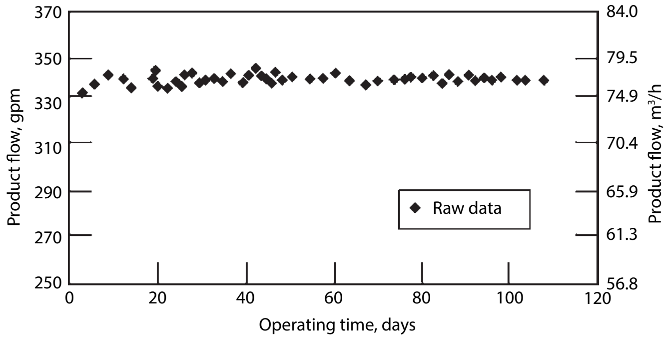

Figure 11.2 Actual product flow rate data from a facility operating on cold-lime softened Delaware River water.

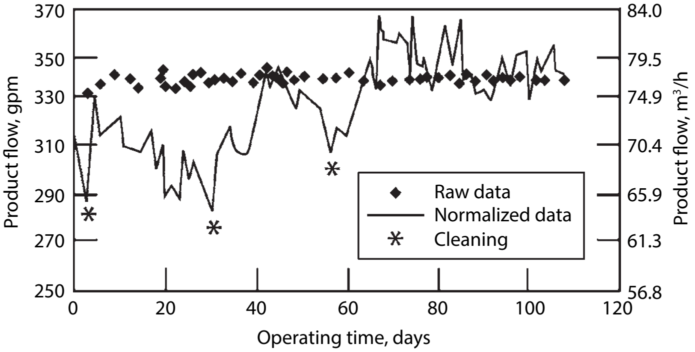

Figure 11.3 Normalize product flow rate data from a facility operating on cold lime softened Delaware River water.

thick layer of foulant or scale on top of the membrane. Hence, constant product flow rate was maintained despite fouling or scaling, due to the increase in operating pressure.

Given that the operators were able to maintain a constant product flow rate, albeit by increasing the operating pressure, one might ask why we should even care about the NPF?

Why not simply monitor actual feed pressure rather than normalized data? Figure 11.4 shows a hypothetical pressure increase for a system operating on a surface water. The figure clearly shows an increase in pressure. Figure 11.5, however, shows the change in feed water temperature for this surface water and the change in pressure required to force water through the membrane as the temperature fluctuates. Putting Figures 11.4

and 11.5 together, Figure 11.6 shows how the pressure due to fouling and the pressure due to temperature change in effect cancel each other out over the first six or seven months, and then are additive over the later months of the year. The net observed pressure stays fairly constant over the first six months of the year. If one were only monitoring feed pressure, the assumption would be that no cleaning was necessary over this time period. A 15% increase in observed pressure would be reach in July (Figure 11.7).

Figure 11.8 superimposes the NPF on the graph. It is clear to see that the NPF drops by 15% within the first three months of operation, as opposed to July for the 15% increase in observed pressure. Thus, if only observed

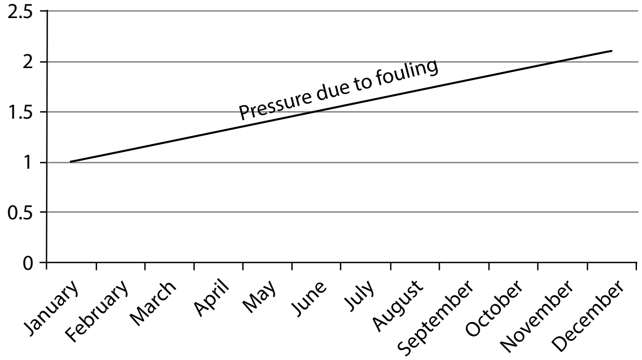

Figure 11.4 Hypothetical pressure increase on a surface water due to fouling.

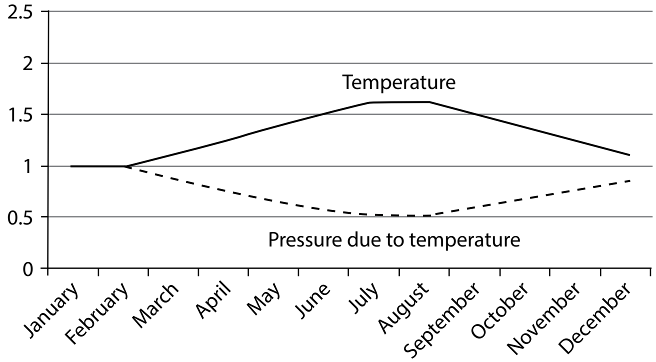

Figure 11.5 Hypothetical pressure changes on same surface water due to seasonal temperature changes.

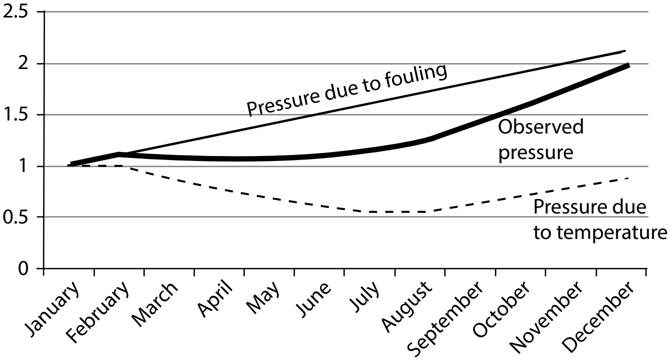

Figure 11.6 Net observed pressure when fouling and temperature changes both affect pressure.

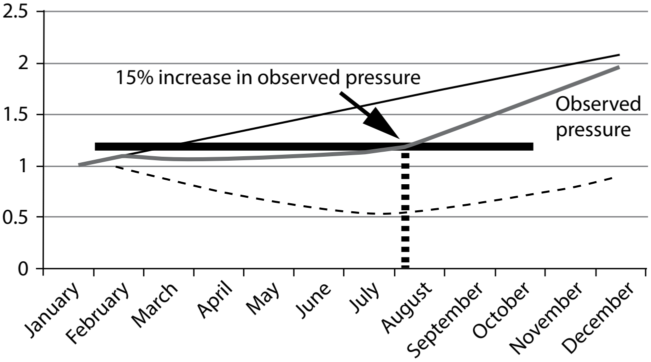

Figure 11.7 A15% increase in observed pressure would occur in July for a system operating on surface water that experiences both fouling and seasonal changes in temperature.

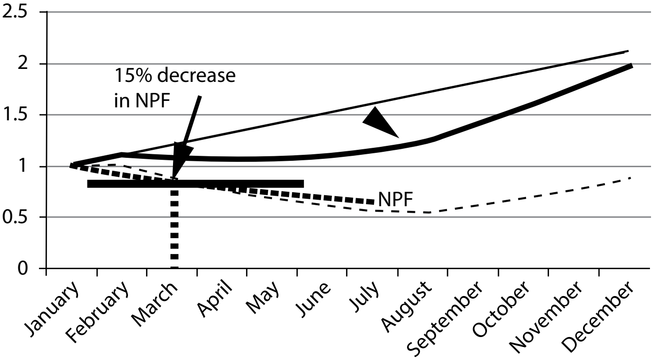

Figure 11.8 Normalized permeate flow for the same system depicted in Figures 11.4 – 11.7, showing that the actual performance of the membranes falls off much more rapidly that just following the observed pressure would indicate.

pressure were monitored, the membranes may experience increased rates of fouling and/or scaling, which could become permanent.

When systems are allowed to operate in fouling or scaling mode for extended periods of time, the foulant or scale can become resistant to removal via cleaning. Thus, NPF is used to determine when it is time to clean the membranes before the surface contamination becomes permanent.

Further, continued operation under fouling or scaling conditions will result in the operating pressure reaching the maximum output allowed by the feed pump. If permitted to continue operating in this manner, the product flow rate would decrease as the pump could not supply higher pressure to overcome the resistance of the fouling layer. Hence, the key to keeping the membranes operating is to monitor the NPF and clean when the drop in NPF indicates it is time to do so. Cleaning of the membranes is recommended when the NPF drops 10% to 15% from initial operating conditions. Ideally, a cleaning should be scheduled at 10% drop and completed by the time the NPF drops 15% (see Chapter 13.2.1).

Although the "initial operating conditions" should be taken when new membranes are installed, it can sometimes be impractical to use this baseline condition for determining when to clean the membranes. Examples of when new membrane performance might not be suitable for baseline performance include occasions when normalization is just being initiated and the membranes have been in operation for some time or when the pretreatment is not adequate. In the later case, if the baseline condition is membrane start-up, the cleaning frequency may be much too frequent when pretreatment is not adequate. In such cases, it is advisable to use the performance after cleaning as a new baseline condition. Figure 11.9 demonstrates how this would work. Performance would follow both the new membrane baseline for overall cumulative performance loss and the post-cleaning baseline to determine when to clean next.

Figure 11.9 Normalized permeate flow showing both cumulative performance loss from new membrane baseline performance and post-cleaning performance on which subsequent cleaning is based.

11.3.1.2 Normalized Salt Passage

Salt passage is another operating variable that is normalized. Since concentration is constantly changing, it is difficult to compare observed salt passage (or salt rejection) on a day-to-day basis. Normalizing the salt passage takes out the concentration and temperature variables, allowing the passage at any one time to be compared that at another time. Equation 11.3 shows how concentration affects the normalized salt passage through an RO membrane.[3]

$$\begin{array}{l}\text{Percent}\\ \text{Normalized}\\ \text{Salt Passage}\end{array} = \left\{ \frac{\text{EPF}_a}{\text{EPF}_s} \bullet \frac{\text{CFC}_s}{\text{CFC}_a} \bullet \frac{\text{STCF}_a}{\text{STCF}_s} \bullet \frac{C_{fa}}{C_{fs}} \right\} \bullet \%\text{SP}_a \tag{11.3}$$

where

EPF = average permeate flow divided by the number of membrane modules

STCF = salt transport temperature correction factor (from membrane manufacturer)

C_f = feed salt concentration

%SP = percent salt passage

CFC = concentration of the feed-concentrate:

$$\text{CFC} = C_f * \frac{\ln \frac{1}{1-Y}}{Y} \tag{11.4}$$

$$Y = \frac{\text{product flow}}{\text{feed flow}} \tag{11.5}$$

and

“s” = subscript for “standard” conditions

“a” = subscript for “actual” conditions

Monitoring salt passage is important in tracking membrane scaling and/or degradation. In both of these cases, salt passage will increase with time. If membrane degradation is occurring, this increase in salt passage is easy to understand. In the case of membrane scaling, however, the increase in salt passage is not so intuitive. Consider the following example.

Figure 11.10 depicts a cross-section of a membrane with a layer of calcium carbonate scale on the surface. The concentration of calcium at the membrane surface, Z, is higher than that in the bulk feed, X, since

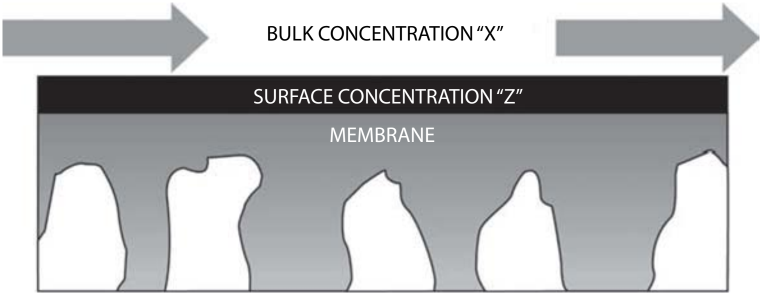

Figure 11.10 Cross-section of an RO membrane with a layer of scale on the surface of the membrane. Concentration of scale formers is higher at the membrane surface, Z than in the bulk solution, X.

the concentration at the surface has reached saturation. The membrane passes salts based on what concentration is actually next to the membrane. In this case, the membrane is exposed to a saturated concentration, not the lower bulk solution concentration. Even though the percent passage of calcium through the membranes stays constant, the scaled membrane will yield higher permeate concentration of calcium. This is because the concentration of calcium that the membrane is exposed to at the membrane surface is higher than the bulk solution concentration of calcium, [Z],[X], respectively.

Normalized salt passage is generally not used as the primary indicator of when to clean membranes. This is because normalized product flow and/or differential pressure drop (see below) will usually indicate problems with the membranes before product quality becomes an issue. However, normalized salt passage should be used in conjunction with NPF and pressure drop to diagnose and troubleshoot problems with the RO system.

11.3.1.3 Normalized Pressure Drop

Pressure drop through the RO system can also be used as an indicator of when it is time to clean membranes. Pressure drop is a direct measure of the pressure loss due to friction caused by scale or foulants on the membrane or the feed spacer.

The energy lost from pressurized feed water is absorbed by the membrane module materials, which can cause the materials to shift within the module when the degree of fouling or scaling is severe. This can lead to telescoping of the membrane leaves, resulting in physical damage to the membrane itself (see Chapter 14.8.1 and figure 11.7). Figure 11.11 shows how the pressure drop on an 8-inch (20 cm) diameter membrane module operating at 200 psig increases the axial load on the modules themselves. Assuming a "good" pressure drop of 4 psig per membrane module, the axial pressure on the end of the last module is over 1,150 psig. Figure 11.12 shows the different axial loads for 8-inch diameter modules operating at 200 psig with a recommend pressure drop of 3 – 4 psig per membrane module (21 psig drop per single stage of 6 modules in series), and a maximum recommended pressure drop of 8.3 psig per membrane module (50 psig maximum drop per single stage of 6 modules in series). At 50 psig pressure drop, the axial load on the end of the last module is 2400 psig.

As a result, pressure drop should also be considered in making the determination when to clean the membranes to avoid physical damage to the modules. Membranes should be cleaned when the pressure drop increases by 10% to 15% from initial operating conditions.

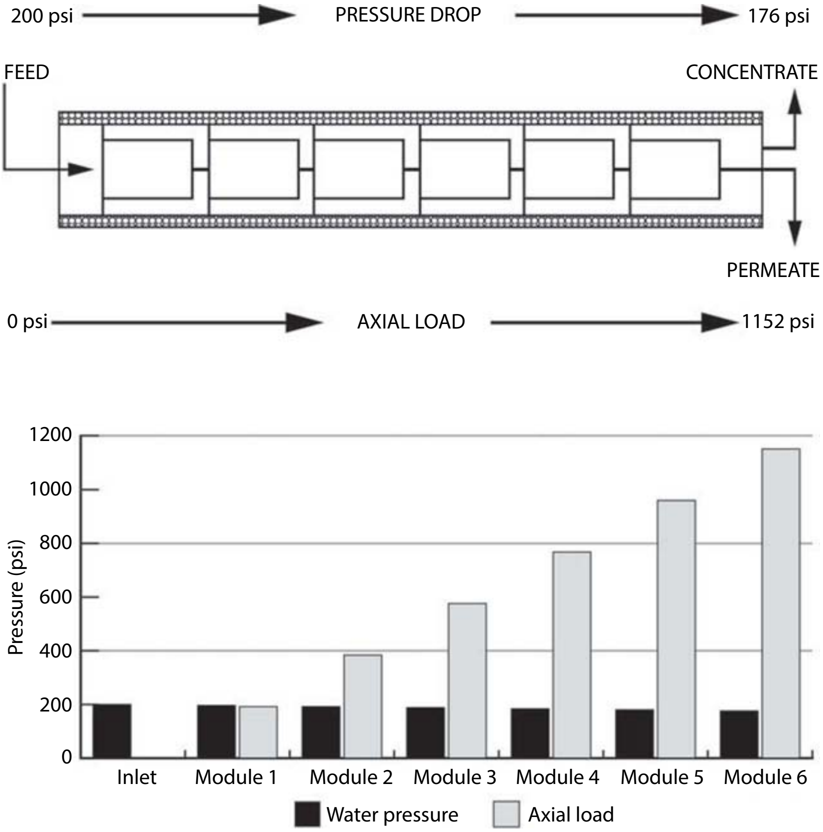

Figure 11.11 Axial pressure load on 8-inch diameter membrane modules operating at 200 psig. Assumes six, 8-inch modules per pressure vessel.

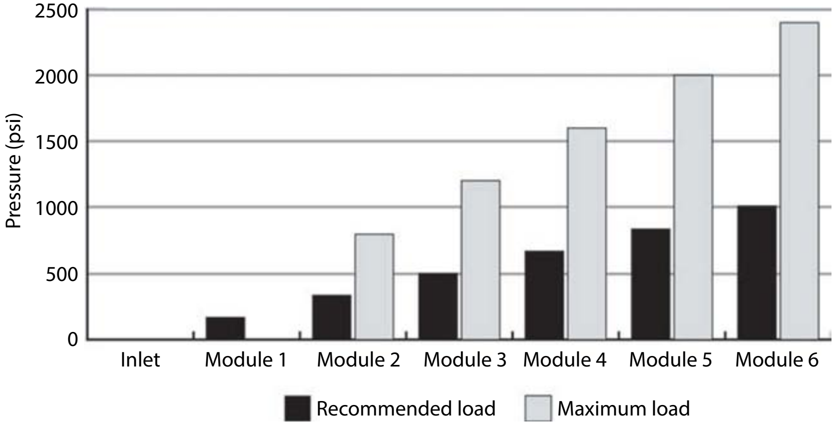

Figure 11.12 Comparison of axial pressure load on end module with recommend 3–4 psig pressure drop per module and a maximum recommended pressure drop of 8.3 psig per membrane module. Assume six, 8-inch diameter modules per pressure vessel.

Equation 11.6 can be used to normalized the system pressure differential.[5]

$$\begin{array}{l}\text{Normalized}\\ \text{Differential}\\ \text{Pressure}\end{array} = \frac{\Delta P_{actual} \times (2 \times CF_{su} + PF_{su})^{1.5}}{(2 \times CF_{actual} + PF_{actual})^{1.5}} \tag{11.6}$$

where

ΔP_{actual} = actual differential pressure
CF = concentrate flow
PF = permeate flow
"su" = subscript for start up

Normalized pressure drop and NPF should be monitored simultaneously, and the membrane cleaned when the first of these measures reaches the 10% change in performance as compared to initial operating performance.

11.3.2 Normalization Software

Normalization calculations can be tedious, so membrane manufacturers have made available, at no charge, normalization software for their specific membranes. Some chemical vendors and other membrane consultants have software as well, which may or may not be available for public use. Some even have hardware that will download the appropriate data from the PLC or discrete probes to eliminate the need for manual entry of the

Table 11.2 Optimal monitoring variables for an RO system.

	Feed	Interstage	Product	Reject
Pressure	X	X	X	X
Flow			X	X
Conductivity	X		X	X
Temperature	X			

data. Still other incorperate normalization in to the PLC/HMI. Operators will be able to use the normalization software to review the normalized data, schedule cleanings, and optimize the RO operation.

Table 11.2 lists the typical data inputs required by the normalization software programs. These inputs cover a multi-stage RO skid as if it were a single stage in terms of calculating normalized data. Some programs have the ability to handle interstage data, which allows the user to analyze each stage separately (typically limited to 2 stages). The ability to analyze individual stages aids the user in determining whether fouling is occurring in the first stage or scaling is occurring in the second stage. Interstage pressure transmitors allow for NdP across each stage. More complete systems with interstage flow and conductivity allow for MPF an NSP across each stage.

Virtually all normalization programs will calculate the normalized permeate flow, normalized salt rejection and/or passage, and differential pressure (some programs normalize pressure, some do not). Some programs also include net driving pressure as an output as well as the following outputs:

- Recovery
- Concentration factor
- Salt passage
- Salt rejection
- Average system flux
- Average feed osmotic pressure

Hydranautics' ROData program includes the normalized water transport coefficient and the normalized salt transport coefficient. The water transport coefficient corresponds to the permeability coefficient, A, in equation 4.1. The salt transport coefficient corresponds to the permeability coefficient, K, in equation 4.2. The coefficients should remain constant over normal (ambient) operating conditions. Changes in the

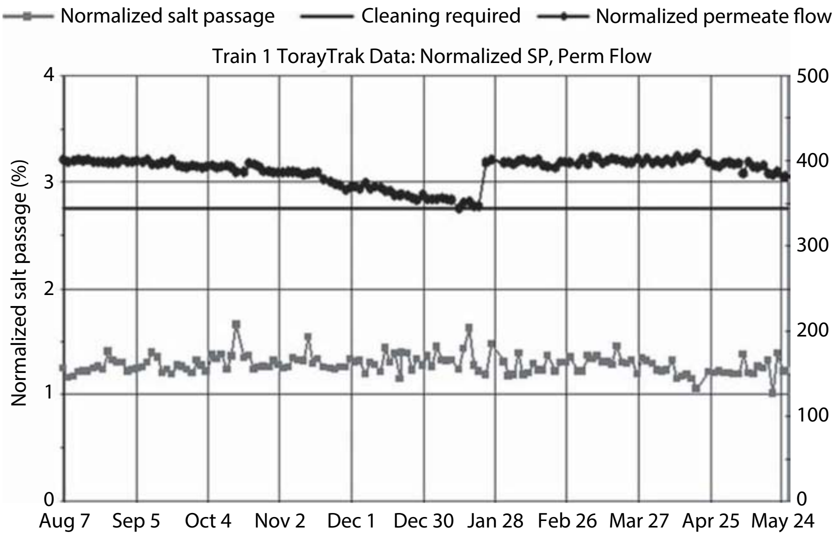

Figure 11.13 Normalized permeate flow and normalized salt rejection as functions of time. *Data courtesy of Madalyn Epple, Toray Membrane, USA, Inc.*

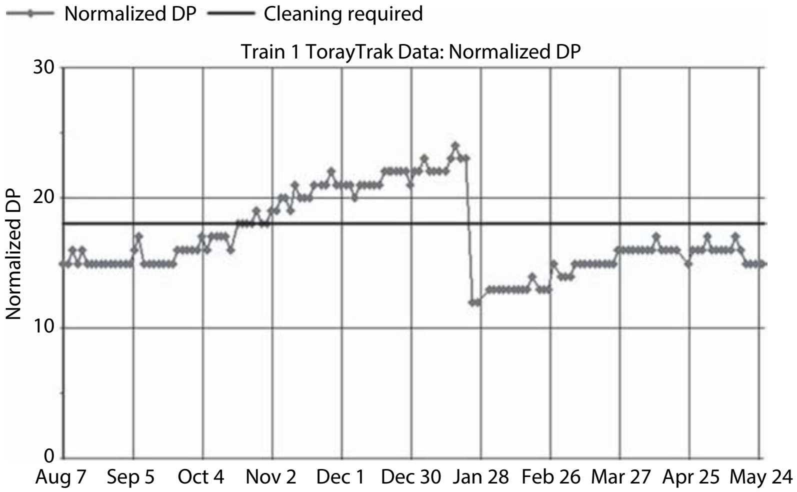

Figure 11.14 Normalized differential pressure as a function of time. *Data courtesy of Madalyn Epple, Toray Membrane, USA, Inc.*

coefficients are indicative of changes on or to the membranes. An increase is the water transport coefficient generally implies that the membranes are degraded, while a decrease in the coefficient means the membranes are fouling or scaling. Similarly, an increase in salt transport coefficient means the membranes are degraded or scaled while a decrease typically means that the membranes are fouled.

The normalization programs provide graphs for the performance variables. Some programs offer the ability to combine various data curves on the same graph. For example, Toray Trak by Toray Membrane USA has the ability to include four (4) curves on the same graph. Figure 11.12 shows normalized permeate flow and normalized salt rejection as functions of time using Toray Trak. Figure 11.13 shows the normalized differential pressure as a function of time. Multiple curves, whether on the same graph or not, allow the user to compare different performance parameters and aid in troubleshooting the system, as trends are easier to discern. For example, the loss in permeate flow shown in Figure 11.12, coupled with the corresponding increase in differential pressure, Figure 11.13 and the constant salt rejection, Figure 11.12, could be caused by membrane fouling rather than scaling (see Chapter 13.3).

Both graphs (Figure 11.13 and 11.14) show the suggested time to clean the membranes based on initial performance. The increase in normalized differential pressure reached the "cleaning required" condition after about 3 months of operation, which is typical for a system with good pretreatment. However, this cleaning indicator was overlooked in favor of the normalized permeate flow, which did not drop to its cleaning indicator condition until about five and one half months after start up. Fouling does not appear to have been permanent, however, as both the normalized permeate flow and differential pressure returned to start up performance following cleaning.

Other outputs available from at least some normalization programs include:

- System recovery: this can be compared to the hand-calculated recovery as well as the recovery based on rejection of species such as sulfate (which is rejected to a high degree);
- Net pressure driving force: looks at the effect of concentration on the pressure driving force for water flux;
- Permeate and feed/concentrate average osmotic pressures: used to calculate the net pressure driving force;
- Specific flux: calculated by dividing the flux by the net driving pressure. The higher the specific flux, the greater the permeability of the membrane. Low permeability corresponds to fouling, scaling, or compaction.

- Event identification: Allows the user to input events such as cleaning, new membranes, etc., and the performance graphs will indicate that an event has occurred by placing a marker on the graph corresponding to the date the event occurred. This helps in identifying any step changes that may occur in performance after an event.

11.4 Preventive Maintenance

Preventative maintenance (PM) is critical to RO operations. It may require additional staff time and capital, just as the pretreatment to RO requires additional capital, but in the long run, PM will pay for itself in improved RO operations, including longer membrane life. Successful RO operation requires diligent PM, so PM tasks must be assigned to be completed on a regular basis. Table 11.3 lists a suggested PM schedule for general maintenance tasks.

Tasks listed in the Table 11.3 are critical for the performance of the system and to keep total operating costs, including membrane cleanings and replacements, to a minimum.

- *Daily logs*: Collecting data is perhaps the most fundamental aspect of PM. Without data, there is no way to determine the conditions of the membranes. See Chapter 11.2 for details about the type of data to collect.
- *Normalization*: Should be conducted on a daily basis following start-up or the installation of new membranes. Once the system has reached equilibrium, which could take up to 4 to 6 weeks, normalization can be done on a weekly schedule. See Chapter 11.3.1 for more details about data normalization.
- *SDI*: Silt density index tests should be conducted on a daily basis following start up, but once the system has reached equilibrium, weekly readings can be taken. Note that if the make-up water is a surface source, SDI may need to be taken daily to catch changes due to weather conditions (e.g., heavy rains), ship traffic, and so forth.
- *Water analyses*: See Chapter 7 for details on what species to analyze.
- *Mass balance*: Mass balance is an effective way to troubleshoot an RO system to determine whether species are being

Table 11.3 General preventative maintenance schedule (adapted from Anne Arza, Nalco, an Ecolab Company).

Preventive Maintenance Item	**Daily**	**Weekly**	**Monthly**	**Quarterly**
Daily Logs	X			
Normalization	X	X*		
SDI	X	X*		
Water Analysis (feed permeate, reject)			X	
Mass Balance			X	
Check 5-micron Prefilters		X**		
Check and Calibrate Critical Sensors			X	
Check and Calibrate all Sensors				X
Check Pretreatment Unit Operations (e.g., filters, softeners, etc)			X	
Calibrate Chemical Feed Pumps				X
Pump Maintenance (all)			X	
Elution Studies (if necessary)				X+
Membrane Cleaning				X++

* after start-up and system equilibrium

** Biweekly

\+ Semi-annually

++ Or as required per normalized data

deposited on the membranes. See Chapter 14.4 for information about mass balances.

- *Check cartridge filters*: The cartridge prefilters should be checked biweekly for pressure drop across them and to be sure they are seated properly. High pressure drop means it is time to replace the filters. Improper seating of the filters will lead to particulates bypassing the filters and fouling or abrasion (and destruction) of the membranes.

- *Clean and calibrate critical sensors*: Critical instruments include the ORP and pH sensors used to make sure the RO feed water is acceptable.
- *Clean and calibrate all sensors*: Instruments must be calibrated on a regular basis. Improper sensor readings will lead to inaccurate normalization and present a false picture as to how the RO system is functioning.
- *Calibrate chemical feed pumps*: Chemical feed systems should be calibrated on a regular basis to make sure the required dosage of chemical is being fed.
- *Check pretreatment unit operations*: The integrity of filters, softeners, tanks, and other pretreatment systems should be checked. Performance of each should also be evaluated and modifications made as required.
- *Elusion studies*: Elusion studies should be conducted on softeners on a quarterly basis or more frequently, if required.
- *Membrane cleaning*: RO membranes should be cleaned based on normalized performance. Cleanings should not be more frequent than every three months if the pretreatment system is adequate. RO systems with more frequent cleanings could benefit from upgrades to the pretreatment system.

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12

Performance Degradation

Performance of an RO system, specifically the permeate flow rate, salt rejection and pressure drop, is a function of temperature, pressure, and concentration as well as membrane fouling, scaling, and degradation, as previously discussed (See Chapter 11.3). This chapter covers the detailed effects of membrane fouling, scaling, and degradation have on normalized product flow, normalized salt rejection, and pressure drop.

12.1 Normalized Permeate Flow

Normalized permeate flow (NPF) is a function of the average applied transmembrane pressure, the osmotic pressures of the feed and permeate, and temperature, as shown in Equation 11.1. Factors that cause an increase or decrease in the NPF are discussed below.

12.1.1 Loss of Normalized Permeate Flow

Membrane fouling and scaling can both lead to a loss in normalized permeate flow. Additionally, membrane compaction will result in decreased permeate flow as well.

12.1.1.1 Membrane Fouling

Membrane fouling involves the deposition of suspended solids, including bacteria, on the membrane or components within the membrane module (i.e., the feed channel spacer). These foulants form a layer on the surface of the membrane that becomes an additional barrier for water to flow through to the permeate side of the membrane. Hence, if the feed pressure is held constant, the permeate flow will decrease.

In general, operators focus on observed permeate flow and adjust operating variables to deliver the required permeate flow. Thus, if the permeate flow is decreasing due to fouling, the operating pressure is usually increased to overcome the additional barrier to transport and to maintain a constant observed permeate flow. Problems associated with this practice were discussed in Chapter 11.3.1 Case Study.

As discussed in Chapter 11.3.1.1, membrane fouling will result in a negative slope for the NPF (see Figure 11.1).

12.1.1.2 Membrane Scaling

Membrane scaling involves the deposition of saturated salts on the surface of the membrane, typically in the later stages of the RO system. Scale forms a layer on the surface of the membrane that becomes an additional barrier for water to have to flow through to get to the permeate side of the membrane, similar to that described above for foulants.

Typically, operating pressure is increased to adjust for the loss in observed permeate flow due to scaling, so observed permeate flow is not a good indicator of membrane scaling. However, the normalized permeate flow will reflect the need to increase pressure with scaling, and register this as a negative slope in the normalization curve. Thus, membrane scaling will result in a decrease in NPF.

12.1.1.3 Membrane Compaction

Membrane compaction involves the compressing of the membrane itself that, in essence, makes the membrane “denser” or thicker which reduces the flow and salt passage through it. Compaction can occur under higher feed pressure, high temperature, and water hammer. (Water hammer occurs when the RO high-pressure feed pump is started and there is air trapped in the membrane modules—see Chapter 6.2.) Most brackish water membranes, when operated properly, experience a minimal degree of compaction. However, seawater membranes and cellulose acetate membranes at pressures greater than about 500 psig, can experience significant compaction.[1] Factors which favor compaction are high temperature together with high pressure. Most effects of compaction are realized within the first 200 hours of operation. Compation will cause a decrease in NPF.

12.1.2 Increase in Normalized Permeate Flow

An increase in normalized permeate flow is typically the result of a leak, either due to a breach in the membrane itself or because of problems with the membrane module hardware, or to exposure to oxidizers such as chlorine.

12.1.2.1 Membrane Degradation

Membrane degradation involves the loss of membrane polymer integrity. This can be a result of membrane oxidation, where the oxidizer attacks the membrane polymer, leading to aromatic ring substitution and chain cleavage.[1] In this case, feed water is allowed to pass into the permeate leading to an increase in permeate flow and a decrease is product quality. Oxidation degradation typically occurs first at the lead membranes, as these membranes are exposed to the oxidizer first, and, in many cases, the oxidizer has been reduced before it can reach the later membranes. Typical oxidizers include free chlorine (and other halogens), chlorine dioxide, ozone, hydrogen peroxide, and so on (see Chapters 8.2.1 and 8.5.2.1).

Membranes can also be oxidized in the presence of iron, manganese, and other transition metals. These metals catalyze the oxidation of RO membranes. This type of oxidation tends to involve the entire RO skid rather than focus on the lead membranes. Again, when this type of degradation occurs, feed water passes into the permeate, resulting in an increase in permeate flow and a decrease in product quality.

Exposure to high temperature at pH extremes can hydrolyze the membranes, leading to loss of membrane integrity. (See Chapter 4.2.1, Table 4.2, and Chapters 9.2, 9.8, and Table 13.1 for more detailed discussions on the effect of temperature and pH on polyamide composite membranes.) Hydrolysis also tends to involve the entire RO skid rather than focus on only the lead membranes. Just as with oxidation of the membrane, feed water will pass into the permeate resulting in an increase in permeate flow and decrease in the product quality.

Membrane degradation can also be a physical phenomenon. Particles, such as sharp, granular, activated carbon fines, abrade the membrane surface and cause microscopic tears in the membrane through which feed water can breach the membrane, and increase the permeate flow (see

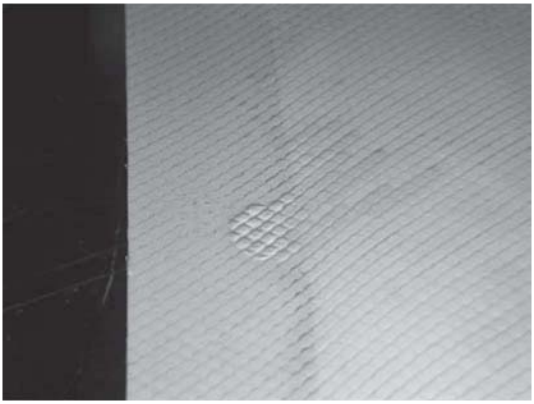

Figure 12.1 Glue line breaches where feed water and permeate can mix.

Figure 14.18). Also, excessive permeate back-pressure can lead to ruptures in the glue lines holding the membrane leaves together, again leading to breaches through which feed water can enter the permeate and the permeate flow increases (see Figure 12.1).

12.1.2.2 Hardware Issues

Breaches in hardware will allow feed water pass into the permeate. Common problems include O-ring leaks and leaking module product tubes, both of which can be damaged during installation. Product tubes may also be damaged under conditions of high pressure drop caused by excessive fouling or scaling. Water hammer may cause damage to the permeate tube and O-rings as well.

12.2 Normalized Salt Rejection

Normalized salt rejection is a function of the concentration driving force across the membrane, as shown in Equation 11.3. Factors that lead to loss or increase in salt rejection are discussed below.

12.2.1 Loss of Salt Rejection

Membrane scaling and degradation can lead to a loss in normalized salt rejection as can breaches O-rings and permeate tube.

12.2.1.1 Membrane Scaling

Membrane scaling involves the deposition of saturated salt(s) onto the surface of the membrane or components within the membrane module (See Chapter 3.8). This scale forms a layer on the surface of the membrane where the concentration of the saturated salt(s) is higher then the concentration of the salt (s) in the bulk solution. The concentration that the membrane is exposed to is thus higher than that recorded for the bulk solution. Since the actual percent rejection exhibited by the membrane remains fairly constant during nominal, industrial-type applications, the salt passage also remains the same. However, since the concentration of salt(s) is higher at the membrane surface, the actual amount of salt(s) that passes through the membrane is higher than would be expected based on the bulk concentration. Hence, the apparent salt passage increases and the apparent rejection decreases. This phenomenon is registered as a loss in normalized salt rejection.

12.2.1.2 Membrane Degradation

Membrane degradation involves the loss of membrane integrity (see Chapter 12.1.2.1). Because of the loss in integrity, feed water is allowed to pass into the permeate leading to an increase in permeate concentration. Thus, salt(s) passing into the permeate increases while the apparent salt rejection decreases.

12.2.1.3 Hardware Issues

Breaches in hardware can allow feed water to mingle with permeate. As is the case with an increase in water flux, breaches in O-rings and permeate tubes will allow high concertration feed water to mingle with low concentration permeate, thereby increasing the concentration of the permeate (see Chapter 12.1.2.2). The overall salt rejection will appear to decrease and salt passage appears to increase.

12.2.2 Increase in Salt Rejection

Increases in salt rejection are typically due to membrane compaction (see Chapter 12.1.1.3). As the membrane becomes denser due to compaction, the passage of salts through the membrane is reduced, leading to a loss in salt passage and in increase in salt rejection.

Note that brief, initial exposure to chlorine under tightly controlled conditions can also lead to an increase in salt rejection for some membranes (while longer exposure leads to a decrease in salt rejection see Chapter 8.2.1.1.)[3] The reasons for this are not clear, but could involve changes to the membrane surface charge which results in a repelling of anionic compounds, decreasing their passage and increasing the rejection.[3]

12.3 Pressure Drop

Pressure drop measures the loss in pressure from the feed to the concentrate. In effect, it measures the loss in driving force for water across the membrane (see Chapter 11.3.1.3 and Equation 11.6). Factors that result in an increase or decrease in pressure drop are discussed below.

12.3.1 Loss in Pressure Drop

It is unusual to find a loss in pressure drop under nominal operating conditions for most industrial applications.[4] If a loss in pressure drop is recorded, it is typically a result of faulty instrumentation.

12.3.2 Increase in Pressure Drop

A number of factors can lead to high pressure drop, including membrane scaling, colloidal fouling, and microbial fouling. These three factors all involve deposition of material onto the surface of the membrane as well as onto components of the membrane module, such as the feed channel spacer. This causes a disruption in the flow pattern through the membrane module, which, in turn, leads to frictional pressure losses and an increase in pressure drop.

High pressure drop causes disruptions to the system hydraulics. Because of the high pressure drop, the lead membranes tend to operate at very high fluxes while the lag membranes operate at low flux. This increases the rate of membrane fouling for both the lead and lag membranes. Lead membranes foul faster because more water is forced to the membrane module faster and the rate of contaminant accumulation in the boundary layer on the membrane surface increases. The lag membranes, on the other hand, experience low flows since most of the water is removed through the lead membranes, leading to an increase in the thickness of the boundary layer

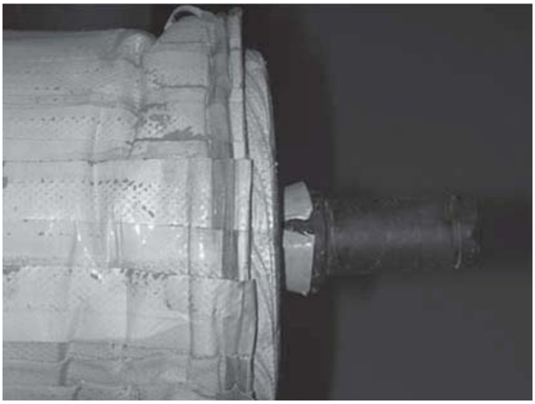

Figure 12.2 Damaged membrane module due to high pressure drop.

leading to faster rates of fouling. (See Chapter 3.5 for a discussion on boundary layers and concentration polarization).

High pressure drop can also lead to damage of the membranes and membrane modules themselves. The loss in feed water pressure is translated into pressure down the axis of the membrane module. When the pressure drop gets very high, greater than about 50 psig per 6-element stage, the membrane modules can telescope which can physically crack and tear the membrane or compact the fiberglass module shell, as shown in Figure 12.2 (see Figure 3.5, Chapter 11.3.1.3, and Figure 11.6 for more discussion regarding pressure drop and effect on membrane modules).

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13

Off-Line Operations

Operations that are conducted while the RO system is off line are just as important as on-line operations in keeping an RO system functioning well. Off-line operations covered in this chapter include system flush, membrane cleaning, and membrane lay-up.

13.1 System Flush

System flushes are typically used when an RO system goes off-line, comes back on-line, and during stand-by mode. The purpose of the off-line and stand-by flushes is to rid the feed/concentrate side of the membrane of either high concentrations of feed water species or to stir up materials that may have settled on the membrane during down time and wash them away. The on-line flush (when the membranes come back on line) is to reduce the conductivity in the RO permeate before sending the permeate on to further processing or to the ultimate use. Flush water is typically sent to drain.

It is important during flush to keep the permeate line wide open to prevent delamination of membranes at the concentrate end of the pressure vessel (see

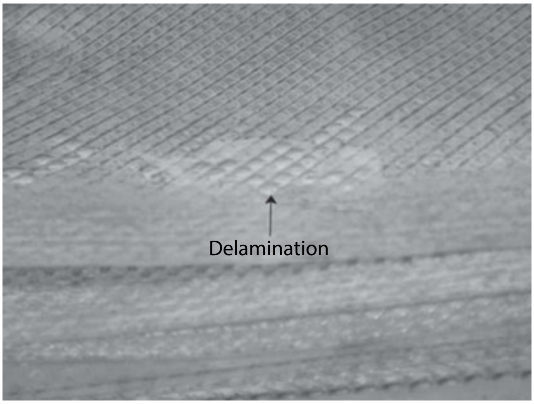

Figure 13.1 Membrane delamination caused by high permeate pressure.

Figure 13.1). Delamination occurs when the permeate pressure is higher than the pressure of the feed side of the membrane. During fouling conditions, the feed-side pressure drop can be significantly higher than the 21–24 psig for a 6-module pressure vessel under "clean" conditions. Thus, if the permeate line is closed, the potential exists for the permeate pressure to exceed the feed pressure due to the pressure drop on the feed-side of the membrane. If this difference is greater than about 10–15 psi, delamination can occur.[1]

13.1.1 Off-Line Flush

The off-line flush is conducted when the membranes are brought off line for any reason. The flush is used to displace the high concentration of solids in the feed/concentrate side of the membrane with lower-concentration water (water under minimal pressure so as not to produce permeate which would increase concentration of the flush water). A flush of 3 to 5 minutes is usually sufficient. Any permeate generated is sent to drain. Typically, pretreated (softened) feed water is used for the flush, although permeate water is preferred (as a last resort, low-pressure raw feed water can be used). The flush water should be free of pretreatment chemicals, so any chemical injection systems should be stopped before flushing. After the flush is completed, all feed valves should be completely closed. If the concentrate line drains to a level that is below that of the pressure vessels, the vessels might be emptied by a siphoning effect. Then when restarted, the system may experience water hammer if air has entered the pressure vessels. To prevent this, an air break should be installed in the concentrate line at a position higher than the highest pressure vessel.

The flush can be programmed into the PLC and thus occurs automatically when the RO skid shuts down, or it can be manually initiated. Note that not all RO systems are equipped with this flushing feature. Without this feature, fouling and scaling of membranes will be exacerbated, if the RO unit cycles off and on in a regular rotation, or if the RO sits idle for any length of time.

13.1.2 Return to Service Flush

The on-line flush takes place when the RO skid is returned to service. The objective of the flush is to remove particulates and salts that have settled on the membrane surface while the skid was off line as well as to bring down the concentration of the RO permeate. Figure 13.2 shows the concentration of the RO permeate as a function of flush time after stand-by (assumes a feed water conductivity of 250 micro Siemens per centimeter).[2] Typically, pretreated feed water is used for the flush; there is no need to use higher-quality water for this flush. Pressure is generally at nominal operating condition, and any permeate that is generated is sent to drain.

The on-line flush can also be programmed into the PLC and occurs automatically when the RO skid is brought back on line. Most RO systems are equipped with this feature.

13.1.3 Stand-by Flush

The stand-by flush is used intermittently when the RO skid is off line in stand-by mode. It can also be used during extended lay-up of the skid. The

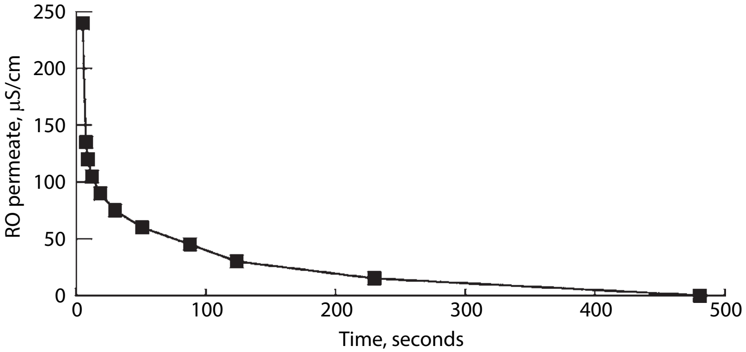

Figure 13.2 Permeate concentration as a function of flush time after membrane stand-by (250 ppm micro Siemens per centimeter feed conductivity). *Courtesy of Jonathan Wood and UltraPure Water® Journal, www.ultrapurewater.com, March, 2009.*

objective is to remove particles and salts that have collected on the membrane surface while the membranes are idle. This minimizes the potential for membrane fouling and scaling while the membranes are at rest.

The frequency for this type of flush is application and environment dependent. Flushing may be programmed to occur every 15 minutes to once every 24 hours, depending on how concentrated the pretreated feed water is and how high the temperature is. Higher feed water concentrations and higher temperatures require shorter intervals between flushes. Flushes of 3 to 5 minutes are sufficient. Permeate water is preferred to flush the membranes, although softened feed can be used (raw feed water can be used as a last resort). Pressure is minimal to avoid concentrating the water used to flush the membranes. Any permeate generated during the flush cycle is sent to drain.

13.2 Membrane Cleaning

Membrane cleaning is one of the most important aspects of membrane operations. Regardless of how good the pretreatment and hydraulic design of an RO system, membranes will eventually foul and/or scale. Timely and effective cleaning is necessary to keep membranes free of foulants and scale, thereby resulting in longer cleaning intervals, and longer membrane life, both of which save money, time, and the environment.

13.2.1 When to Clean

Membranes should be cleaned when the normalized permeate flow drops by 10%–15% from initial stabilized performance (see Chapter 11.3.1.1), or when the differential pressure increases by 10%–15% (see Chapter 11.3.1.3). Ideally, a cleaning is scheduled when the performance changes by 10% and should be completed by the time the performance has changed by 15%. Waiting too long to clean can result in irreversible fouling and/or scaling of the membrane. Membranes with good pretreatment can expect to clean about 4 times per year or less depending on the quality of the feed water.

Membranes are typically not cleaned due to a drop in salt rejection. This is because in most instances, there is a mechanical explanation for the drop in salt rejection (see Chapter 12.2.1). However, in the case where membrane scaling is responsible for a drop in salt rejection, normalized permeate flow is generally the first indicator of this phenomenon (see Chapter 11.3.1.2).

Figure 13.3 compares the projected performance of an RO membrane that has been cleaned on time (performance decline within 15% of initial performance) with that for membranes that were cleaned after performance

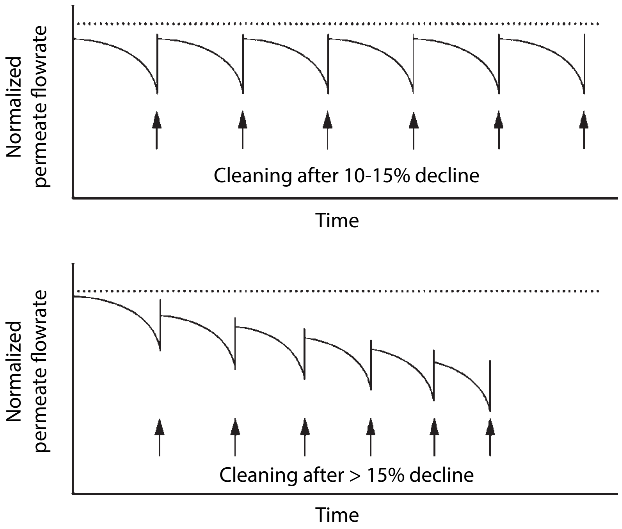

Figure 13.3 Comparison of cleaning when performed within 15% of performance decline and when performance has fallen more than 15% from start-up conditions.

had dropped more than 15%. As the figure shows, cleaning on time results in better cleaning efficacy and in longer intervals between cleanings. Both of these outcomes result in lower operating and maintenance costs for the system. Waiting too long to clean can cause some of the foulants and/or scale to become permanently attached to the membranes or module components. Once foulants or scale have deposited onto the membrane or module components, they attract more materials, exacerbating the problem, and leading to a more rapid decline in performance and, therefore, more frequent cleaning events.

13.2.2 How to Clean

Membrane manufacturers and cleaning-chemical vendors typically have cleaning procedures formulated for their specific product(s). While it is impossible to review all cleaning procedures here, a basic cleaning procedure is presented which can be modified to suit the membrane, the cleaning chemical(s), and the specific contaminant(s) to be removed:

1. *Prepare the cleaning solution.* If the solution is in liquid form, it just needs to be pH-adjusted and heated. If the solution is in dry form, it needs to be mixed (using RO-permeate or better quality water), pH-adjusted and heated.

2. *Introduce the solution to the RO skid*. It is important to clean each stage individually, so that foulants formed in the first stage do not carry over to the second stage and scale formed in the second stage does not carry over to the first stage. The solution should be introduced at a flow rate of about 3 to 5 gpm per pressure vessel.[3] For an 8-pressure vessel stage, the total introduction rate would be no more than about 40 gpm. This slow flow rate gives the user enough time to view the cleaning solution and observe changes in color. If the cleaning solution changes color (e.g., becomes dark), it should be sent to drain or discarded and a fresh batch should be prepared.
3. *Recirculate the solution*. The solution should be recirculated at about 35 gpm per pressure vessel. In other words, for an 8-pressure vessel stage with 8-inch diameter membrane modules, the recirculation rate should be 8 times 35 gpm or 280 gpm. Recirculation should be conducted using as little pressure as possible, thereby minimizing the formation of permeate. If permeate is generated, it increases the likelihood of re-deposition of removed species on the membrane.[1] If the cleaning solution comes out dark, it should be discarded and a new batch should be prepared. Temperature and pH should be monitored and adjusted during the recirculation as needed. Recirculation should continue for about 45 to 60 minutes.
4. *Soak the membranes*. Membrane should be allowed to soak in order to give the cleaning solution time to "loosen" material on the membrane surface and to penetrate biofilm. In some cases, a soak of one hour is sufficient. In other cases an overnight soak may be required. During longer soak periods, use the cleaning skid pump to recirculate the solution at about 10% of the typical recirculation rate to help maintain temperature. Note that longer periods of soaking is not a substitute for using the temperature and pH as recommended by the manufacturer for efficient cleaning.
5. *High-flow recirculation*. The solution should be recirculated at about 40–50 gpm per 8-inch pressure vessel for about 45 minutes. Note that higher flow rate recirculation may result in pressure drop issues. The solution should be recirculated at no more than about 50 psig for 8-inch diameter, six-element pressure vessels.

6. *Flush the membranes*. Membranes should be flushed following cleaning using RO-permeate quality or better water. Pretreated feed water should not be used as components may interact with the cleaning solution and precipitation of foulants my occur in the membrane modules. The minimum flush temperature should be 20°C.[1]
7. *Repeat steps 1 through 5* using the next cleaning chemical(s).

Factors that effect cleaning efficacy include:

- *Chemicals used*: using appropriate cleaning formulations will greatly enhance the efficacy of the cleaning procedure. The concentration of cleaning chemicals is also important to the overall effectiveness of cleaning.[4]
- *Temperature*: cleanings conducted at higher temperatures are more effective at removing materials from membranes.
- *pH*: extremes in pH (both high and low) are more effective in cleaning membranes. However, temperature and pH limits for cleaning should be followed to prevent damaging the membranes or module components (see Table 13.1).[4]
- *Recirculation rate*: the velocity of recirculation will impact the ability of the cleaning solution to remove debris from the membrane. Higher flow rates (see step 5 above) are usually necessary to scour debris off of the surface of a membrane.
- *Time*: the time spent cleaning and soaking the membrane is vital to the overall success of cleaning. Sufficient time must be devoted to the cleaning process to ensure that the cleaning solution has time to penetrate foulants and scale and that the recirculation flows scour as much of the debris off of the membranes as possible. A 2-stage RO skid takes a minimum of 10-12 hours to clean.

These factors should be monitored and recorded at 15 minute intervals during the entire cleaning process. Temperature, pH, and recirculation rate should be adjusted to maintain the initial cleaning specification which will ensure the best cleaning action.

13.2.3 Cleaning Chemicals

Effective cleaning is a function of pH, temperature, and cleaning solution(s). Cleaning is most effective when it is focused on the specific

Table 13.1 Temperature and pH limitations for dow water solutions polyamide composite membranes.[1]

Temperature (°C)*	**pH**
25	1–13
35	1–12
45	1–10.5

For all brackish water membranes (BW30, BW30LE, LE, and XLE)

* for temperatures greater than 50°C, Dow-FilmTec recommends that they be contacted

fouling or scaling problem experienced by the membrane. If the "wrong" cleaning chemicals are used, the situation can become worse.[1] If in doubt, most membrane manufacturers recommend conducting the alkaline cleaning first.[1] Acid cleaning should only be used first if it is known that calcium carbonate or iron oxides are present in the membrane modules. If acid cleaning were to be used first, and microbial or organic fouling was present, the fouling situation may become irreversible due to the reaction of microbial extra-cellular material to the acid condition.

Cleaning solutions are usually classified by pH. There are high-pH, and low-pH cleaners. Increasing temperature and pH extremes together enhance the effectiveness of cleaning. However, there are limits to temperature as a function of pH, as shown in Table 13.1 for Dow Water and Process Solutions polyamide composite membranes (membrane manufacturers should be consulted prior to cleaning to confirm their temperature/pH limitations).[1] At high temperature and pH extremes, a conversion of the membrane takes place, resulting in a loss of performance. The mechanism for this change in the membranes is not clearly understood but may be related to hydrolysis.[5]

In addition to acid or caustic, cleaners will sometimes have other compounds that are effective in removing and suspending materials off of the membrane. These compounds include metal chelating agents, surfactants, and enzymes. These compounds clean a membrane by one of three mechanisms:[4]

- physically removing the foulants or scale off of the surface of the membrane
- changing the morphology of the foulant or scale such that further accumulation is discouraged

- changing the surface chemistry of the fouling layer to, again, dissuade additional accumulation.

The user can mix these cleaning formulations or some may be available pre-packaged from a vendor. For *vendor-provided pre-packaged cleaners, the user should determine the compatibility of the cleaning formulation with the specific membranes being cleaned to avoid potential fouling or degradation of the membrane with the components in the cleaning solution*.

Sample cleaning formulations are described below.

13.2.3.1 High-pH Cleaners

High-pH cleaners are typically used to address removal of the following species:

- Biofilm fouling
- Organic fouling
- Silica scale
- Colloidal material fouling
- Sulfate scale

High-pH cleaners are generally formulated with a surfactant (detergent) such as sodium dodecylsulfate (Na-DSS) or sodium laurel sulfate. *Note that cationic surfactants should not be used, as irreversible fouling of the membrane may occur*. The surfactant serves to lift solids of the membrane and support them in the solution. (Antifoams may not be added to suppress the foaming action of the surfactant as they are not compatible with the membrane polymer.) Some high-pH cleaners may also be formulated using a chelating agent such as sodium EDTA (ethylenediaminetetraacetic acid). The chelating agent serves to maintain salts in solution. Sequestering agents may also be added to bind up calcium and other scale-forming cations. Table 13.2 lists five sample, high-pH cleaning solutions formulations applicable to polyamide, composite membranes.[1,6]

Figure 13.4 shows the effect of high pH on the removal of biofilm.[1] As the figure shows, a high pH of 12 is much more effective at restoring permeate flow than a lower pH.

Note that performance of the RO unit may be different after a high pH cleaning. Specifically, the flux may be higher and the rejection may be lower. This is a result of the membrane “loosening” at high pH and is a temporary condition. Performance should return to nominal within a couple hours to a day.

Table 13.2 Sample high-pH cleaning formulations for polyamide, composite membranes.

	Sulfate scale	**Organic Fouling**	**Biofouling**	**Silica**
0.1% caustic, pH 12, 35°C	X	X	X	X
1.0% Sodium EDTA*, ph 12, 35°C	X			
0.025% sodium DSS**, pH 12, 35°C		X	X	X
2.0% sodium TPP+ and 0.8% sodium EDTA, pH 10.0, 45°C	X	X		
2.0% sodium TPP+ and 0.25% sodium DDBS++, pH 10.0, 45°C		X		

* ethylene diamine tetraacetic acid

** dodecylsulfate

\+ Tripolyphosphate

\++ dodecylbenzene sulfonate

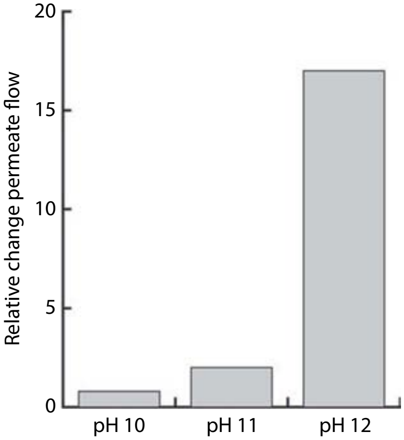

Figure 13.4 Effect of pH on ability of cleaning solution to remove biofilm and restore membrane performance. *Courtesy of Dow Water and Process Solutions.*

13.2.3.2 Low-pH Cleaners

Low-pH cleaners are typically used to address calcium carbonate scale and iron oxide deposition. These cleaners are usually formulated using only acid, such as acetic, hydrochloric, or sulfamic. Figure 13.5 shows the effects of temperature and pH on the removal of calcium carbonate from a membrane.[7] As the figure shows, lower pH, and higher temperatures are more effective at restoring permeate flow than higher pH and lower temperatures.

Hydrogen peroxide or a combination of hydrogen peroxide and peracetic acid can be used to address biologically fouled RO membranes when operated at lower pH. The following precautions should be taken when using hydrogen peroxide:

- Dilute commercial products to 0.2wt% with RO permeate. Higher concentration will result in membrane damage (higher salt passage).
- Maintain temperature less than 25°C. Higher temperature will result in membrane damage.
- Remove all transition metals from the solution. The presence of metals will catalyze the degradation of the membrane.
- Recirculate diluted hydrogen peroxide solution for 20 minutes.
- Maintain a pH of 3–4 for optimal efficacy and longest membrane life.
- Completely clean the membranes with high pH and low pH cleaners prior to recirculating hydrogen peroxide.

As with high pH cleaning, the performance of the RO membranes after cleaning with low pH products may temporarily change from nominal. In

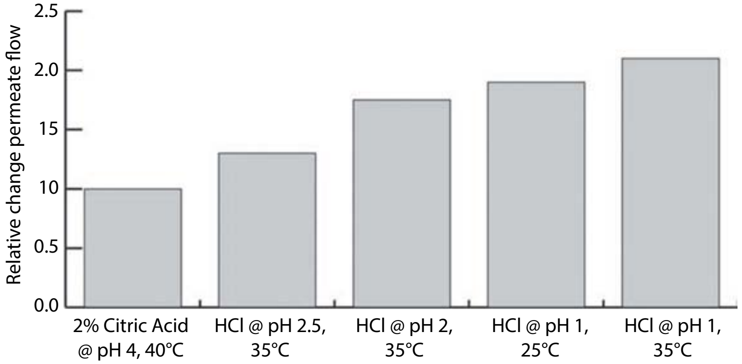

Figure 13.5 Effects of temperature and pH on removal of calcium carbonate from an RO membrane. *Courtesy of Dow Water and Process Solutions.*

Table 13.3 Preferred cleaning solutions for specific foulants and scale.[3,8]

Species	Dow-FilmTec	Hydranautics*
Sulfate Scale	0.1% caustic, pH 12, 30°C	2.0% sodium tripolyphosphate, pH 10, 45$_{o}$C
Carbonate Scale	0.2% hydrochloric acid, pH 2, 30$_{o}$C	0.5% hydrochloric acid, pH 2.5, 45$_{o}$C
Silica Scaling	0.1% caustic, pH 12, 35$_{o}$C	0.1% caustic, pH 11.5, 35$_{o}$C
Iron Fouling	1.0% sodium hydrosulfate, pH 5, 30$_{o}$C	1.0% sodium hydrosulfate, pH 11.5, 35$_{o}$C
Organic Fouling	0.1% caustic pH 12, 30$_{o}$C followed by 0.2% hydrochloric acid, pH 2, 45$_{o}$C	0.1% caustic plus 0.03% sodium dodecylsulfate, pH 11.5, 35$_{o}$C
Biofouling	0.1% caustic, pH 12, 30$_{o}$C	0.1% caustic plus 0.03% sodium dodecylsulfate, pH 11.5, 35$_{o}$C

* CPA membranes only

the case of low pH, the membrane essentially becomes "tighter," exhibiting lower flux and higher rejection for up to a few hours to a day after the cleaning is completed.

13.2.3.3 Cleaners for Specific Foulants and Scale

For stubborn foulants and scale, there are some preferred cleaning solutions that may improve the efficacy of cleaning. Some of these generic solutions are listed in Table 13.3.[1,8] Check with specific membrane manufacturer for limits on pH and temperature.

13.2.3.4 Specific Cleaning using Non-Oxidizion Biocides

Most of these cleaners use a non-oxidizing biocide such as DBNPA (dibromonitriloproprionamide) or isothiazolins, and are pre-packaged by vendors. They are typically used following high pH cleaning as a final step. Procedures usually can be a recirculation of the product followed by a good flushing rinse.

13.2.4 Cleaning Equipment

Reverse osmosis cleaning equipment is simple and straightforward. Figure 13.6 shows a schematic of a cleaning skid. The skid can be a stand-alone

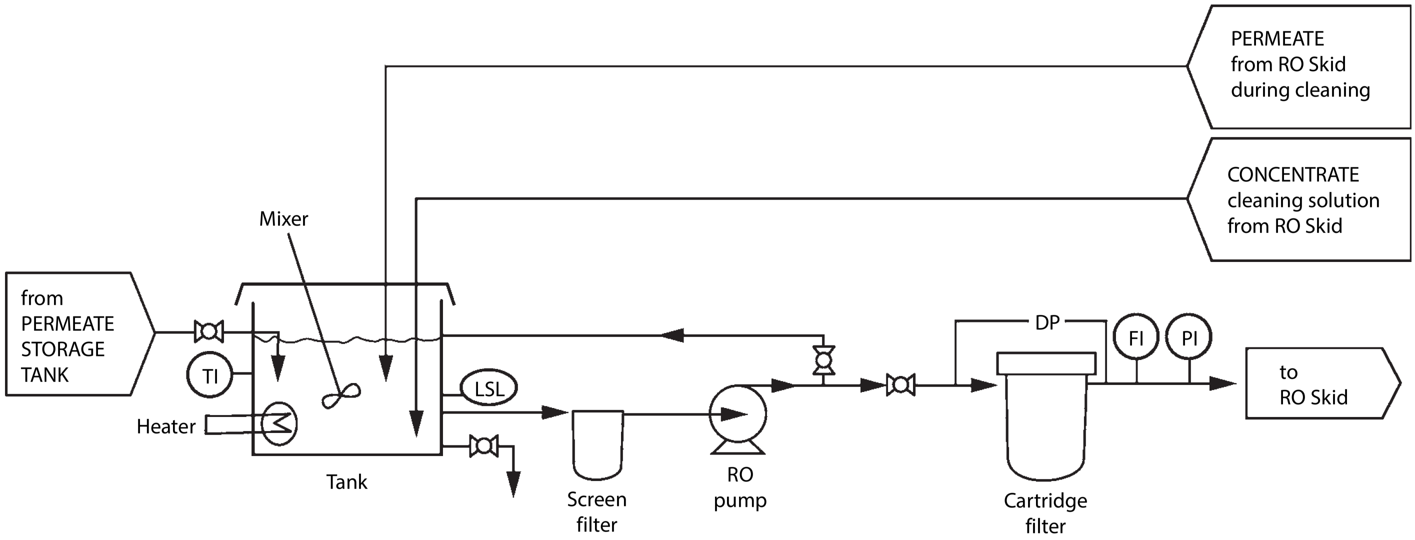

Figure 13.6 Cleaning skid schematic.

unit, which is connected to the RO skid via removable hoses, or it can be permanently plumbed into the RO skid. Skids that are plumbed in to the RO skid itself, and use the high-pressure feed (and cartridge filters) to recirculate cleaning solution may not provide sufficient cleaning due to the inability of these arrangements to allow for cleaning of each stage individually. A cleaning skid includes three main pieces of equipment: a tank, a recirculation pump, and a cartridge filter.

13.2.4.1 Cleaning Tank

The cleaning tank is typically made of plastic, but fiberglass and stainless steel versions are available. (Keep in mind chemical compatibility when selecting the type of tank to use.) The tank should be sized to handle the hold-up volume in the pressure vessels plus the volume in the piping or hoses. The approximate hold-up volume in an 8-inch diameter, 6-module long pressure vessel is about 52.2 gallons. Thus, for a 4:2-6M array, the cleaning tank would need to be sized for the first stage (The largest stage), so about 210 gallons for the pressure vessels (since only one stage is cleaned at a time) plus piping volume for about 250 gallons total.

13.2.4.2 Cleaning Recirculation Pump

The recirculation pump is typically a centrifugal pump. It should be sized to handle the maximum recirculation rate for the largest stage in the RO skid. For example, given a 4:2-6M array, the recirculation pump must be able to deliver 40–50 gpm per pressure vessel or up to 200 gpm at less than 50–60 psig. AVFD is general recommended.

13.2.4.3 Cartridge Filter

The cartridge filter is typically a 5- to 10-micron nominal cutoff filter. The housing can be PVC, FRP, or SS (again, take heed of the materials of compatibility). It should be equipped with a differential pressure gauge to measure the pressure drop across the filter. Cartridge filters should be changed out with every new cleaning solution.

13.3 Membrane Lay-Up

Sometimes, it is necessary to shut down an RO system for a host of reasons. For example, a peaking power facility might need to shut down an RO system for several days or months depending on the demand for power.

13.3.1 Short-Term Lay-Up

Membranes that are laid-up for less than two weeks should follow short-term lay-up procedures. These procedures are designed to minimize fouling, scaling, and microbial growth on the membranes. General procedures are given below.

1. Upon shut-down of the RO, the membranes should be flushed with feed water under minimal pressure (see Chapter 13.1.1) or with RO-permeate or better quality water. Flushing with higher-quality water will help remove foulants and scale and better preserve the membranes.[9] While flushing, the air from the system should be vented.
2. When the pressure vessels are filled, the valves should be closed to prevent air form entering into the system.
3. Repeat steps 1 and 2 every 5–7 days.[9]

13.3.2 Long-Term Lay-up

Membranes that are left off line for extended periods of time should follow these long-term lay-up procedures. Again, these procedures are designed to minimize fouling, particularly with microbes, and scaling.

1. The RO membranes should be cleaned using the procedures outlined in Chapter 13.2.2. Flush the clean membranes with permeate or better quality water.
2. The cleaned membranes should then be flushed with an approved biocide, such as sodium metabisulfite (1 to 1.5 wt%) while venting air outside of the pressure vessels. Non-cobalt-catalyzed sodium metabisulfite should be used.
3. When the RO is completely filled with biocide, all valves should be closed to prevent air from deactivating the biocide. To check to see if the pressure vessels are completely filled, the solution should be allowed to overflow through an opening in the top of the RO skid that is higher that the highest pressure vessel being filled.
4. Repeat steps 2 and 3 as necessary. If sodium metabisulfite is being used, the steps should be repeated when the pH reaches 3 or lower. For other biocides, the steps should be repeated every 30 days when the temperature is below 80°F and every 15 days if the temperature is greater than 80°F.

5. When the RO system is being brought back on line, it should be flushed with low-pressure feed water for about an hour. Any permeate generated should be sent to drain. The permeate should be checked for residual biocide prior to returning the RO unit to service. If any is present, flushing should continue.

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5

TROUBLESHOOTING

14

Troubleshooting

Despite all the pretreatment and attention to system hydraulics, most RO systems will eventually show degradation in performance. This degradation is manifests itself as a loss in permeate flow, a loss of salt rejection, or an increase in pressure drop. As discussed in Chapter 12, membrane fouling, scaling, or degradation can cause these conditions. Figure 14.1 shows the relative causes of membrane fouling and scaling for a study of 150 membranes that were autopsied.[1] As the figure shows, organic fouling is by far the leading cause of membrane fouling for the membranes autopsied. Scaling accounted for less than 5% of the total materials found on these membranes. This is because pretreatment, such as sodium softening and antiscalants, are generally effective at minimizing the formation of scale on RO membranes. Data not shown in the figure is microbial fouling. This is because *all* of the membranes autopsied showed some degree of microbial fouling. Conclusions in the report indicate the following:

- All operating membranes have a viable biofilm.
- A biofilm level of 10^3 CFM/cm^2 is normal and seldom a problem.

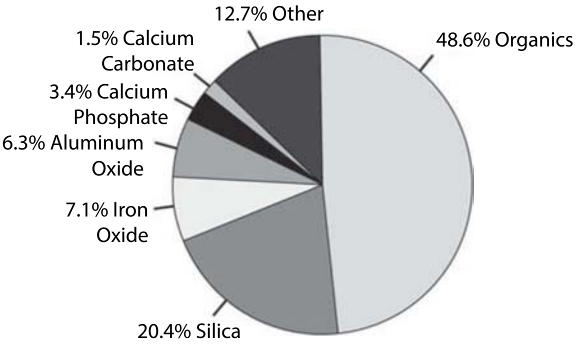


Figure 14.1 Causes of membrane fouling and scaling for 150 autopsied membranes. *Courtesy of M. Fazel and The Engineering Society of Western Pennsylvania.*

- Problematic biofouling occurs with bacterial counts of greater than 10^5 CFM/cm^2. Thirty-four percent of the autopsied membranes had counts greater than 10^5 CFM/cm^2.
- At counts greater than 10^7 CFM/cm^2, it was not possible to visibly remove the biofoulant. While cleaning may improve flux and salt rejection, the improvement is short-lived, with minimal enhancement in differential pressure.[1]

In practice, it is not always possible or advisable to pull membranes for autopsy to determine the degree of biofouling on the membranes. Thus, culture techniques are often employed to estimate the counts on the membranes (see Chapter 7.2). Cultures of the RO reject are recommended, even though these results represent about 1–10% of the total counts on the membranes themselves. Since the RO reject culture counts represent a small fraction of the actual number of counts on the membranes themselves, culture counts of 10^3 CFM/cm^2 or greater in the RO reject stream are generally considered indicative of severe biofouling of the membranes.

This chapter offers techniques useful in troubleshooting RO systems. The objective of troubleshooting is to identify membrane system irregularities and to investigate modes of membrane system failures, with the intent of eventually restoring membrane performance.[2] The ability to correct diagnose and rectify problems with an RO system is critical to keeping the unit on line.

There are two types of irregularities that an RO system can experience, those that are acute, and those that are chronic. Acute irregularities occur when there is a temporary change in feed water quality or an upset in the pretreatment system. Acute situations must be dealt with quickly before they have a chance to foul, scale, or degrade the RO membranes. Chronic problems, on the other hand, can take a long time to manifest themselves, and can result in membrane fouling, scaling, or degradation before the user can determine a definitive cause(s). Note that in most cases, there is more than one cause for performance decline.

There are several investigative techniques that can be used to troubleshoot an RO system. These include:

- Mechanical evaluation
- General Performance Issues
- System design and performance projections
- Data normalization
- Water Sample testing
- Membrane integrity testing
- Profiling and probing
- Autopsy

In general, more than one of these techniques is necessary to get a complete picture of how the system is operating and to determine what might have led to the loss in performance.

14.1 Mechanical Evaluation

Perhaps the first line of investigation should be a mechanical evaluation of the system to rule out causes such as instrumentation or valves. Typical investigations include an instrument check; they should be tested and calibrated. Filters should be checked for channeling. Valves should be checked to determine if they are functioning properly. Filters and softeners should be checked to determine whether the specific flow rate or flux is within design guidelines.

Once mechanical issues have either been ruled out or identified as causes for poor performance, the performance of the RO system should be evaluated to establish whether other factors are contributing to poor performance.

14.2 General Performance Issues

There are several general performance issues that should be investigated when troubleshooting an RO system. These include the following issues:

- *Membrane cleaning frequency*: RO systems that require more than four cleanings per year have a membrane fouling and/or scaling problem.
- *Cartridge filter replacement frequency*: high replacement rates (every 2 weeks or less) could indicate a fouling problem. Low replacement rates (every 1 month or more) could lead to microbial fouling as microbes grow in the "old" cartridges.
- *Chemical application*: dosages and controls should be checked to ensure proper feeding of chemical. This includes acid/caustic, chlorine or other oxidizer, coagulant in pretreatment, and antiscalant.
- *Visual inspection*: simple visual inspections of pretreatment and RO systems can indicate potential for fouling or scaling.
    - Check tanks and piping for mold or biogrowth.
    - Open the feed side of a pressure vessel and inspect for fouling. Biofouling will feel slippery and may also have an odor.
    - Open the concentrate side of a pressure vessel and inspect for scaling. Scale will feel rough to the touch.

14.3 System Design and Performance Projections

14.3.1 System Design

Design of an RO system has a great effect on the potential for fouling or scaling the membranes. As discussed in Chapter 9, feed water flow, concentrate flow, water flux, and recovery all affect the ability of the membranes to foul and scale. Flow rates affect the concentration polarization boundary layer where fouling and scaling occur (see Chapter 3.5). Flux and recovery affect the concentration of contaminants within the boundary layer. Following proper design guidelines, fouling and scaling can be minimized. And, when design guidelines are disregarded, fouling and scaling are very likely to occur.

Should an RO system show signs of performance problems, the design of the system should be explored. Do the flow rates and fluxes agree with the guidelines presented in Tables 9.1, 9.2, and 9.3? If not, then the effect the variation(s) has on performance should be evaluated.

14.3.2 Performance Projections

The same performance projection software programs described in Chapter 10 for the design of RO systems can also be used to evaluate the performance of an RO system. Note that in actual application, the flow performance may vary by up to + /−15% from nominal values (which are shown in the projections).[3] Salt rejection my also vary for individual membrane modules, but will never be less than the minimum specified salt rejection in the manufacturer's literature. Thus, actual, stabilized performance may not agree with performance projections, but should be close for systems larger than about 125 gpm (assuming 8-inch diameter modules).[3] For example, the actual permeate TDS should be not greater than about 1.5 times the projected concentration. Permeate flow should vary by no more than about + /−15%. If actual performance varies greatly from that projected, membrane fouling, scaling, or degradation may be occurring.

Note that there is a period after installation of new membranes, where the performance of the membranes is not stable. During this period, which can last up to 2 weeks of continuous operation, the permeability and salt passage of the membrane both decline.[4] The decline in performance is due some what to compaction and the establishment of baseline and is worse for seawater and wastewater applications. Other reasons for the decline are not clear but may include the degree of hydration of the membrane upon start up. Up to 10% of initial permeability and salt passage can decline during this time of destabilized performance.[4] The decline in permeate flow is shown in Figure 14.2.

Permeate back pressure must be taken into account when evaluating system performance. If not considered while running projections, actual performance will show a higher feed pressure than what was projected. Hence, if observed operating pressure is greater than predicted, review the projection to determine if permeate pressure was included. Permeate pressure may be the result of pressure required to deliver the permeate to a tank or other downstream unit operation. If permeate pressure was considered in developing the projection, then fouling or scaling of the membranes could explain the difference between actual and predicted operating pressure.

Pressure drop must also be assessed. Most projection programs assume a piping loss of about 5 psi (35 kPa) per stage plus the pressure drop through the membrane modules in the projection program. Should the

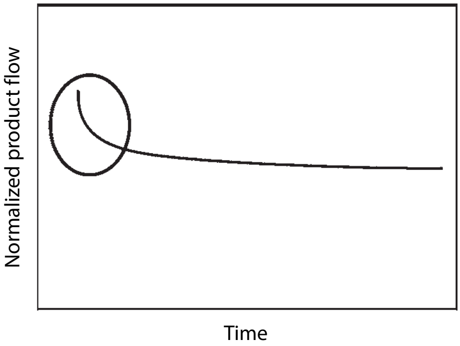


Figure 14.2 Typical permeate flow decrease upon start up of new membranes due to compaction and possibly degree of membrane hydration.

actual pressure drop exceed the predicted pressure drop, there could be two explanations:

- membrane fouling or scaling, or
- location of the pressure sensors leading to misleading readings. Restrictions in the feed and concentrate headers could lead to higher than predicted pressure drop. The pressure sensors should be located as close as possible to the pressure vessel to avoid these restrictions, and away from high-turbulence areas such as valves.

14.4 Data Assessment

Data, particularly normalized data, is evaluated to determine the nature of the loss in membrane performance (see Chapter 11.3 for a complete discussion on data normalization). Normalized permeate flow, salt rejection, and differential pressure should be evaluated to determine trends in performance.

Table 14.1 is a troubleshooting matrix that shows trends in normalized performance and possible causes. The table lists different sets of performance parameters and possible causes for each. Some symptoms are the same, such as items one through three in the table, but each occurs in a different place in the RO system, and thus, each has a different root cause.

As discussed in Chapter 13.2, normalized data should be used to determine when the membranes should be cleaned. Normalized data should be scanned to determine if the membranes were cleaned on time, or

Table 14.1 Reverse osmosis troubleshooting matrix.

Case	Normalized Permeate Flow	Normalized Salt Passage	Normalized Differential Pressure	Location	Probable Causes
1	Up	Greatly up	Stable	1st stage	Oxidation
2	Up	Greatly up	Stable	All stages	Hydrolysis
3	Up	Greatly up	Stable	Random	O-ring, membrane failure
4	Greatly down	Up	Up	Last stage	Scaling
5	Down	Stable*	Greatly up	All stages	Biofouling
6	Greatly down	Stable*	Stable	All stages	Organic fouling
7	Greatly down	Up	Up	1st stage	Colloidal fouling
8	Greatly down	Greatly down	Stable	All stages	Compaction

* can increase as a secondary effect resulting from the fouling layer disrupting the cross-flow action on the membrane, which increases concentration polarization

if potential fouling and/or scaling could have become permanent because the membranes were not cleaned on time.

The effectiveness of cleaning can also be determined by following the trend in normalized data. If membrane are cleaned on time, not only should the performance after cleaning return to initial conditions, the performance should remain at such a level for an extended period of time. Figure 14.3 compares the performance of a well-cleaned RO system to one where the cleaning was less than successful. Normalized permeate flow rate returns to near initial performance and remains high for the well-cleaned RO system. The performance of the other RO system does not return to initial flow and drops off again rapidly. This could be a sign of irreversible fouling or scaling.

Normalized performance can also be used to track the improvements in pretreatment, for systems that can be successfully cleaned but performance still drops off too rapidly. Recall the case study discussed in Chapter 11.3.1.1 and the normalized permeate flow in Figure 11.3

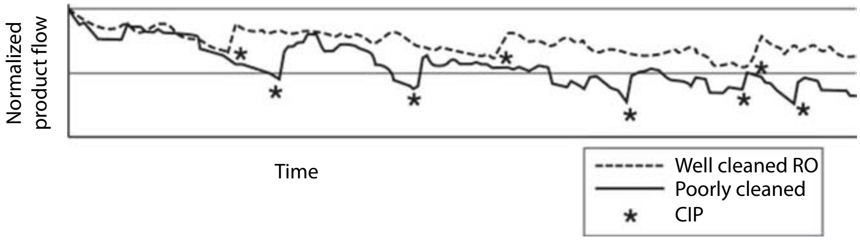


Figure 14.3 Trends in normalized data showing effectiveness of membrane cleaning. Note the decline in permeate flow during the first few days of operation due to compaction (see Chapter 14.3.2).

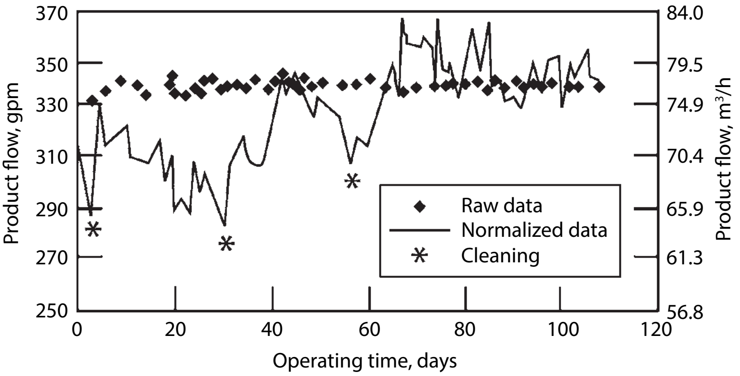


Figure 14.4 Normalize product flow rate data from a facility operating on cold lime softened Delaware River water.

(reproduced here as figure 14.4). The membranes were fouled with colloids that carried over from the cold-lime softener and that passed through the three multimedia filters, which were all channeling. Iron oxide was also fouling the membranes; the iron was introduced by corrosion of the stainless steel pipe when exposed to the hydrochloric acid used to adjust the pH after the cold-lime softener. As improvements were being made to the pretreatment system, the normalized permeate flow returned to a higher value after each cleaning. Eventually, the normalized permeate flow reached the initial normalized permeate flow and stayed fairly constant without benefit of additional cleanings. Additionally, the normalized permeate flow now tracked with the actual permeate flow. Both these conditions are indicative of the improvements in pretreatment being successful.

14.5 Water Sampling

Water sampling cannot be under-rated as to the importance it has to the performance of the RO system. As described in Chapter 7, water source plays a big role in determining the degree of membrane fouling, scaling, and degradation that RO systems might experience. When troubleshooting, the water source should be determined. If the water is municipal, the ultimate source needs to be determined. The pretreatment system including treatment by the municipality should be reviewed to ensure that it meets the challenges of the feed water.

A detailed water analysis is also required. The species should be compared to Table 7.1, to determine the potential for fouling, scaling, and degradation. Specific species can be identified that may have already fouled, scaled, or degraded the membranes.

A troubleshooting technique that will help in determining what species have fouled or scaled a membrane is a mass balance around the membrane. A species is selected, such as iron or aluminum, and a mass balance is taken around the RO system. The amount of that species on the feed side should be equal to that amount in the permeate plus the concentrate. Keep in mind that this is conservation of mass not concentration (there is no conservation of concentration). So, to calculation the amounts, the user will have to take the concentration and multiply by the flow rate. This will generate an amount per unit time that will be suitable, if all time frames are the same (for example, if gallons per minute is used). If a species come up short in the concentrate plus permeate versus feed mass, it is probable that this species has deposited on the membranes or elsewhere in the membrane module.

14.6 Membrane Integrity Testing

If the normalized salt rejection is low or the normalized permeate flow is high, the integrity of the membrane may be in question. The vacuum decay test is a direct test for the integrity of a spiral wound RO membrane module. The test is best used to identify leaks within the membrane modules rather than leaks due to chemical attack. The test requires the isolation of an individual membrane module or the entire pressure vessel. A vacuum is then pulled on the membrane(s) and the rate of decay in pressure is observed. A decay of greater than 100 millibar per minute is indicative of a leaky membrane. Refer to ASTM Standards D3923[5] and D6908[6] for a more detailed review of the technique.

14.7 Profiling and Probing

Profiling and probing are two techniques typically used together to determine if and where in an RO system membranes are scaled or leaking. These techniques should be used when the conductivity in the product of an RO system is high.

Profiling is used to determine which RO pressure vessel(s) has high conductivity. To profile, the user must have access to the permeate channel on each pressure vessel in the skid(s) of interest. A hand-held meter is then used to determine the conductivity in the permeate out of each pressure vessel. The conductivity is then recorded in any manner that allows for comparison of all the values form a single skid, such as a bar graph. Figure 14.5 shows such as bar graph for a hypothetical 4:2-6M array. The conductivities from first stage are compared to each other, and the higher values are singled out for vessel probing. The same procedure should be followed for the second stage. As shown in Figure 14.5, the first stage vessel exhibiting a conductivity of 3.6 should be probed, as should the second stage vessel with a conductivity of 6.6.

Probing involves determining the permeate concentration at various points *within* the pressure vessel. The most common points selected for analysis are at the ends of the pressure vessel and at the tie point between individual membrane modules. To probe a vessel, the user must have access to the permeate port and be able to thread a long piece of stainless steel or Tygon®-type tubing down the permeate channels of all the membrane modules in the vessel (Tygon is a registered trademark of Saint-Gobain

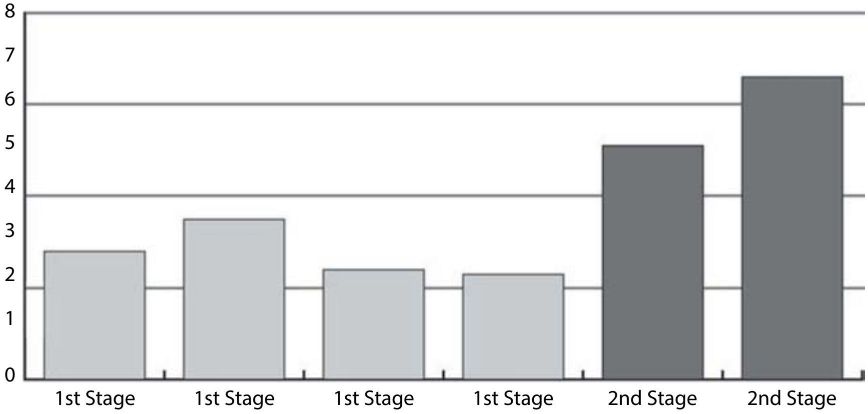


Figure 14.5 Bar graph showing permeate conductivities after profiling RO system.

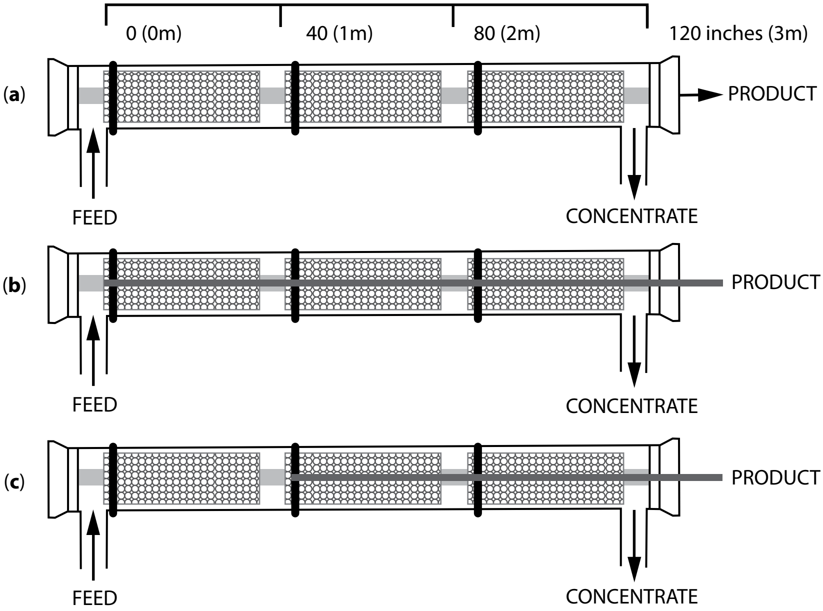


Figure 14.6 How to probe an RO pressure vessel: (a) pressure vessel prior to probing, (b) Pressure vessel with probing Tyron® tubing inserted all the way to the end, (c) pressure vessel with probing tubing partially extracted.

Corporation, Valley Forge, PA). Some RO skids are equipped with a ball valve that makes threading the tubing very easy. However, some skids are not equipped with any sort of valve and may be even hard piped, making probing difficult if not impossible. If possible, the tubing is threaded down the permeate channel of each membrane module all the way to the opposite end of the pressure vessel, as illustrated in Figure 14.6. The conductivity is measured at this point in the vessel, using a hand-held meter. The tubing is then extracted out of the pressure vessel by about 40 inches, corresponding to the length of a module, and the conductivity is measured again. This procedure is repeated until all the points of connection between modules within the pressure vessel have been measured. Note that additional locations may be sampled, such as mid-module.

Data collected during probing is plotted as a function of distance through the pressure vessel. Figure 14.7 shows what some specific problems would look like when graphed.

1. A pressure vessel with no leaks or scaling would show a slight increase in conductivity from the feed end to the concentrate end. This is a result of the feed water becoming

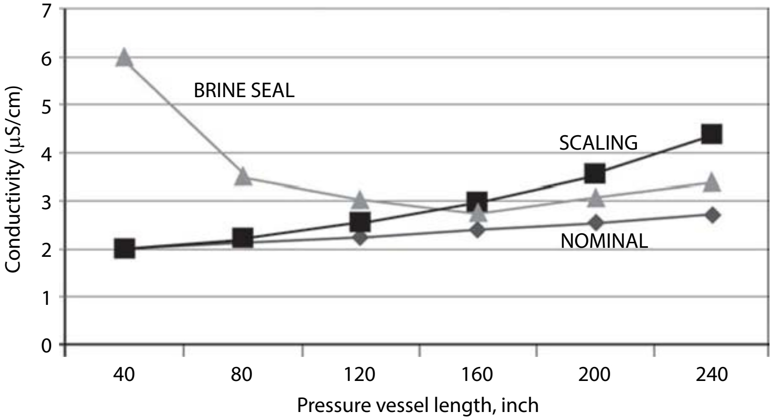


Figure 14.7 Graphed results of RO membrane probing. Feed end of the pressure vessel is at zero inches, while concentrate end is at 240 inches.

more concentrated (and hence, the product becoming more concentrated) as water is removed from the feed side of the membrane.

2. A pressure vessel with a leaking or missing O-ring at the feed end (or any place in the vessel) would show a spike in conductivity at that point, but then show a drop in conductivity as the distance increases away from the leak. The curve then takes on the general shape of a pressure vessel with no leaks or scale.
3. Scaled membranes would show a more rapid increase in conductivity than a pressure vessel with no leaks or scale.

Should the results of the probing be inconclusive (i.e., an increase in conductivity is noted but does not correlate with the ends of the modules), then a damaged membrane may be at fault. To test this theory, probing should be conducted again, this time measuring the conductivity every 8- to 10-inches or so. This will capture performance of individual membranes, not just the interconnectors between them.

14.8 Membrane Autopsy

Membrane autopsy and subsequent tests are generally the last resort in determining a definitive cause for membrane failure. This is because these tests are all destructive to the membrane module and membrane itself. The tests are used to determine the morphology of material on the membrane and the feed channel spacer, the types of chemicals present, the amount of a specific species found on the membrane, and the nature of the materials that oxidized the membrane.[7]

If the user is unsure about what may be causing performance problems, it is best to autopsy at least two membranes, the lead module in the first stage of the RO system and the last module at the concentrate end of the last stage. The lead module will capture suspended solids that may be fouling the membrane while the last module will contain any scaling that may be occurring. If fouling or scaling is suspected, however, then a membrane (s) from the appropriate location in the RO system should be selected for autopsy.

Modules should be prepared for autopsy following the vendor's instructions. Typically, preparation involves bagging each module individually in plastic and boxing it into the original shipping container, if available. Modules should be sent via express mail within 2 days of removing them from service. Membranes should *not* be cleaned prior to autopsy.

14.8.1 Visual Inspection

The first inspection of a membrane submitted for autopsy is a visual one. The module itself is inspected for damage, such as crumpling or crushing damage that could have occurred due to excessive pressure drop or water hammer during operation. Figure 14.8 shows a crumpled membrane module (a) and a cracked membrane module (b). The end caps of the module are checked for damage that also may occur due to excessive pressure drop. A cracked end cap from the concentrate outlet end of an RO membrane module is shown in Figure 14.9. The feed-end cap and face of the module are studied to determine if there are any foulants present that may be blocking the feed channels. Figure 14.10 shows the feed inlet end of an RO membrane module with debris blocking the feed channels to the membranes. The concentrate end of the module is viewed to determine whether any telescoping of the module has occurred (see Chapter 4.3.3). Figure 14.11a shows a severely-telescoped membrane module. In most cases, however, telescoping is not as extreme as shown in Figure 14.11a; it typically takes the form of protruding spacer and sometimes membrane sheets, as shown in Figure 14.11b.

Once the module has been opened, the surface of the membrane, glue lines, and feed spacers should be inspected for damage and for scale and foulants. Damaged glue lines can mean excessive backpressure was applied to the membrane module. Figure 14.12 shows blisters where the glue line has been breached. Permeate back pressure must never exceed

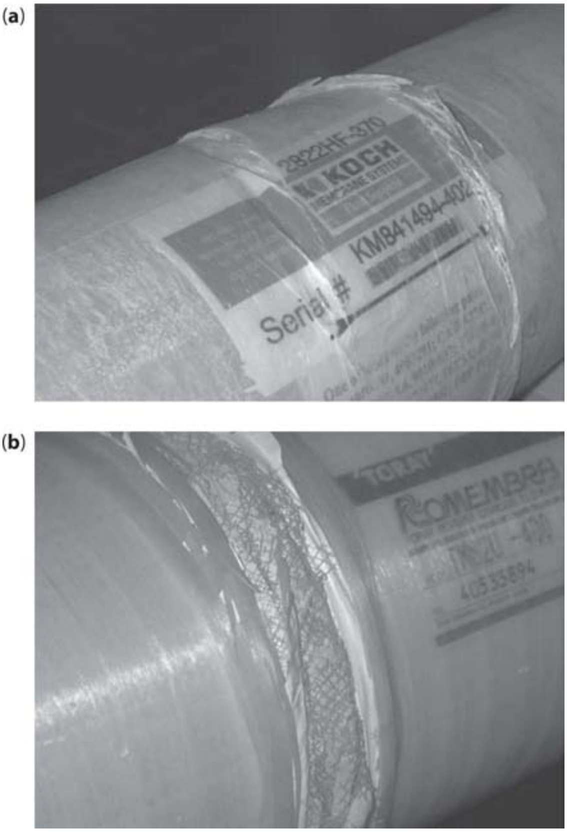


Figure 14.8 (a) Crumpled membrane module due to excessive pressure drop or water hammer (b) cracked membrane module.

the concentrate pressure by more than 15 psi, particularly at the tail end of the pressure vessel. Should such an event occur, the membranes can delaminate at or near the glue lines in the membrane module, thereby allowing feed water to mix with RO permeate water. One of the most common ways delamination occurs is when there is high pressure drop on the feed/concentrate side of the membrane due to excessive fouling or scaling. Others ways in which delamination can occur include

- *Permeate Divert Valves*: Permeate divert valves (or any other valve on the permeate line) should be set to close only after the other valve has opened completely or the RO system has shut down. If all permeate valves were to be closed while the RO was operating, permeate would have nowhere to go and

Figure 14.9 Cracked end cap as the concentrate outlet.

Figure 14.10 Feed end of membrane module showing foulants.

pressure would build up quickly on the permeate side of the membrane.

- *Tanks*: Tanks provide an important break in back pressure for RO permeate, if the tank is positioned properly. Permeate rarely has enough pressure to feed directly into another unit operation, so tanks provide the break in back pressure that would occur if the permeate were sent to another unit operation. However, tanks need to be carefully positioned so as not to cause significant back pressure themselves. For example, tall, narrow tanks require that permeate have enough head pressure to reach the inlet at the top of the tank. Depending on the height of the tank, this may result in permeate back

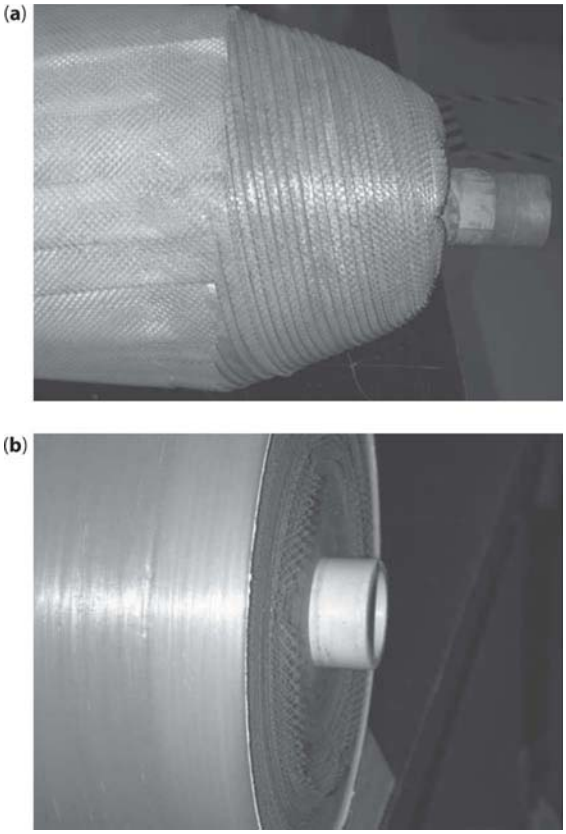


Figure 14.11 (a) excessively-telescoped membrane module due to high pressure drop resulting from considerable membrane fouling or scaling, (b) concentrate end of RO membrane module showing protruding (telescoped) feed spacer material.

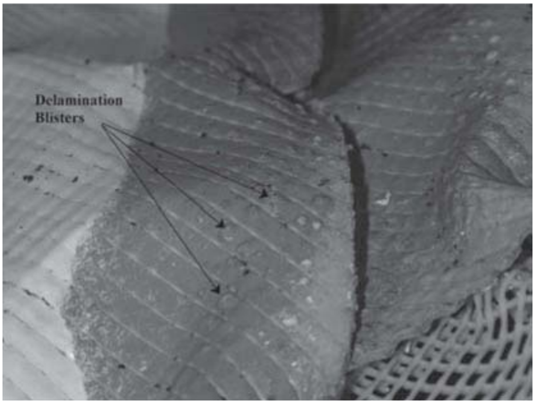


Figure 14.12 Damaged glue lines due to excessive backpressure.

pressure that is too high. Also, placement of the tank on a another level in the facility that is higher than the RO skid level can also result in high permeate back pressure. For example, placing the tank on the roof when the RO skid is on the ground floor may result in high permeate back pressure.

Other issues that may be identified upon visual inspection include:

- *General Oxidation*: Figure 14.13 shows damage to the membrane. In this case, the damage took the form of a hole in the membrane. At the same time, iron-fouled resin beads of the same size as the holes were found on the surface of that membrane (see Figure 14.14). It was deduced that the damage to the membrane in Figure 14.13 was probably caused by iron oxidation of the membrane.

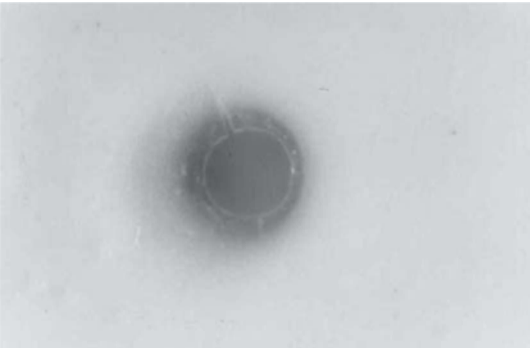


Figure 14.13 Hole in membrane surface.

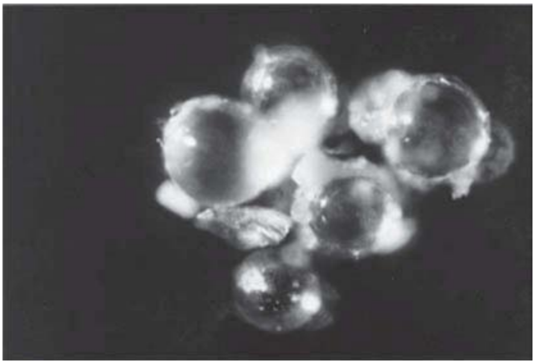


Figure 14.14 Iron-fouled resin beads on membrane surface.

- *Fouling and Scaling*: Figure 14.15a shows a feed spacer with foulants adhering to the spacer, while Figures 14.15b and c show feed spacers virtually completely blocked with foulants and scale, respectively. This would seriously hamper the flow

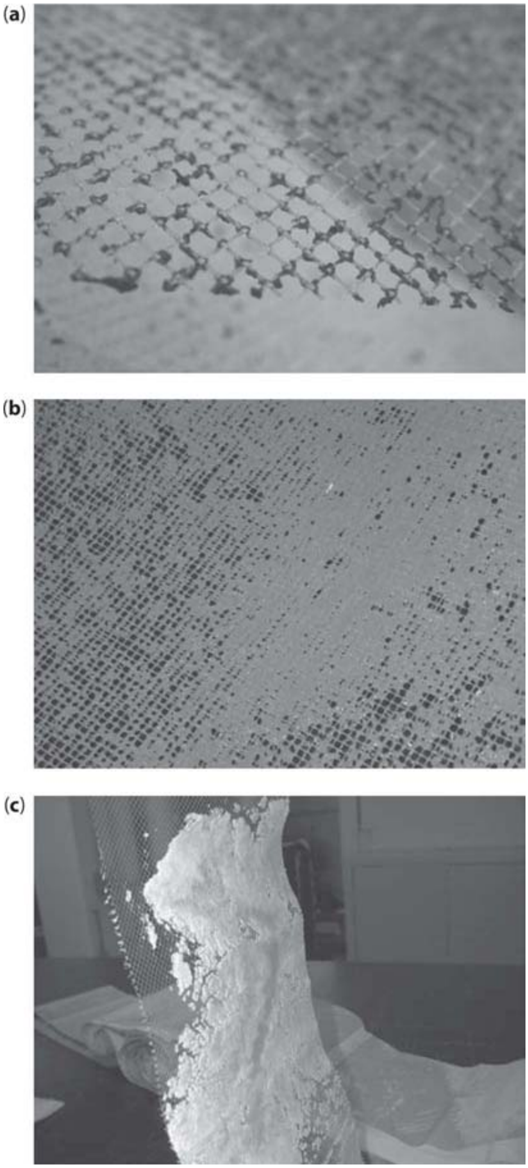


Figure 14.15 (a) foulants adhering to feed spacer; feed spacers virtually blocked with (b) foulants and (c) scale.

Figure 14.16 Surface of a scaled membrane

through the membrane leading to poor production, high operating pressure, and high pressure drop. Figure 14.16 shows the surface of a scaled membrane.

- *Microbial Fouling*: Finally, Figure 14.17 shows rod-type microbial residue on the surface of a membrane magnified 5000 times.

14.8.2 Pressure Dye Test—Rhodamine B

This test is used to determine whether a membrane has been damaged by exposure to an oxidizer or by some sort of physical attack. In the Rhodamine B test, the membrane module is pressurized with a dye prior to autopsy. If the permeate turns pink, the membrane is probably damaged. Upon autopsy, damaged areas of the membrane will be stained pink.

14.8.3 Methylene Blue Test

The Methylene Blue test is used to determine if there is any chemical or physical damage to the membrane surface. In this test, a sheet of membrane taken after autopsy is tested in a flat-sheet test apparatus. The feed side of the membrane is exposed to a 0.05% solution of methylene blue. If the membrane is damaged, the permeate will turn blue and the membrane will stain blue in the damaged areas. Figure 14.18 shows such a membrane. The darker shaded areas on the permeate side are actually stained blue from the methylene blue solution, indicating that the membrane has been damaged. Causes in this type of damage include abrasion

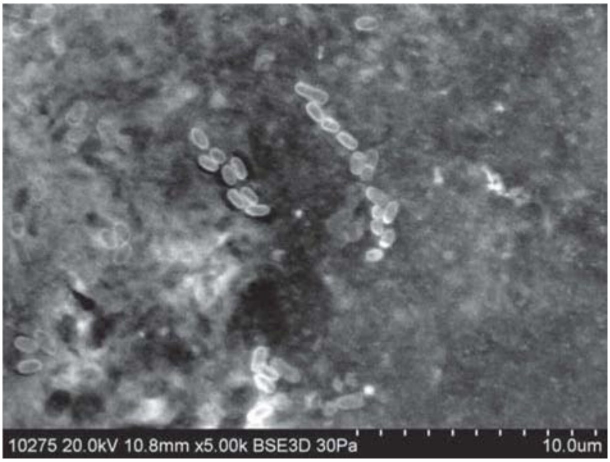
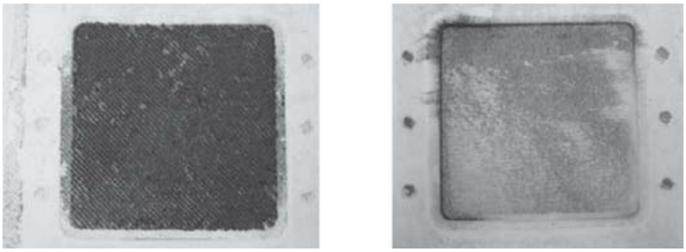


Figure 14.17 Microbial residue on the surface of a membrane (5000X view).



Feed side

Permeate side

Figure 14.18 Methylene Blue test showing stained permeate side of a membrane, indicating damage to the membrane.

due to particles such as show carbon fines from a carbon filter (see chapter 8.1.4 and 12.1.2.1).

14.8.4 Fujiwara Test

The Fujiwara test is used to determine whether a membrane has been oxidized by exposure to halogens. The test measures the presence of halogenated organics in a membrane sample. The test involves a small piece of membrane placed in the bottom of a test tube. One drop of 5N sodium hydroxide solution and 2 drops of a pyridine solution are added to the test tube. The tube is then placed in a water bath at about 90°C, and held there for 30 seconds. A positive test occurs when the pyridine layer in the test tube shows a red or pink color. Note that prolonged heating of the sample will cause the color to fade or turn to brown/yellow.[7] This in an inexact test that can result in some false-positives and can also miss some positives.

14.8.5 Spectroscopy

There are several spectroscopy tests that can be used to determine the nature of materials that have fouled or scaled a membrane. These are described below.

- Scanning electron microscopy (SEM), along with stereo or standard light microscopes, can be used to determine the morphology of materials on the surface of a membrane.
- Energy dispersive X-ray fluorescence (EDXRF) spectroscopy is used to determine which chemicals are in the deposit on the membrane. This technique uses short wavelength X-rays to ionize component atoms in a material. This process emits energy in the form of a photon. The energy is characteristic of the atoms present. The term "fluorescence" is applied to this phenomenon because the absorption of higher-energy radiation results in the re-emission of lower-energy radiation.
- Inductively coupled plasma emission (ICP) spectroscopy is used to determine the amount of trace metals and silica on a membrane. This technique uses inductively coupled plasma to excite atoms and ions that emit electromagnetic radiation and wavelengths that are characteristic of a particular element. The intensity of the emission is indicative of the concentration of that element in the sample.
- Electron spectroscopy for chemical analysis (ESCA) is used to determine impurities that have been organically bound to a membrane surface. This technique measures the elemental composition, chemical state, and electronic state of elements within a material.
- Infrared spectroscopy is used to detect most organic material and some inorganic materials such as iron, silicates, carbonates, and sulfates. The technique uses the absorbance of the infrared light frequencies to detect the nature of chemical bonds present.

14.8.6 Other Tests

X-Ray diffraction can determine whether or not the material on the membrane is crystalline. This technique uses X-rays to strike the material of interest. X-rays are scattered, and from the angles and intensities of the scattered beams, the nature of the crystal can be determined.

Microbial testing for aerobic and anaerobic bacteria and fungi is typically conducted. Specific species searched for include:

- Aerobic bacteria
  - Pseudomonas
  - Spores
- Anaerobic bacteria
  - Clostridia
  - Sulfate-reducing bacteria
- Fungi
  - Molds
  - Yeasts
- Iron bacteria
- Algae: filamentous and non-filamentous
- Diatoms
- Protozoa

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6

SYSTEM ENGINEERING

15

Issues Concerning System Engineering

Various engineering issues concerning RO and pre- and post-treatment are discussed in this chapter. Commonly encountered issues include:

- sodium softening and whether to place the softener before or after the RO unit
- whether to use sodium softening or antiscalant
- sizing of an RO in variable flow demand conditions
- cleaning of RO membranes on-site or off-site
- disposal of RO reject

15.1 Sodium Water Softening

Sodium softening is used to remove soluble hardness from water, including calcium, magnesium, barium, and strontium. As discussed in Chapter 8.1.6, sodium softeners are commonly used to pre-treat RO feed water to reduce the potential for scaling the membrane with hardness scales. However, due to discharge limitation on chlorides, many sites cannot aford to use softening prior to an RO because of all the chlorides in the waste. In the next two sections, the placement of the sodium softener, either before or after the RO system, as well as the use of sodium softeners versus antiscalants is discussed.

15.1.1 Sequencing of the Sodium Softeners and RO

Traditionally, sodium softeners have been used as pretreatment to RO. Sodium softeners remove hardness and metals, such as iron and manganese, that scale, foul, or catalyze degradation of RO membranes. Anecdotally, softeners are also used to help reduce suspended solids and SDI from surface or other highly fouling feed waters prior to RO. In this case, the sodium softener, in essence, acts as another barrier in front of the membrane.

The disadvantage with using sodium softening as RO pretreatment is that the softener must treat not only the permeate volume but also the volume of water that will become the reject. In other words, the softener must be large enough to treat the entire feed volume to the RO. This brings up two issues:

1. The softener system must be relatively large, as the service flow rate through a softener vessel should be about 6–8 gpm/ft^2.[1] A 500-gpm RO operating at 75% recovery (see Chapter 3.2) would require two 120-inch diameter vessel to soften the feed water and maintain the desired service flow rate while one unit is in regeneration.
2. Chloride discharge may become a concern. One 120- inch diameter vessel will generate about 3,400 gallons of 10% brine waste just from the brining step alone. A 10% brine solution contains about 6,000-ppm chloride. Current Environmental Protection Agency (EPA) guidelines call for a chronic (or continuous) chlorine discharge limit of 230 ppm to a controlled watercourse. To meet the current guidelines, the brine solution would have to been diluted by a factor of 18, or the 3,400 gallons of 10% brine would need to be diluted by 61,200 gallons of chloride-free water.

These two issues have prompted several users to move or consider moving the sodium softener from in front of the RO to after the RO, to polish the RO permeate. Post treatment of RO permeate is often necessary because the RO does not reject 100% of the hardness in the feed water.

(See Table 3.2). With post-treatment the RO feed water is not softened, the concentration of hardness in the RO[2] effluent will be higher than if the feed water were softened prior to the RO. Depending on the application of the permeate, polishing with a softener to remove hardness may be required.

The advantages of this configuration include the following:

1. The sodium softener is only treating the RO permeate, typically about 75% of the feed flow rate.
2. A polishing sodium softener can operate at a higher service flow rate than a primary softener. Instead of being limited to 6–8 gpm/ft^2, a polishing softener can operate at 10–15 gpm/ft^2. The same 500-gpm RO system that requires two 120-inch diameter softener vessels for pretreatment, would only require two 84-inch diameter vessels to post-treat the RO permeate.
3. One 84-inch diameter vessel will generate about 1,700 gallons of 10% brine waste. About 44,200 gallons of chloride-free water will be required to dilute the chloride to meet discharge limits, or only about 60% of that required when the sodium softener was located in front of the RO.

The disadvantage of the post-RO arrangement is that the RO membranes are now more prone to scaling, fouling, and degradation with hardness and metals such as iron and manganese. This can be addressed by using antiscalants to minimize scaling (see Chapter 8.2.4) and appropriate filtration, such as pyrolusite filtration, to remove iron and manganese (see Chapter 8.1.5). However, costs would have to be carefully evaluated to determine which option (softener in front of or behind the RO) is more cost effective.

15.1.2 Sodium Softening and Antiscalants

The choice of sodium softening or antiscalant is specific to each application. It is very difficult to make a blanket statement that one technology is better than the other, since both are effective at minimizing the potential for scaling RO membranes. Some designers prefer using sodium softeners because of the additional barrier they provide in front of the RO. Others prefer antiscalant to eliminate the need to handle brine waste (see Chapter 15.1.1).

For practical purposes, it generally makes sense to use sodium softeners for RO feed flow rates of less than about 30 gpm rather than conventional, flow-proportional control; difficulties in feeding based on flow control are exacerbated at low flow rates because of limited turn down on proportioning chemical feed pumps at low flow rates. However, when Nalco Company's 3D TRASAR technology is used, antiscalant can be fed to RO systems operating feed flow rates as little as 3 gpm.[2]

The other issue to consider is cost, both capital and operating. Capital is generally lower for the antiscalant feed system than for a softener. An antiscalant feed system can be had for just for the pump, make-down calibration equipment, and a day tank. A comparable softener would cost significantly more for a duplex system that allows for continuous operation.

Table 15.1 lists operating cost issues for sodium softeners and antiscalant feed systems. The three largest expenditures listed in Table 15.1 are the salt and resin amortization for the sodium softener options and the antiscalant itself for that option. To provide examples of these costs in greater detail, consider the cases described below.

The significance of these three cases are to show that each application requires full accounting of operating costs when considering whether to use a sodium softener or antiscalant. A complete water analysis is required on which to base the operating cost assumptions (see Chapter 7). The presence of iron and/or manganese can significantly affect the design, performance,

Table 15.1 Operating costs considerations for sodium softeners and antiscalant feed systems.

Operating Cost Issue	**Sodium Softeners**	**Antiscalant Feed System**
Pump Maintenance	Yes*	Yes
Pump Accrual	Yes	Yes
Vessel Maintenance	Yes	No
Tank Maintenance	Yes (brine)	Yes (day)
Salt	Yes	No
Antiscalant	No	Yes
Resin Amortization	Yes	No
Membrane Fouling Protection	Moderate**	Little
Membrane Scaling Protection	High	Moderate to High $^{+}$

* for pumped-brine systems only (versus educated brine systems)

** Some anecdotal evidence on higher-fouling waters

$^{+}$ some difficulty with calcium phosphate scale and cost to operate an RO system with pretreatment. Additionally, local pricing for commodities will also affect the cost to operate the system. Focusing on just one operating cost variable, such as the cost of salt, may not give a complete picture of the total affect the softener might have on performance of the RO and pretreatment system.

Case 1 High Hardness Well Water

In this case, well water has a total hardness of 285 ppm as calcium carbonate, with 250 ppm calcium and 35 ppm magnesium. The remaining feed water analysis is listed below (all species listed as ppm ion):

- sodium: 75.4
- barium: 0.08
- iron: 0
- sulfate: 21
- fluoride: 0.17
- nitrate: 0.3
- phosphate: 0.5
- potassium: 5.7
- strontium: 0.13
- manganese: 0
- chloride: 240
- bicarbonate: 84
- silica: 15
- pH: 8.1

The feed is make-up water to a 110 gpm RO operating at 75% recovery. Hence, the pretreatment system must treat 150 gpm of feed water.

Sodium Softener

The sodium softener selected to treat this water is a duplex, 150- gpm system with 54-inch diameter by 72-inch side sheet vessels. Each vessel contains 50 ft^3 of resin. Since the duplex system operates with one vessel on line and one vessel in stand-by, the total system regenerates 2.4 times per day. At a salt dosage of 15 pounds per cubic foot, the system uses about 1,800 pounds (820 kg) of salt per day or 27.4 tons per month, assuming a 100% operating factor. At a salt cost of $80 per ton, the total month cost for salt is about $2,200.[3]

Amortization of resin typically assumes a 5-year life or replacement cycle. With two vessels at 100ft^3 of resin total, the monthly amortization is $100.

Antiscalant

Table 15.2 lists the saturation indexes for the untreated feed water, feed water with 10.2 ppm antiscalant, and 4.2 ppm of antiscalant plus 3.4 ppm

Table 15.2 Saturation indexes for untreated feed water and feed water treated with antiscalant.

Feed Water Condition	**Untreated**	**With 10.2 ppm Antiscalant**	**With 4.2 ppm Antiscalant and Supplemental Acid Feed**
Calcium Carbonate	164	75	74
Calcium Sulfate	1.7	0.6	0.6
Barium Sulfate	200	2.4	2.4
Strontium Sulfate	0.4	0.0	0.0
Calcium Fluoride	30.1	0.0	0.0
Silica	35	23	31
Calcium Phosphate	117	103	96

sulfuric acid for pH reduction from 8.1 to 7.5. As the untreated water shows, the major species of concern are the calcium carbonate, barium sulfate, and calcium phosphate. The antiscalant does a good job with all but the calcium phosphate. To address this potential scale, acid must be added. This reduces the antiscalant demand by 60%.

Average price for an antiscalant in 2014 runs about $4.00 per pound.[4] At a dosage of 10.2 ppm, the daily cost for antiscalant is about $72.00 or about $2,200 per month. With acid feed, the antiscalant requirement is about $905 per month. Sulfuric acid, at about $700 per ton, and 3.4 ppm feed rate, would add about $64 per month. Monthly total for the antiscalant only option is about $2,400, while that for the acid/antiscalant option is about $970.

Summary

For this high-hardness case, the softener and antiscalant options appear to be about the same when only antiscalant (no acid) is used. When acid is feed in conjunction with the antiscalant, the lower cost option is the chemical one when comparing cost of salt versus cost of antiscalant/acid. Note that any local variation in cost of either salt or antiscalant can change the results. What is not accounted for is the affect a softener has on the ability to remove suspended solids and SDI out of feed water, such as any iron or manganese that may be in the well water. If the water were to contain soluble iron and manganese, the softener would remove these species and prevent both fouling and catalyzed degradation of the RO membrane, thereby reducing membrane O&M costs via lower membrane cleaning and replacement costs. The chemical option would require an iron filter, thereby increasing the costs of this option. If the softener were to have a positive affect on membrane performance, this cost would have to be taken into account as well. See Case 3 below.

Case 2 Low Hardness Surface Water

In this case, surface water had a total hardness of 105 pm as calcium carbonate, with 95 ppm calcium and 10 ppm magnesium. The remaining analysis is listed below (all species listed a ppm ion):

- sodium: 19
- barium: 0.0
- iron: 0
- sulfate: 46
- fluoride: 0.82
- nitrate: 12
- phosphate: 0.0
- potassium: 3
- strontium: 0.0
- manganese: 0
- chloride: 33
- bicarbonate: 42
- silica: 5.5
- pH: 8.5

As with Case 1, the RO system produces 110 gpm at 75% recovery that requires 150 gpm of feed water.

Sodium Softener

The sodium softener selected to treat this water is a duplex, 150-gpm system with 54-inch diameter by 72-inch side sheet vessels. Each vessel contains 50 ft^3 of resin and the system regenerates 0.9 times per day. At a salt dosage of 15 pounds per cubic foot, the system uses about 675 pounds of salt per day, assuming a 100% operating factor. At a salt cost of $80 per ton, the total monthly cost for salt is about $820.

Amortization of resin typically assumes a 5-year life or replacement cycle. Given two vessels with 100 ft^3 of resin total, the monthly amortization is $100.

Antiscalant

Projections shows that calcium carbonate and calcium fluoride, with saturation indexes of 158% and 200%, respectively, are the species to be concerned with. The addition of 2.6 ppm of antiscalant would bring down the saturation indexes to 82% and 0% for calcium carbonate and calcium fluoride, respectively. At $4.00 per pound of antiscalant, the cost for antiscalant is about $19 per day, or about $570 per month.

Summary

For this low hardness, surface water case, the antiscalant operating cost is lower than that for the softener. Again, the affect of the softener on improved membrane performance is not known and should be considered for this surface water source.

Case 3 Well Water with Iron and Manganese

This case is taken from an actual analysis conducted for an O&M contract for a facility in Venezuela. The system is to take potable well water from the city and generate boiler make-up water. The water has 77 ppm (as calcium carbonate) total hardness, with 60 ppm calcium and 17 ppm magnesium. The water contains 0.5 ppm iron and 0.4 ppm manganese. The remainder of the analysis is listed below (all species listed as ppm ion):

- sodium: 17
- barium: <0.4
- sulfate: 30
- fluoride: NA
- nitrate: <0.16
- phosphate: NA
- potassium: 4.8
- strontium: 0.12
- chloride: 56
- bicarbonate: 40
- silica: 11
- pH: 6.8

Sodium Softener

The softener is a 48-inch diameter unit with 35 ft^3 of resin. The softener will regenerate once per day with 15 lb/ft^3 of salt. At a salt cost of $80 per ton, the sodium softener would require about $638 per month to operate.

Antiscalant

Projections indicate that about 3 ppm of antiscalant is required to minimize scaling due to hardness. At a local cost of $4.50 per pound, the monthly cost for antiscalant is $46.

Table 15.3 lists the pertinent operating costs for this system. As the table shows, the cleaning and membrane replacement costs for the two options

Table 15.3 Projected operating costs for an RO pretreatment system with and without sodium softener.

Concern	With Sodium Softener			Without Sodium Softener		
	Frequency/Dose	**Cost Each**	**Cost per Year**	**Frequency/Dose**	**Cost Each**	**Cost per Year**
Antiscalant	0 ppm	$0	$0	3 ppm	$4.50/lb	550
Salt	1 regeneration /day	$21*/day	$7,665	0 regenerations	$0	$0
Membranes	3 year life	$600	$7,200	2.5 year life	$600	$8,640
Membrane Cleaning	4 per year	$3,240	$12,960	6 per year	$3,240	$19,440
Total			$27,825			$28,630

* 15 lb/ft3 dosage, $80/ton

are different. The iron and manganese make the difference in this case. A softener will remove these species from the RO feed water, thereby protecting the membranes from degradation and fouling. This results in fewer membrane cleanings and longer membrane life.

15.2 Reverse Osmosis Sizing and Capacity

Proper sizing of an RO system, particularly when the demand for product is variable, can be a challenge. Variable product demand can involve actual swings in demand typically brought on by low-level and high-level sensors located in product tanks that cycle the RO feed pump on and off. The ideal condition is to keep all RO skids operating continuously. Idling the membranes makes them more susceptible to fouling and scaling, especially when a shut-down flush is not employed (see Chapter 13.1.1). Furthermore, repeated start-ups subjects the membranes to physical stress and perhaps even water hammer; soft-start motors can minimize this (see Chapter 6.2).

The best approach to meeting variable product demand is to design the RO system for the average flow rate required. For example, if demand for product water is 500 gpm for 10% of the time and 350 gpm for 90% of the time, the RO should be designed for about 365 gpm. A product tank that is large enough to hold the excess 15 gpm for 90% of the time is required. Whether an RO system is on line or not is often a function of the level settings in the RO permeate or product tank. At the low set point, the RO feed pump trips on, and at the high set point, it trips off. The key is to position the level set points far enough apart that the RO system remains on line for the maximum amount of time.

Should a large tank not be an option, the alternative is multiple skids, some of which will sit idle. The key is to rotate skids on and off so that no one skid experiences most of the down time or start-ups. It is also recommended that an off-line or shut-down flush be employed, and that the motor be equipped with a soft start. For the example above, two 350-gpm skids would be required. Both skids would be on line during the 500-gpm draw. A product tank with enough capacity to handle the 200-gpm overage would be required.

If demand is continuously variable, the best option is still designing for the average flow rate, as described above. However, in some cases variation in demand may be such that it still may become necessary to cycle the feed pumps on and off with level in the product tank.

Table 15.4 Merits of on-site versus off-site membrane cleaning.

Off-Site Membrane Cleaning		**On-Site Membrane Cleaning (CIP)**	
Advantages	**Limitations**	**Advantages**	**Limitations**
• Expert service • More effective cleanings • Documented results	• Higher cost • Requires second set of membranes	• Membranes cleaned in situ—no need for replacement membranes • Faster cleaning • Less expensive	• Less efficient • Capital outlay for cleaning skid • Storage and handling of chemicals and waste

15.3 Membrane Cleaning: On-Site versus Off-Site

Chapter 13.2 discussed techniques and chemicals used for cleaning of RO membranes. This section discusses the merits of on-site verses off-site membrane cleaning. Table 15.4 summarizes the advantages and limitations of on-site and off-site membrane cleaning.

15.3.1 Off-Site Membrane Cleaning

Off–site membrane cleaning involves removing membrane modules from the pressure vessels and shipping them off site for cleaning by a 3rd party. If the RO must remain in operation, a second set of membranes is used to replace those sent out for cleaning (one of the shortcomings of off-site cleaning).

Advantages of off-site cleaning are detailed below.

- Off-site cleaning offers expert service. Personnel specifically trained for that purpose clean membranes. Experience goes a long way when it comes to membrane cleaning, because cleaning can be as much an art as it is a science.
- Off-site cleaning is generally more efficient. Off-site cleaning operations have a variety of cleaners at their disposal to use for most types of foulants and scale. If one cleaning is not successful, another cleaner(s) may be employed to improve upon results.
- Membrane manufacturers at times give special variances to off-site cleaning operations to use conditions outside the

normal cleaning recommendations for membranes, as listed in the membrane specifications. For example, higher temperature and pH may be used to address biofilms and lower pH and higher temperature may be used to remove calcium carbonate scale (refer to Table 13.1).
- Results are documented. Documentation typically includes performance testing prior to and after cleaning, and comparison of the results with specifications for that specific membrane make.

Shortcomings of off-site cleaning are as follows:

- Off-site cleaning costs more than on-site cleaning. Quotes should be obtained form specific vendors, but pricing can be as high as $150 or greater per membrane 8-inch diameter module.
- A second set of membranes is required for continued operation of the RO.

15.3.2 On-Site Membrane Cleaning

The techniques and chemicals described in Chapter 13.2 apply directly to on-site or Clean-In-Place (CIP) membrane cleaning.

Advantages of CIP are as follows.

- Cleaning is conducted with the membrane modules in situ; there is no need for a second set of membranes.
- Cleaning is faster with CIP than with off-site cleaning. A two-stage, 500-gpm RO skid can be cleaned is about 2 days. Off-site cleaning can take a couple of weeks to turn around the membranes.
- CIP is less expensive that off-site cleaning. Depending on the chemical(s) used, an 8-inch diameter membrane module can be cleaned for anywhere from $5 to $25 each.

Shortcomings of CIP are listed below.

- Cleaning is less efficient than with off-site cleaning. Typically, cleaning operations are limited to one cleaner per pH (e.g.,

one high-, and one low-pH cleaner) on site. It is too costly to stock all cleaners that "might" be needed. Additionally, membrane manufacturers will generally require adherence to their cleaning specifications.
- Initial capital outlay will need to include a cleaning skid.
- On-site personnel must store and handle the cleaning chemicals as well as the wastewater that is generated.

15.4 Reverse Osmosis Reject Disposal Options

While there may be many options to deal with RO reject, each one has advantages and limitations. Some offer cost savings, while others may increase costs, but eliminate the need to dispose of a relatively large waste stream. Reject is considered non-hazardous, and contains only those constituents that were present in the feed water (only more concentrated, which can be a problem) and any antiscalants, biocides (such as DBNPA—see Chapter 8.2.2.2), or any other chemical added as pretreatment. Disposal techniques over the years have included:

- Surface water discharge
- Land application
- Sewer
- Deep well injection
- Evaporation pond
- Zero-liquid discharge

The three most common techniques for dealing with RO reject waste are discussed here.

15.4.1 Discharge to Drain or Sewer

Perhaps the most common disposal method for RO reject is simply sending it down the drain to sewer or waste treatment. However, discharging in this manner may actually not be a simple as it sounds. There are regulations and permits that may be required that limit discharge of specific contaminants.

Discharge to a natural watershed generally requires a permit that must be periodically renewed. Permit requirements vary greatly from location to location and take into account the impact discharge will have on the local ecosystem. Generally, discharge to a larger body of water results in less stringent permits, while discharge to a smaller or more delicate ecosystem, typically will encounter tighter permitting. For example, Louisiana does not regulate chlorides or hardness into the Mississippi River near the Gulf of Mexico, so sodium softener brine waste and cold-lime softener sludge may be discharged directly to the river.[5] On the other hand, New Jersey has such stringent regulations and permits, that zero-liquid-discharge (ZLD) is often necessary.[5]

Discharge to a sewer or publicly owned treatment system (POTW) is not as regulated as discharge to a natural watershed. Most jurisdictions do not require permits and regulate only pH. However, there may be an up-charge for high concentrations of certain contaminants such as chlorides.

15.4.2 Discharge to Cooling Tower

Sending RO reject to the cooling tower is the second most common method of disposing of the reject. The concerns with this method of handling of RO reject are 1) scaling in the heat exchange equipment, 2) tower chemistry, and 3) logistics.

Calcium and silica can cause scaling problems for the cooling tower, particularly if the RO reject is a major portion of the cooling tower make-up. Scaling of the heat exchanger equipment results in a loss in productivity on the process side of the facility. New chemistries that are better able to handle high concentrations of scale-forming species are being introduced, but there will always be a limit as to what the cooling system can tolerate.

The effect of the RO reject on the cooling tower chemical program is also a concern. Because the reject contains the same species as the cooling tower make-up (only cycled up 3 to 5 times), and a possible antiscalant or biocide, adding reject to the cooling tower should not adversely affect the tower chemical program, if the reject is not a large percentage of the total make-up. However, when the RO reject comprises a large percentage of the total make-up to the tower, these issues become important.

Location of the RO system relative to the cooling towers is a concern. In most facilities, the RO is not located near the major cooling towers. There may be a small, local tower located nearby, but discharging to this tower may be difficult as the RO reject could be a major portion of the make-up flow to the tower. Pipelines must be run from the RO to the major cooling towers to allow discharge of the RO reject to these towers.

Prior to making the decision to discharge RO reject to the cooling tower, an analysis should be conducted to determine what impact the reject will have on tower operations. There is a need to balance conservation and recovery of RO reject water with the impact on the cooling system.

15.4.3 Zero Liquid Discharge

The use of RO to treat and recover reject from another RO system is becoming more common, particularly in ZLD applications. A secondary RO is used to treat the reject from the primary RO to reduce the thermal evaporative requirements of the ZLD system.

Figure 15.1 shows a ZLD system with RO as a primary and secondary treatment for wastewater. As the figure shows, wastewater from a variety of sources, including cooling tower and boiler blow downs, boiler feed water makeup treatment wastes, and process wastes, is sent to the pretreatment system. This pretreatment system typically consists of a cold lime softener, either in traditional form or using microfiltration. If the wastewater is high in organics, additional treatments might include digestion (aerobic and/or anaerobic), dissolved air flotation, and stripping. Waste from the pretreatment system is sent to a sludge press, which, in turn, yields cake solids and another wastewater stream that is recycled to the headworks of the ZLD system. The effluent from the pretreatment system is sent to an RO, the product of which can be sent back to the cooling tower. Reject from the primary RO is sent to a concentrate or secondary RO. The secondary RO is typically a seawater system, capable of operating in the range of 45,000 to 85,000 ppm TDS.[6] Reject from the secondary RO is sent to the thermal system, consisting of a brine concentrator and a crystallizer. The brine concentrator can achieve a concentration of about 300,000 ppm; the crystallizer yields salt solids. Using the secondary RO reduces the load on the brine concentrator by about 20%. This translates into a corresponding 20% energy savings for a single-effect brine concentrator. Capital cost of the system is also significantly reduced, as the size of the brine concentrator, one of the most expensive pieces of capital equipment in the process, can be smaller. (Refer to Chapter 16.5 to see discussion on how high efficiency reverse osmosis can be used in the ZLD system).

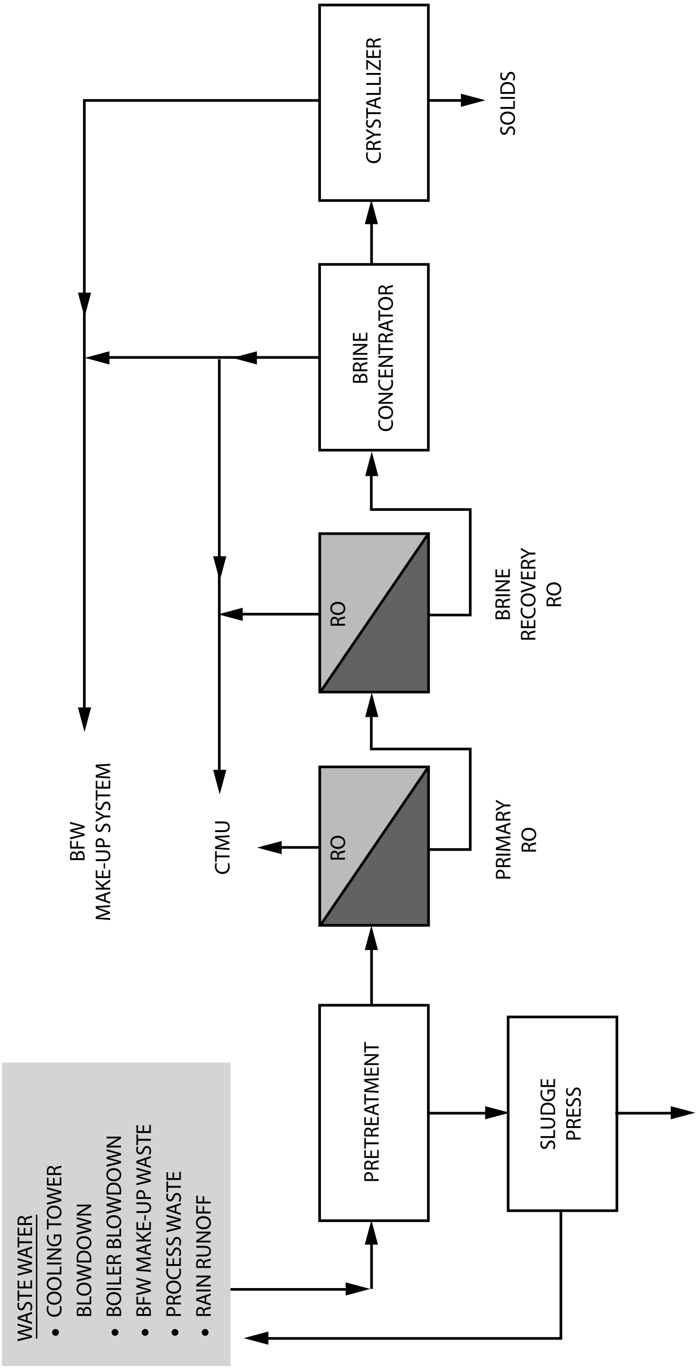

Figure 15.1 Zero-liquid discharge (ZLD) system showing primary and brine recovery RO systems.

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16

Impact of Other Membrane Technologies

In this chapter, the impact of other membrane technologies on the operation of RO systems is discussed. Technologies considered include microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) as pretreatment to RO, and continuous electrodeionization (CEDI) as post-treatment to RO. Forward osmosis is discussed as another membrane-based application often used in conjunction with RO, that has emerged relatively recently to desalinate water. This chapter also describes the HERO™ (high efficiency RO—Debasish Mukhopadhyay patent holder, 1999) process used to generate high purity water from water that is difficult to treat, such as water containing high concentrations of silica.

16.1 Microfiltration and Ultrafiltration

Microfiltration and UF are pressure-driven membrane separation technologies that use positive pressure or suction to separate particles (and very high molecular-weight soluble species in the case of UF) from solution (see Figure 1.1). The history of MF and UF membranes goes back to the early

1900's. Bechhlold developed the first synthetic UF membranes made from nitrocellulose in 1907.[1] He is also credited with coining the term "ultrafilter." By the 1920's and 1930's both MF and UF nitrocellulose membranes were commercially available for laboratory use. The first industrial applications of MF and UF came in the 1960's and 1970's. Microfiltration membranes became viable for industrial application in the 1970's when Gelman introduced the pleated MF cartridge.[1] Ultrafiltration membranes became industrially viable in the 1960's when Amicon began preparing UF membranes using a modified Loeb-Sourirajan method (see Chapter 4.2.1).[1]

Microporous membranes are used to effect the separation by MF and UF processes. These microporous membranes differ from polyamide composite RO membranes in that they are not composites of two different polymeric materials; they are usually constructed using a single membrane polymeric material. In simple terms, both UF and MF technologies rely on size as the primary factor determining which suspended solids and high molecular-weight dissolved organics are retained by the respective membranes. Due to the microporous nature of MF and UF membranes, the pressure required to drive water through them is significantly lower than for RO membranes, typically less than 100 psi; initial clean membrane differential pressures can be as low as 1.5 to 2.0 psi, depending on the membrane material.

Common polymers currently used to prepare MF and UF membranes include:

- Polypropylene (PP): a hydrophobic membrane with good chemical resistance and tolerance of moderately high temperatures; sensitive to chlorine.
- Polytetrafluoroethylene (PTFE) (MF only): an extremely hydrophobic membrane, with high tolerance of acids, alkalis, and solvents; can be used at temperatures up to 260°C.
- Polyvinylidene fluoride (PVDF): a hydrophobic membrane (can be surface-modified to become more hydrophilic) with good resistance to chlorine. Stable pH range up to 10.
- Polysulfone (PS): good resistance to chlorine and aliphatic hydrocarbons (not compatible with aromatic hydrocarbons, ketones, ethers, and esters), stable pH range from 1–13, and tolerance of up to 125°C.
- Polyethersulfone (PES): same as PS membranes. Stable pH range up to 11.
- Polyethylene (PE): poor resistant to chemical attack and relatively low strength.

- Polyacrylonitrile (PAN): good chemical resistance, but resistant to flexing.
- Cellulose triacetate (CTA): Polymer with complete acetylation of cellulose that is hydrophilic, but suffers from very narrow acceptable temperature (<30°C), and pH (4-6 nominal, 2–9 occasional) ranges. This material is also highly susceptible to microbial attack. (Infilco Degremont is the only manufacatuer using this material as of this publication.)

Figure 16.1 compares the strength and elongation characteristics of various polymers used in the manufacture of MF & UF membranes. High strength and good elongation characteristics are important for the integrity of the membrane. Both properties ensure that the membrane material, particularly in the form of hollow fibers (see discussion below) can flex without breaking. Flexing is an important property for hollow fiber UF and MF membranes, which have a tendency to move in the turbulence of the flow of feed water.

Wettability or hydrophilic properties of UF and MF membranes is also important characteristics. Wettability is measured using contact angle. Contact angle is the result of the interface/surface tensions between liquid and solid. Consider a liquid droplet at rest on a flat, solid surface, as shown in Figure 16.2. The contact angle, Θ, is the angle formed by the solids surface and the tangent line to the upper surface at the end point. A smaller contact angle means the wettability and hydrophilicity of the solid material is greater. Table 16.1 lists the contact angle for some common polymers. A

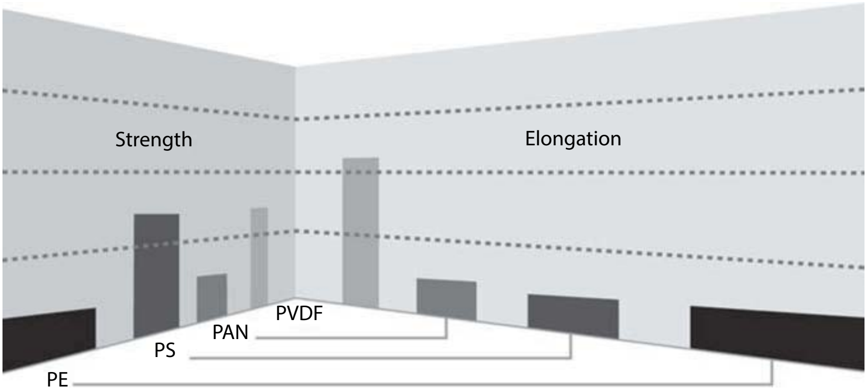


Figure 16.1 Strength and elongation characteristics of various UF and MF polymers. *Courtesy Dow Water and Process Solutions.*

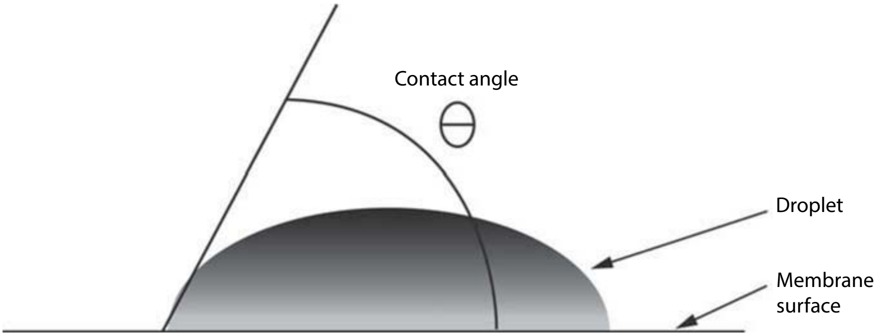


Figure 16.2 Contact angle between a liquid droplet and a flat, solid surface.

Table 16.1 Contact angle for common membrane polymers.

Polymer	Contact angle (degrees)	
PES	44	HYDROPHILIC
PAN	46	↓
PVDF	66	
PP	108	
PTFE	112	HYDROPHOBIC

hydrophilic membrane is usually preferable over a hydrophobic membrane for UF and MF applications.

Microfiltration and UF membranes can be asymmetric, with a denser side and a more open side, or uniform without macrovoids (See Figure 16.3). The open area behind the denser surface in an asymmetric design means there is less resistance to water permeating the membrane. Operating pressure can be lower and the membrane systems can be more productive. The limitation of the asymmetric design is that the material, predominately used in the hollow fiber configuration, is not as strong as the uniform cross section.

Microfiltration and UF membranes are available in tubular, spiral wound, and hollow fiber membrane module configurations. Tubular and spiral MF and UF modules are similar to RO tubular and spiral wound membrane modules described in Chapters 4.3.2 and 4.3.3. However, while the thickest commercially available feed spacer in a spiral RO module is 34-mil, UF and MF modules nominally have up to a 45-mil spacer due to the relatively high concentration of suspended solids these membranes are called upon to treat (TriSep™ Corporation offers a special 65-mil spacer for dairy applications).

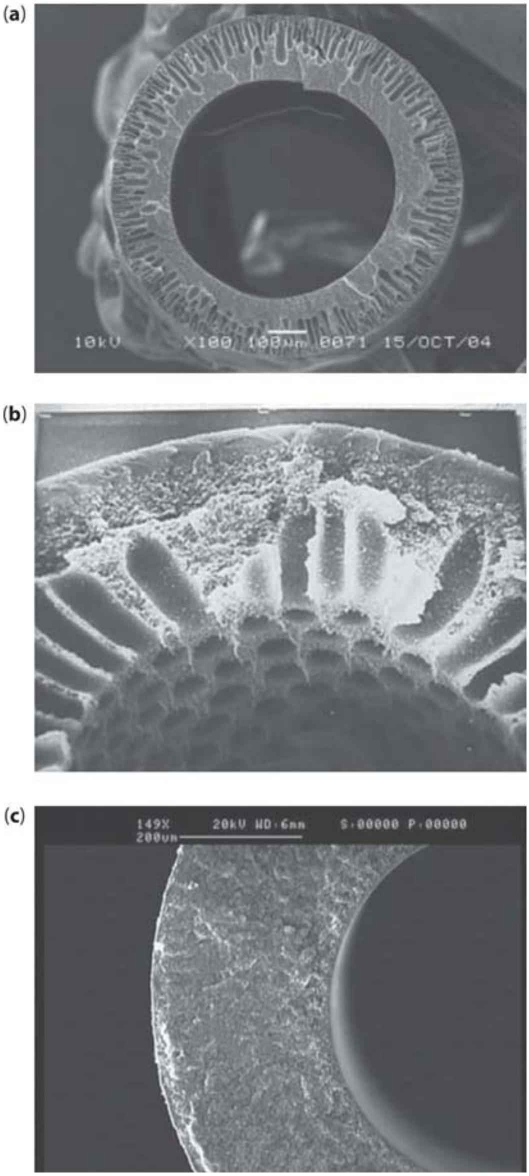


Figure 16.3 Asymmetric (inside-skinned (a) and outside-skinned (b)) and uniform (c) cross-section UF membranes. *Figure c courtesy of Dow Water and Process Solutions.*

Improvements made over the last 20 years in MF and UF membranes and modules, including the development of a new generation of hollow-fiber (HF) membranes and modules for industrial applications has led to wider application of these membrane separation technologies.[2] The new generation HF membranes are characterized by high porosity, strength, and flexibility, all important characteristics for MF and UF applications.

Microfiltration and UF hollow fiber membranes are different than the hollow fine fibers discussed in Chapter 4.3.4. The MF and UF membranes are thicker and not quite as flexible, resembling fine-diameter straws rather than human hair. Diameter of fibers ranges from about 200 to 3,000 microns with a cross-sectional membrane thickness of 100–200 microns. The fibers are not folded into the pressure vessel as they are with hollow fine fibers, but are usually potted and open on both ends. (Note that Koch's Puron® submerged hollow fiber membrane is "potted" at one end only, with the other end unencumbered and sealed (Puron® is a registered trademark of Koch Membrane Systems, Wilmington, MA). The membrane module assembly in operation resembles a "weed" blowing in the wind. This configuration is proported to be less prone to fouling on the outside of the fibers at the sealed end than a hollow fiber that has both ended potted).

Hollow fibers can be created with the dense side on the inside or lumen of the fiber or on the outside of the fiber, or they can be double-skinned, where both the lumen and the outside of the fiber are dense (see Figure 16.3). Location of the denser side of the membrane determines whether the service flow is outside-in or inside-out. Outside-in systems are typically used in a dead-end mode (or some variation thereof), while inside-out systems are typically dead-end, but can also provide true cross flow. Manufacturers of outside-in membranes include Evoqua (Memcor®), GE (ZeeWeed®), and Pall (Aria™-Aria is a trademark of Asahi Kasei Corporation, Tokyo, Japan). Koch manufactures inside-out membranes (Romicon®), as does Pentair Norit (X-Flow). Some hollow fiber membranes, such as Dow Water and Process Solutions' UF membrane, are skinned on both in inside and outside of the fiber, giving the fiber more strength thereby minimizing fiber breakage (see Figure 16.3c). The Dow membranes are operated in an outside-in flow pattern. Table 16.2 lists the advantages and limitations of outside-in and inside-out service flow designs.

Tubular and spiral configuration have advantages and limitations as well. Tubular membranes, with diameters of ½ to 1-inch can handle high concentrations of suspended solids; the chance of plugging the tubes is minimal. Fouled tubular membranes are easily cleaned mechanically using a sponge ball to scour the membrane surface free of foulants. However, the packing density of tubular membranes is not high, so this configuration requires a lot of floor space. Spirals, on the other hand, require less floor space, but require pre-filtration to minimize plugging of the feed channel spacer with larger suspended solids just as RO spiral wound modules.

Table 16.2 Advantages and limitations of outside-in and inside-out service flow designs for hollow fiber MF and UF membranes.

Service Flow	**Outside-In**	**Inside-Out**
Denser Side of Membrane	Outside of the fiber	Inside of the fiber
• Advantages	• Minimal filtration pretreatment • Easier membrane cleaning • Higher surface area means more filtration area per fiber	• True cross flow velocity minimizes concentration polarization and membrane fouling • When no air is utilized for backwashing the less fiber movement leads less fiber breakage.
• Limitations	• Solids collect around and at potted ends of fibers • Requires air scour to clean • Cannot perform true recycle	• High pressure drop limits fiber length • Requires significant filtration for pretreatment

Figures 16.4, 16.5 and 16.6 show spiral wound UF, hollow fiber MF, and tubular UF systems, respectively.

Microfiltration and UF typically encounter some degree of fouling with suspended solids. Fouling can be particularly severe upon start-up under high transmembrane pressure and flux, which can cause compaction of the initial fouling layer (transmembrane pressure is measured from the feed side to the permeate side of membrane). This results in a dramatic loss of flux and rapid drop in driving pressure, depending of the solids loading. Figure 16.7 compares the flux decline with time for MF and UF membranes. As the figure indicates, MF systems can exhibit higher initial flux, but as suspended solids begin to plug the pores of the membrane (which are larger than the pores in a UF membrane, and hence, more prone to plugging), the flux can decline more rapidly for the MF membrane.

Hollow fiber membrane modules can be backwashed to remove foulants whereas tubular and most spiral configurations cannot be backwashed. Backwashing of traditional spiral-wound modules would break the glue lines holding the membrane leaves together or cause blistering and delamination of the membrane from the backing in both spiral and tubular modules (TriSep Corporation has recently developed a back-washable, spiral-wound module (SpiraSep—US patent 6,755,970), that is used in

Figure 16.4 Spiral wound ultrafiltration system. *Courtesy of Koch Membrane Systems*.

Figure 16.5 Hollow fiber microfiltration system. *Courtesy of Koch Membrane Systems*.

Figure 16.6 Tubular ultrafiltration system. *Courtesy of Koch Membrane Systems.*

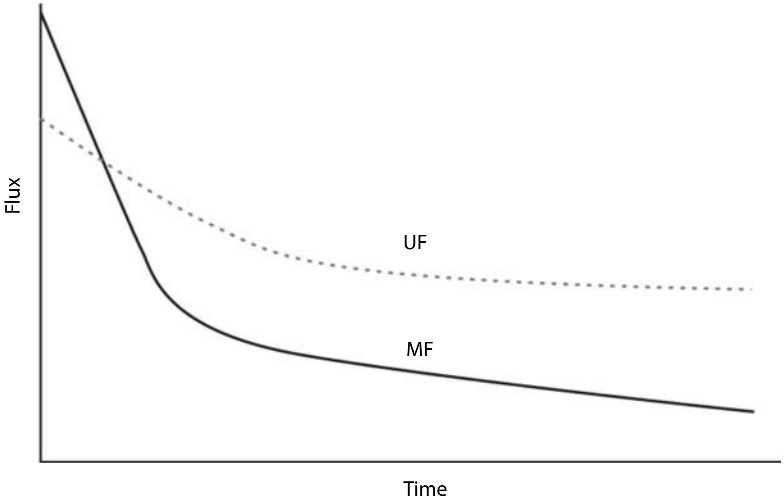


Figure 16.7 Flux decline with time for MF and UF membranes. *Courtesy of Dow Water and Process Solutions.*

immersed systems (see below)). Backwashing of HF membranes may need to be conducted frequently, up to 3 or 4 times per hour, depending of the rate of increase in pressure drop. In general, a hollow fiber MF or UF system will backwash once every 15 to 90 minutes. Backwashing is enhanced using air scour, where air is bubbled along the membrane surface to promote turbulance and left off solids that have collected on the membrane surface. Air scour, for outside-in applications, may be applied as often as once every backwash. Flow reversal can be used to remove solids blocking the fiber lumens for inside-out feed membranes (air scour can also be used on some inside-out modules such as the Pentair–Norit Aquaflex 1.5 mm ID and Pentair–Norit Airlift). Backwashing, along with air scour and flow reversal, minimizes the frequency of chemical cleaning.

Chemical enhanced backwashes (CEB) are also used to minimize the cleaning frequency of hollow fiber membranes. Chemical enhanced backwashes include the use of chemicals, such as hypochlorite, acid, and caustic in relatively high doses, to affect a “mini” chemical clean of the membranes without a full membrane cleaning. Concentrations of up to 1000 ppm acid, 500 ppm caustic, and 1000 ppm hypochlorite are typically used in a CEB.

A full clean or CIP of the membranes involves a high concentration of hypochlorite, acid, and caustic, with concentrations up to 2000 ppm for hollow fiber membranes. In general, packaged cleaners with surfactants are used only on spiral wound and tubular membranes because these products tend to foam, and foam is difficult to rinse out of hollow fiber membranes.

A limitation of HF membrane modules is the fact that just as spiral wound modules require pretreatment, so do HF modules, to reduce the size and/or quantity of suspended solids in the feed water, there by minimizing the chance of plugging the fibers and modules. This is particularly important for inside-out feed HF membranes. Typical pretreatment includes a 200–300 μm or smaller screen filter.

Table 16.3 Summarizes the advantages and limitations of tubular, spiral wound and hollow fiber module configurations.

Microfiltration and UF modules can be operated with a pressurized feed or “immersed” in ambient-pressure solution, with a vacuum (or gravity) on the lumen side of the fiber. Figure 16.8a shows a pressurized MF module, while Figure 16.8b shows a module used in immersed systems. In a pressurized system, water is forced into the membrane under pressure, as shown in Figure 16.9a. Immersed or “submerged” systems rely on suction to pull water through the membrane, as shown in Figure 16.9b. To minimize concentration polarization and fouling of the submerged fibers, two-phase bubbly flow (as illustrated in Figure 16.8b) is used to induce surface shear when operating on water containing a high concentration of suspended solids.

Table 16.3 Advantages and limitation of various module configurations for microfiltration and ultrafiltration membranes.

MF/UF module Configuration	Advantages	Limitations
Tubular	• Plug resistant • Easily (mechanically) cleaned	• Large footprint • High capital cost
Spiral Wound	• Small footprint • Low capital cost	• Plugging of feed channel • Difficult to clean • Cannot perform integrity tests
Hollow Fiber	• Small footprint • Low capital cost • Can be backwashed • Can easily be integrity tested • High membrane area per unit volume (high packing density)	• Plugging of fiber (inside-out feed) • Bridging of fiber bundle (outside-in feed) • Difficult to clean

Table 16.4 shows a comparison of pressurized and submerged hollow fiber MF and UF systems: [3]

- Operation: Pressurized configurations can be operated in either cross-flow or dead-end modes while submerged configuration are essentially only operated in dead-end mode. Submerged systems operate with outside-in flow, while pressurized can be either outside-in or inside out flow.
- Flux: Both pressurized and submerged configurations can be operated below design flux without difficulty. If operation above design flux is required for short periods of time, pressurized systems are preferred, as they operate under a positive trans-membrane pressure; positive pressure can always be increased, while vaccum is limited.
- Cleaning: Pressurized configurations require less chemical during cleaning than submerged systems. This is because the entire tank containing the submerged membrane cartridge must be filled with chemical to clean the membranes (note that spacers are used to occupy space within the tank to minimize this factor).
- Fouling Control: Pressurized and submerged hollow fiber configurations with out-side-in flow both suffer from

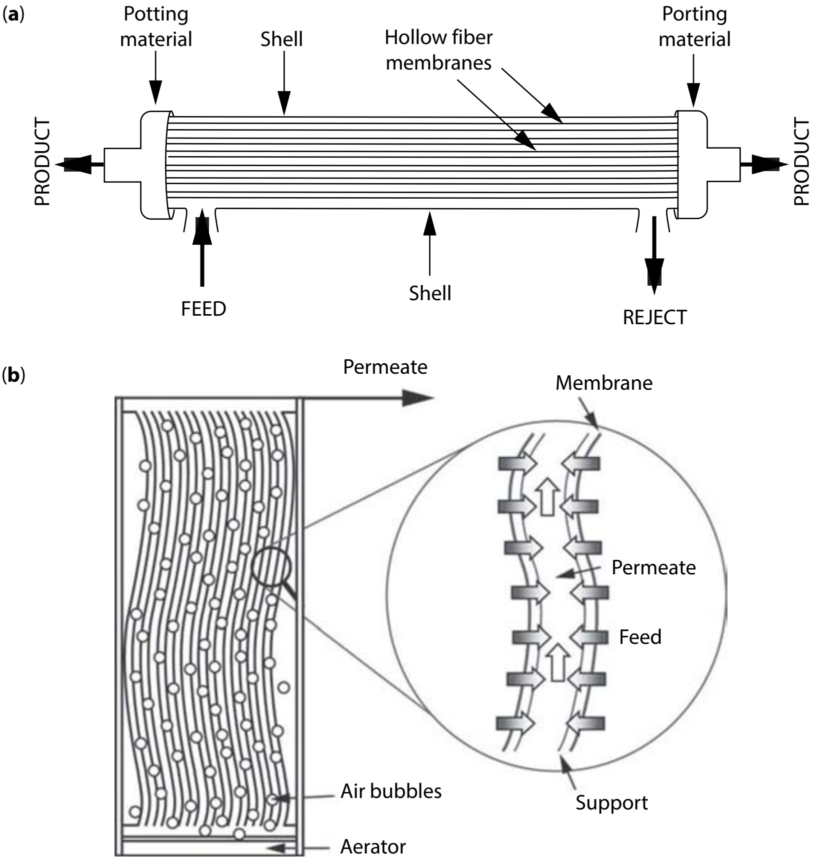


Figure 16.8 Cross-sections of a (a) pressurized MF or UF hollow fiber membrane module and an (b) submerged hollow fiber MF membrane cartridge.

blockage of the fiber bundles that tends to be self-accelerating. Hence, the need for two-phase bubbly flow to minimize accumulation of foulants among the fibers in a submerged system to mitigate this issue.

- Capital Cost: Submerged configurations have a slight cost advantage over pressurized configurations when only the equipment supplied by the membrane supplier is considered. Submerged systems lack pressure vessels and the plumbing is simpler, but tankage must be supplied by the constructor. Additionally, submerged system will need covers over the cells and ventilation systems to avoid chemical fuming and other issues particularly during cleaning that are not a concern with pressurized systems.

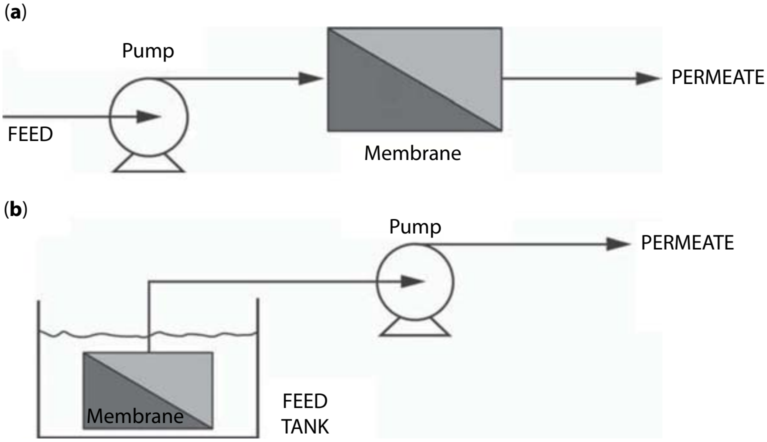


Figure 16.9 (a) Pressurized and (b) submerged hollow fibers systems.

Table 16.4 Comparison of pressurized and submerged hollow fiber MF and UF systems.

Parameter	**Pressurized Configuration**	**Submerged Configuration**
Operation	• Dead-end or Cross-flow • Outside-in, Inside-out	• Dead-end or Cross-flow • Outside-in
Flux	• Flexible	• Limited up-turn in flux
Cleaning	• Less chemical • All chemicals contained in modules & piping	• More Chemical • Limited to soaking rather than recirculation • Covers and ventilation required over cells
Fouling Control	• Moderate to Good	• Moderate to good
Capital Cost	• Moderate to Low	• Low
Integrity testing	• Excellent ability to identify defective module	• Identification of defective module is different and requires removing covers

While submerged applications generally use hollow fibers, flat sheets, and more recently, spiral wound modules have come into use in submerged systems. In general, pressurized and submerged systems compare favorably, with the submerged configuration enjoying a slight cost advantage, particularly for larger systems. Both configurations are used as pretreatment to RO with success.

It is important to take into account permanent fouling of the MF or UF membranes by over designing the system. Despite the dense surface of these membranes, pore fouling can occur, particularly at higher membrane driving pressures (typically caused when the system is operated at high permeate flux or high trans-membrane pressure (TMP)). Under constant pressure, MF and UF membranes can lose 50%–75% of water flux between backwashes. Pilot testing is necessary to determine the degree of permanent fouling as well as the backwash and air scour frequencies and the chemical programs that are required. Pilot testing is particularly important in colder climates where the seasonal range for temperature is great, as temperature affects the flux through the membranes (higher temperature leads to higher flux and, conversely, lower temperature leads to lower flux in a manner similar to RO membranes).

As discussed in Chapter 8.1.9, MF and UF membranes can delay the onset of microbial fouling of RO membranes, but by themselves are not fully effective. These membranes are not 100% effective at removing biologics from feed water. Further, nutrients, in the form of low-molecular weight organics, can pass through these membranes such that any microbes in the RO feed water will lead to microbial fouling. Therefore, the use of chlorine is recommended in conjunction with these membrane processes to minimize the potential for microbial fouling of RO membranes.

16.1.1 Microfiltration

Microfiltration is a pressure-driven membrane separation technology used to separate particles from solution (see Figure 1.1). This technology uses microporous membranes with pore sizes ranging from about 0.1 up to about 3 microns. However, due to particle adsorption onto the surface of the pores, and the collection of particles on the top of the membrane (both of which serve to block pores), MF membranes can often remove particles smaller than the rated pore size.[4] Microfiltration cannot, however, removal all colloidal material because colloids can be as small as 0.01 microns in diameter (see Table 7.2).[5] Since MF membranes do not reject ions, osmotic pressure is not a concern as it is with RO systems. Typical operating pressures for MF systems range from about 10–100 psi with 30–40 psi being typical. Industrial flux rates are up to 100 gfd, depending on the nature of the feed water.

Applications of MF include:

- Water treatment—removal of suspended solids, including up to 4-log removal of bacteria (a major application growth area[1]),

- Wastewater treatment—biomass sedimentation using membrane bioreactors (MBRs), tertiary treatment of municipal waste for reuse,
- Food & beverage treatment—clarification of liquids (fruit juices, beer),
- Resource recovery—recovery of inks, textile sizing agents, and electrodeposition paints.

Microfiltration as pretreatment to RO is used for bulk removal of suspended solids and bacteria. Microfiltration is a barrier technology that can in many cases replace conventional clarification and filtration. Advantages of MF over conventional clarification and filtration include the following:

- Minimal need for treatment chemicals—coagulants, flocculants, acid or caustic (coagulants are used when organic removal is required),
- Consistent effluent quality, regardless of raw feed water quality,
- Compact system,
- Simple automation—minimal operator attention required.

See references 1, and 6–8 for more detailed discussions about microfiltration.

16.1.2 Ultrafiltration

Ultrafiltration is a pressure-driven membrane separation technology used to separate particles and high-molecular-weight soluble species from solution. Ultrafiltration also uses microporous membranes with a pore size distribution of 0.005 to 0.1 microns, which is smaller than the pore sizes for MF (see Figure 1.1). In general, because of the smaller pores, the operating pressure required for transport through a UF membrane is greater than that for an MF membrane, generally up to 150 psi with 30–75 psi being typical (some UF membranes, such as the Pentair–Norit PES membrane, require a very low net driving force of 1.5–2.0 psi on clean membranes assuming proper flux selection). Typical industrial flux rates for UF range from 5 to 70 gfd, depending on the nature of the feed water.

As discussed above, UF membranes have smaller pores than MF membranes indicating that their rejection of suspended solids and bacteria are greater or "tighter" and that for MF. For example, the California Department of Public Health gives UF membranes a 4-log removal credit for viruses, while MF typically receiveds only a 0.5 log-removal credit for viruses. Species that are retained by a UF membrane are typically defined as those whose molecular weight is greater than the molecular weight cut off (MWCO) of the UF membrane. The MWCO of a UF membrane describes the ability of that membrane to retain 90% of a challenge macrosolute (such and glycol, dextran, or protein)[9]. There is no international standard for MWCO, so that membranes from different manufacturers cannot be directly compared on the basis of MWCO only.

Applications of UF include:

- Food & beverage—recovery of proteins for milk and whey, sugar concentration of fruit juice, removal of bacteria and suspended solids and organics from bottled drinking water,
- Wastewater—removal of free oil,
- Municipal water—removal of bacteria and large viruses from potable water and wastewater for reuse.
- RO pretreatment—reduction in concentration of suspended solids and high molecular-weight organics.

The application of UF for RO pretreatment is growing, as users are interested in reducing the size of their treatment facilities and reducing or eliminating chemical treatments. Although capital cost is an issue, UF can be cost effective when used to remove bacteria and dissolved high-molecular weight organics from RO feed water and as a polisher for reduction of suspended solids and silt density index. Ultrafiltration in the tubular configuration can also be used for bulk removal of suspended solids and higher molecular weight dissolved organics prior to RO. Ultrafiltration is a barrier technology providing consistent effluent quality including 6-log bacterial removal and SDIs typically less than 2 (turbidity less than 0.02 NTU). Ultrafiltration prior to RO is commonly seen in the production of bottled drinking water, even when potable water is used as the make-up source. Figure 16.10 shows a water treatment process flow diagram for a typical beverage facility.

See reference 1 and 6–8 for more detailed discussions about ultrafiltration.

16.2 Nanofiltration

Nanofiltration (NF) is a pressure-driven membrane separation technology used to separate ions from solution. Nanofiltration membranes were widely available beginning in the 1980's. This technology uses microporous membranes with pore sizes ranging from about 0.001 to 0.01 microns.

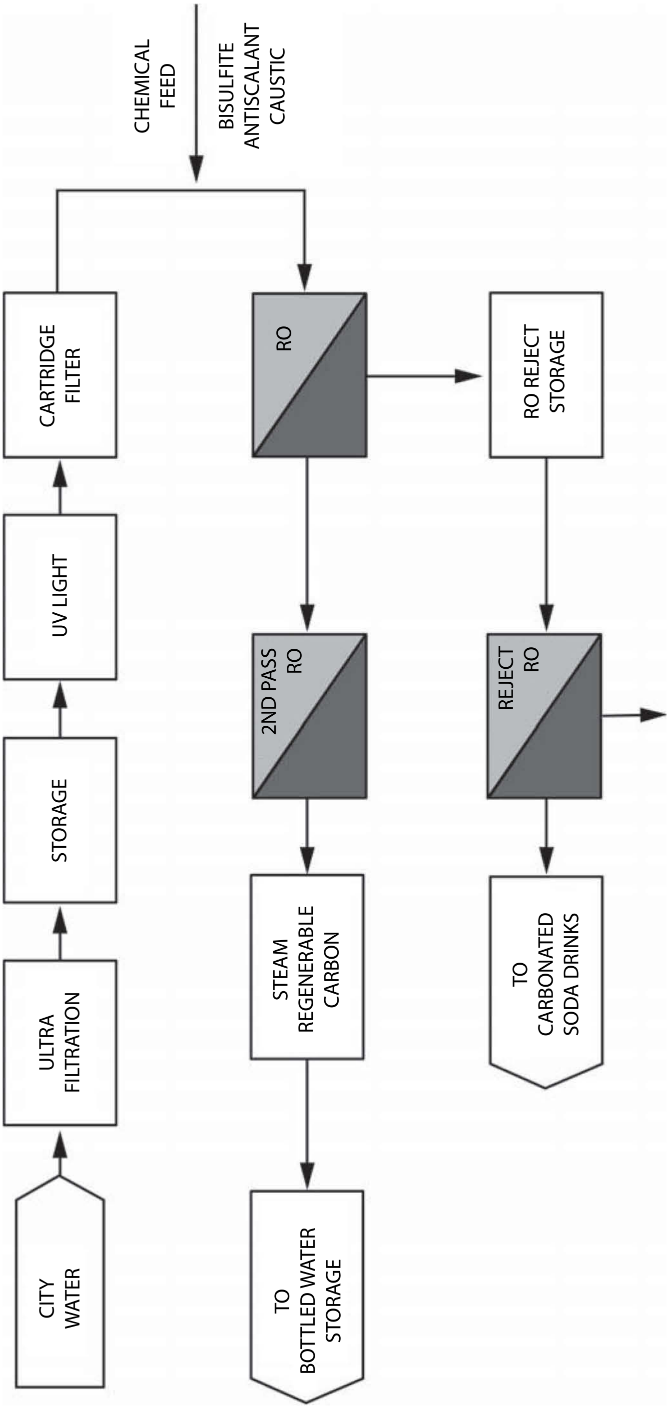


Figure 16.10 Typical water treatment process flow diagram for a beverage facility producing both bottled water and carbonated soda drinks.

Nanofiltration is closely related to RO in that both technologies are used to separate ions from solution. Both NF and RO primarily use thin-film composite, polyamide membranes with a thin polyamide skin atop a polysulfone support (see Chapter 4.2.2.2).

Figure 16.11 shows the chemistry of a typical Dow-FilmTec nanofiltration membrane. Compare this polymer to that of common RO membrane polymers, a shown in figure 4.10. Both chemistries contain free amines and carboxylate end groups. The difference is in the nature of the rings. Reverse osmosis membranes have aromatic ring (C_6H_3), while the NF membranes have a piperazine ring ($C_4H_{10}N_2$ in a 6-member ring with the 2 nitrogens in opposition). The effects of different dissociation constants for piperazine along with the use of trace additives allow NF membranes to be designed with a wide range of salt selectivities.

Nanofiltration is sometimes called "loose RO" or "leaky RO" because of its similarity to RO; the exception is that NF membranes allow more ions to pass through than an RO membrane.[10] Because of the lower rejection of dissolved solids, the increase in osmotic pressure is not as significant with an NF system as it is with RO. Thus, NF operates at lower pressure than RO, typically 50–150 psi. Nanofiltration falls between RO and UF on the filtration spectrum shown in Figure 1.1. Table 16.5 compares the general differences in rejection of species between NF and RO membranes.

As shown in the table, NF membranes offer a wide selection of rejection capabilities. In general, rejection of divalent ions is greater than that for mono-valent ions for NF membranes, particularly for the "loosest" of NF membranes. Reverse osmosis membranes, on the other hand, exhibit high rejection of both mono-valent and divalent ions (although rejection of divalent ions is also greater than that of mono-valent ions—see Chapter 3.3). The addition of trace additives and the different dissociation constants of the piperazine found in the FilmTec NF membrane (Figure 16.11) is used to yield the wide range of solute transport through this membrane.

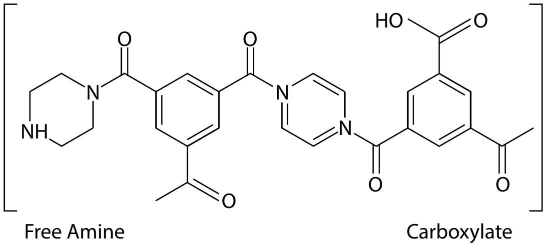


Figure 16.11 Structure of a typical nanofiltration membrane.

Table 16.5 Rejection of ions exhibited by NF and RO membranes.

Species	Nanofiltration Rejection (%)	Reverse Osmosis Rejection* (%)
Calcium	75–98	93–99
Magnesium	70–98	93–98
Sodium	45–95	92–98
Chloride	1–95	92–98
Sulfate	95–99	96–99
Bicarbonate	40–95	85–95
Fluoride	25–95	92–95
Silica	5–95	90–98
Total Dissolved Solids	65–95	90–98

*Polyamide composite membranes

In simple terms, nanofiltration membranes reject species based on size or charge of the particle, depending on the charge of the membrane itself.[1,11,12] For example, cationic NF membranes have negatively charged groups attached to the polymer backbone and consequently, sulfate, which is negatively charged, is rejected to a greater extent by an cationic NF membranes than calcium, which has a larger hydrated radius but is positively charged.[1,11] This is a result of the negative charge on the membrane repulsing the negatively-charged sulfate ion (Donnan exclusion effect). The same principle applies to anionic membranes and cationic species.

Fouling and scaling mechanisms are similar for spiral-wound NF and RO membranes. In general, NF feed water should meet the following characteristics to prevent fouling with suspended solids (refer to Table 7.1 for a more detailed description of spiral-wound RO feed water requirements):

- SDI < 5 (< 3 is preferred)
- Turbidity < 1 NTU (< 0.5 NTU is preferred)

Hence, traditional spiral wound NF membranes require the same level of pretreatment as spiral-wound RO membranes, as well as the same flux and flow rate considerations with respect to feed water quality (see Chapters 9.4 and 9.9).

New generation NF membranes have been developed that exhibit lower fouling tendencies, making them applicable to high organics and high-color applications.[11] While conventional RO and NF membranes have a rough surface and a negative or positive surface change, these new NF membranes have a smooth surface and more neutral surface charge, making them more resistant to organic fouling. These low-fouling NF membranes can operate with TOC concentrations ranging from 10–20 ppm and color up to 90 APHA units.[10] Examples of these new NF membranes include the Hydranautics' ESNA1-LF, LF2, and LF3.

Applications of NF include:

- Water treatment—water softening and color removal for potable water applications
- Wastewater treatment—color removal from pulp and paper wastewater
- Resource recovery—recovery of valuable, lower-molecular weight products in the drug, semiconductor, textile, metal-plating, and food industries.[9]

For RO pretreatment, NF is typically used to pre-soften and reduce color from RO feed water (when appropriate NF membranes are employed). Nanofiltration replaces sodium softening (for hardness removal) and augments clarification (for color removal).

16.3 Forward Osmosis

Forward osmosis (FO) is a process used to separate dissolved solids from water. Forward osmosis, also called direct osmosis (DO) or simply "osmosis," relies on the osmotic pressure differential, $\Delta\pi$, across the membrane to drive the transport of water through the membrane, in contrast to RO and NF, where the driving force is based on the hydraulic pressure differential across the membrane to drive the separation. Osmosis is a natural phenomenon that, while known for hundreds of years, has only recently been examined for everything from wastewater and landfill leachate processing to desalting seawater and purifying water for emergency use. A variation of FO, called pressure-retarded osmosis (PRO), has also been developed to produce electricity by converting the osmotic pressure of seawater into hydrostatic pressure.

Osmosis is the naturally-occurring process wherein water preferentially transports across a selectively permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential (see Figure 16.12). In other words, water moves from a region of low

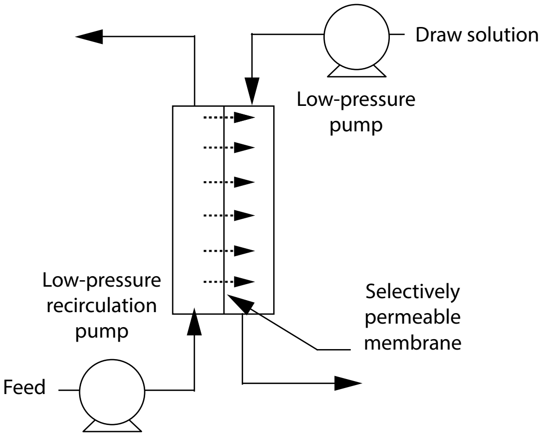


Figure 16.12 Forward Osmosis: Feed water flows on the active side of the membrane, while the draw solution with high osmotic pressure flows on the support side of the membrane. Water passes from the feed side of the membrane into the draw solution.

solute concentration to a region of high solute concentration in an effort to equalize the concentration on both sides of the membrane, resulting in a more concentrated feed solution and a more dilute "draw solution." It is the concentrated draw solution (also referred to as the osmotic agent, osmotic media, driving solution, osmotic engine, or merely brine)[13] that is the driver for FO. The draw solution must have a higher osmotic pressure than the feed solution being treated. Draw solutions that have been considered or used include sodium chloride, seawater (e.g., Dead Sea water), glucose, potassium nitrate, sulfur dioxide, and an ammonia/carbon dioxide solution,[14] to name a few.[13]

Recovery of the draw solution is key to minimizing brine discharge from a continuous-flow FO process. In a continuous flow process, the draw solution is repeatedly cleaned and reused on the permeate side of the membrane. Studies have shown that the recovery of the draw solution used for seawater desalination required significantly more energy than direct desalination of seawater with RO.[15] Figure 16.13 shows an ammonia/carbon dioxide FO desalination process wherein another desalination technique [e.g., membrane distillation (MD)] is used to clean and recover the draw solution.[14] In this process, water is removed from a seawater feed solution using an ammonia/carbon dioxide draw solution, which in turn becomes diluted. Heating of the diluted draw solution yields free ammonia and carbon dioxide. Fresh water can be separated from the dilute draw solution by several separation methods, including RO and MD, wherein gases are removed as distillate, leaving behind fresh water. The distillate is

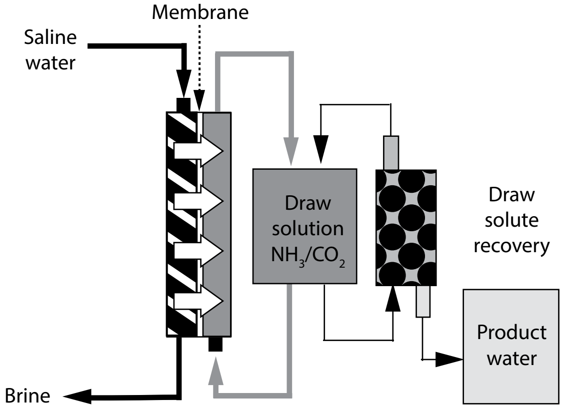


Figure 16.13 Example of a continuous forward osmosis application with recovery and recycle of the draw solution.

now re-purified draw solution, which can be reused to treat more seawater. Work has demonstrated that driving forces of up to 2450 psi (238 bar) can be achieve for seawater with a concentration of 0.05 *M* NaCl, and a driving force of 1800 psi (127 bar) can be achieved for a 2 *M* NaCl feed solution.[13,14] Salt rejection of over 95% and fluxes as high as 14.7 gfd were achieved at driving forces of 2900 psi (200 bar).[16] Note that the experimental water flux divided by the theoretical water flux (known as the "performance ratio") for the membrane used was typically 5% to 10%; thus the actual flux was much lower than the expect flux. This is attributed to concentration polarization within the membrane material.[13]

The draw solution in batch FO applications is not reused; therefore, this type of process lends itself to single-use or "end use" type applications such as osmotic pumps for drug delivery or source water purification using hydration bags.[13]Figure 16.14 shows a HydroPack™ emergency hydration bag developed by Hydration Technologies, Inc. for field use.[17]

Pressure-retarded osmosis (PRO) is a variation of FO that has been evaluated since the early 1960's;[13] it was first patented by Sidney Loeb in 1973.[17] A comparison of PRO to RO and FO is shown in Figure 16.15. The primary difference between PRO and RO is that the applied pressure for RO is greater than the osmotic pressure, while for PRO the applied pressure is less than the osmotic pressure, thus water still diffuses to the more saline draw solution, thereby increasing the volume of the draw solution flow. This flow is then coupled to a turbine to generate electrical power (see Figure 16.16). Power that is generated using PRO is known as "osmotic

Figure 16.14 HydroPack from Hydration Technologies, Inc.[16]

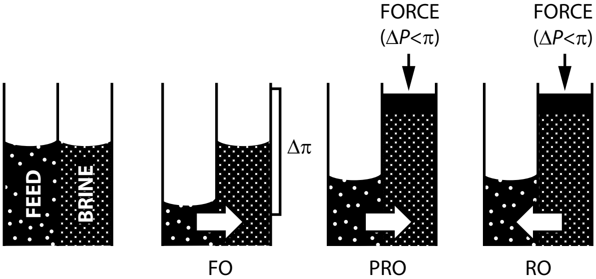


Figure 16.15 Water transport in forward osmosis, pressure-retarded osmosis, and reverse osmosis.

power." Although the PRO process was patented in 1973, the first osmotic power facility was not opened until 2009 by the Norwegian public power company, Statkraft.[19] However, this facility was merely a prototype through which Statkraft hoped to demonstrate high enough efficiency in the process to make it competitive with current technologies by 2020.[20] In December, 2013, Statkraft announced that it was discontinuing its efforts along these lines and was leaving "…the technology development to other players in the global market".[19] The technology, according to Statkraft, would not be developed sufficiently "…to be competitive within the foreseeable future".[20]

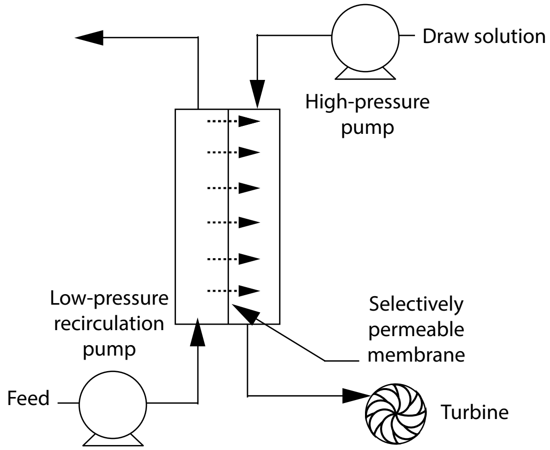


Figure 16.16 Pressurized draw solution in pressure-retarded osmosis serves to drive a turbine to produce electricity.

Nevertheless, research is continuing along the lines of pure FO, if not PRO. The membranes used for successful FO require the following:[13]

- A high-density layer that will achieve high rejection.
- Hydrophilic characteristics to improve flux.
- Overall membrane thinness also to improve flux.
- Mechanical strength for PRO applications.

In essence, the same characteristic that make for successful RO membranes, high flux and high rejection, are also necessary for successful FO. From the 1960's through the 1980's, RO membranes were used for FO testing. However, lower than expected flux was observed for RO membranes used for FO applications. This was due to several variations of concentration polarization occurring within the composite structure of an RO membrane.[13] Then, in the 1990's, Osmotek, Inc. (Albany Oregon) [now Hydration Technologies, Inc. (HTI)] developed a proprietary membrane purported to be made of cellulose triacetate (CTA). Unlike composite RO membranes, which consist of a very thin (less than 1 micron) active film on a relatively thick microporous support layer (making the overall thickness of the membrane 40–80 microns), the HTI membrane is without the porous support layer. Instead, a polyester mesh is embedded within the CTA membrane for support; the overall thickness of the CTA/polyester mesh coupling is less than 50 microns. Thus, a fabric support is also not needed for the HTI membrane. Figure 16.17 shows the difference between

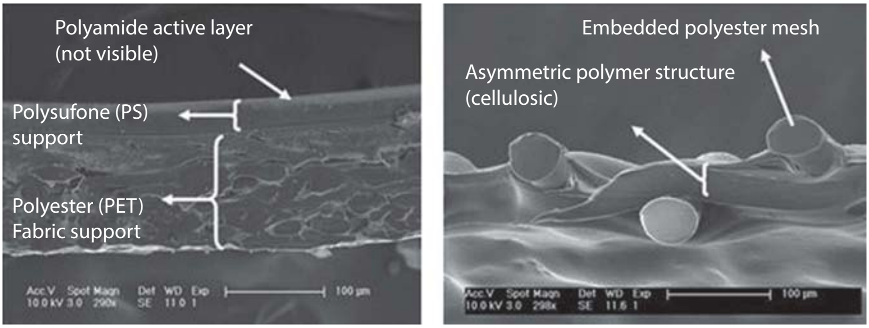


Figure 16.17 Scanning electron micrographs of a representative RO TFC membrane (left) and the HTI FO membrane (right).[20] Courtesy of Scrivener Publishing.

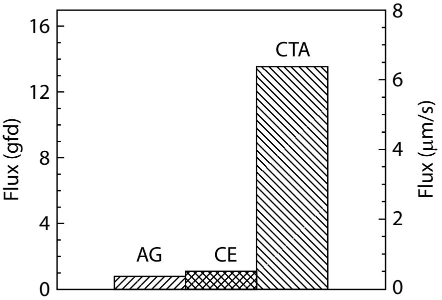


Figure 16.18 Flux performance of 2 commercially available RO membranes from GE Water (AG, CE) and a cellulose triacetate forward osmosis membranes from Hydration Technology Innovations (CTA). The draw solution used was a 6M ammonia-carbon dioxide solution and the feed solution was a 0.5M sodium chloride solution. The temperature of the test was 50°C. Reprinted from REF16-B7. Tests were done in a custom built, crossflow, benchtop FO testing system.

a standard thin film composite RO membrane and the HTI FO membrane. The HTI membrane has shown improved performance over RO membranes for FO applications, as shown in Figure 16.18. This is presumably due to the relative thinness of the membrane and its lack of a fabric support layer.[13]

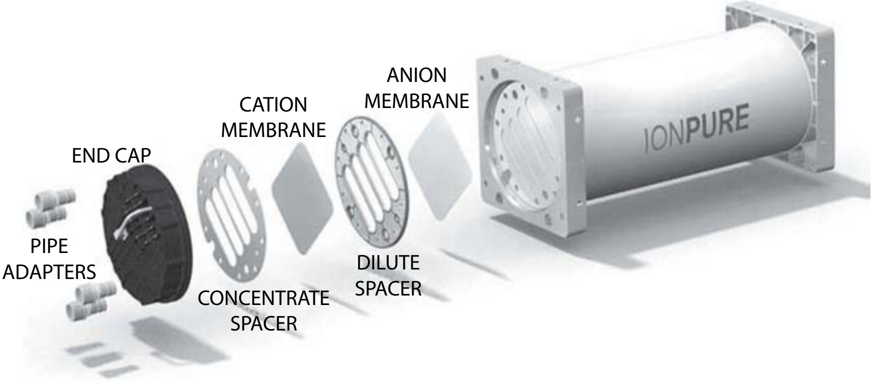
The use of FO has been investigated for several applications. These include seawater desalination, food processing, and osmotic pumps for drug delivery. For the majority of applications investigated, the lack of high performance membranes (i.e., membranes that exhibit high permeability, high selectivity for water over solutes, low tendency for concentration polarization to occur, and high mechanical strength) for continuous-flow processes and the need for a draw solution with high osmotic pressure that can be easily reconstituted (i.e., draw solutions that require low energy for reconstitution and can be easily separated from the pure water that is generated) are limitations that currently hinder wider spread application of FO.[13] To date, hydration bags for emergency military or recreational uses, and the PRO to produce osmotic power, are the few commercial applications of FO. However, on April 7, 2014, four FO companies [Modern Water (UK), HTI (USA), Trevi Systems (USA), and Porifera (USA)] have banded together to form the International Forward Osmosis Association (IFOA) to advance the technology on a global basis.[22] The objectives of the IFOA are to:

- Advocate for global understanding and acceptance of the technology;
- Establish industry standards for the technology;
- Provide a professional network for information exchange;
- Be a single industry voice between the membership and the general public;
- Promote cooperation between industry and government for standards and regulations for the technology.[23]

16.4 Continuous Electrodeionization

Continuous electrodeionization (CEDI—the continuous process subset of electrodeionization (EDI) that is sometimes referred to as just continuous deionization or CDI® (CDI is a registered trademark of Evoqua)) is an electrically-driven membrane separation technique under development since the mid-1950's and successfully comme rcialized in the late 1980's.[24] Continuous electrodionization is used to remove trace dissolved solids from water. This technology relies on a D. C. current that is applied to cation and anion-exchange membranes with ion exchange resin arranged in a "stack" configuration to effect the separation of solutes from water.

Figure 16.19 shows the expanded view of a conventional, stacked-disk plate-and-frame CEDI module (stack). Inside one end of the module is the cathode and inside the other end is the anode. Between the cathode and anode are layers of flat-sheet cation- and anion- exchange membranes separated by spacers that act as alternating diluting (product) and concentrating (reject) compartments. Resin is placed in the diluting compartments, as shown in Figure 16.20a. Note that in the newer "all filled" configurations, all compartments are filled with ion exchange resin as shown in Figure 16.20b. An electrical potential is applied to the stack (100–600 volts DC at 3–10 amps) that drives ions toward the respective cathode or anode. (The amount of current drawn from the power supply is



VNX Electrodeionization
(Ion Exchange Resin Not Shown)

Figure 16.19 CEDI stacked-disk, plate-and-frame configuration. *Courtesy of Evoqua—Ionpure Products.*

proportional to the concentration of ions in the solution. Typically, 4 ppm feed to a CEDI system will draw about 3 amps.[25]) Cations pass through the cation-exchange membranes but not through the anion-exchange membranes, while anions pass through the anion-exchange membranes but not through the cation-exchange membranes. (Note that the ion exchange membranes are not permeable to water; only ions are transported through them.) In this manner, every other compartment becomes dilute in ions while the other compartments become more concentrated in ions. The ion exchange resin facilitates the transfer of ions in low ionic-strength solutions.

Figure 16.21 shows a typical process flow diagram for an all-filled configuration, while Figure 16.22 shows a typical process flow diagram for an unfilled configuration with concentrate recycle. Recycle is used to achieve higher recovery while maintaining good velocity through the concentrating compartments. The concentrate recycle also increases the concentration in the concentrated compartment, thereby reducing the resistance of the stack to the DC current. In some cases, brine injection is used to supplement the concentration recycle, particularly where the ionic concentration of the feed water is very low. The all-filled configuration does not need brine recycle or brine injection. This results in lower capital cost for the all-filled configuration, as the brine recirculation and brine metering pumps and associated piping are eliminated. All-filled configurations offer less electrical resistance and suffer less salt bridging than the unfilled configuration (see discussion on salt bridging below).

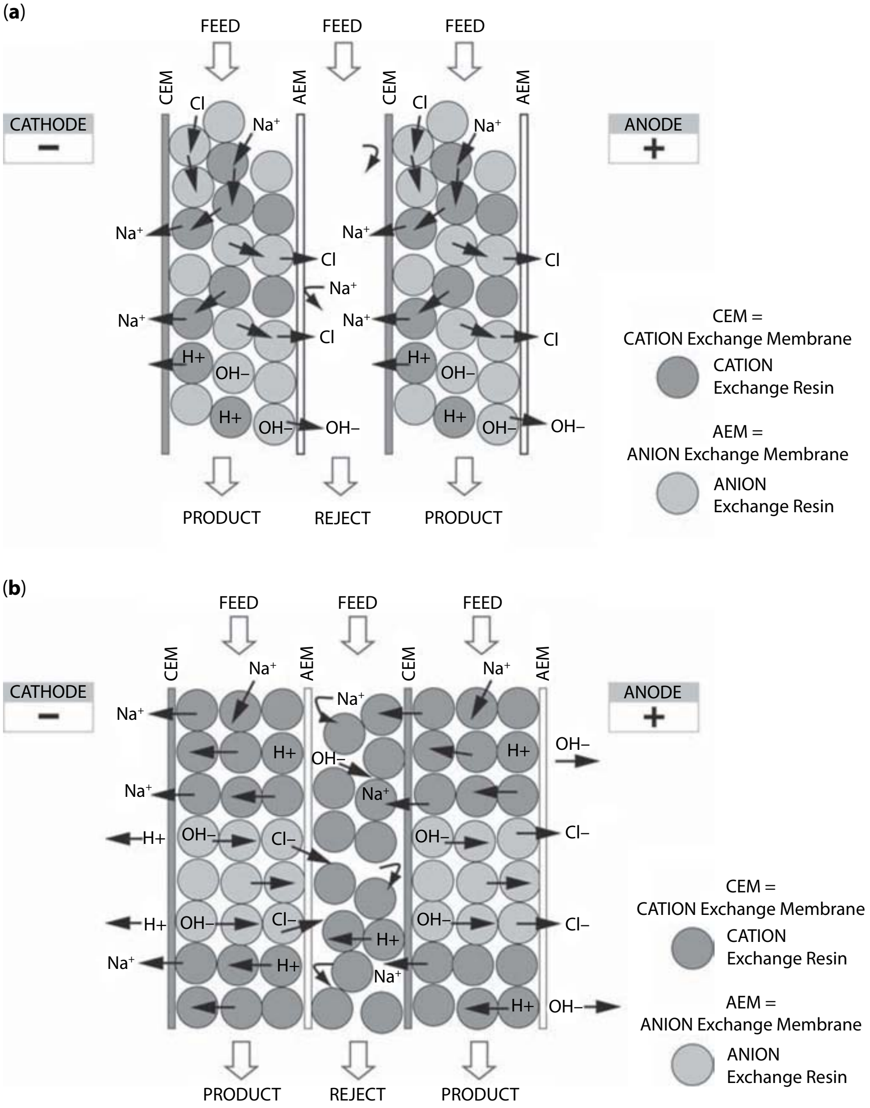


Figure 16.20 Transport through cation- and anion-exchange membranes in (a) "unfilled" and (b) "all filled" CEDI stacks. *Courtesy of Evoqua—Ionpure Products.*

Equations 16.1 and 16.2 show the reactions at the cathode and anode, respectively. These equations indicate that hydrogen and oxygen gases are produced at the electrodes. Typically, 7.5 ml/min of hydrogen and 2.7 ml/min of oxygen are produced at 25°C and 14.7 psig. Equation 16.3 indicates that chlorine gas may also be generated at the anode. Concentrations of

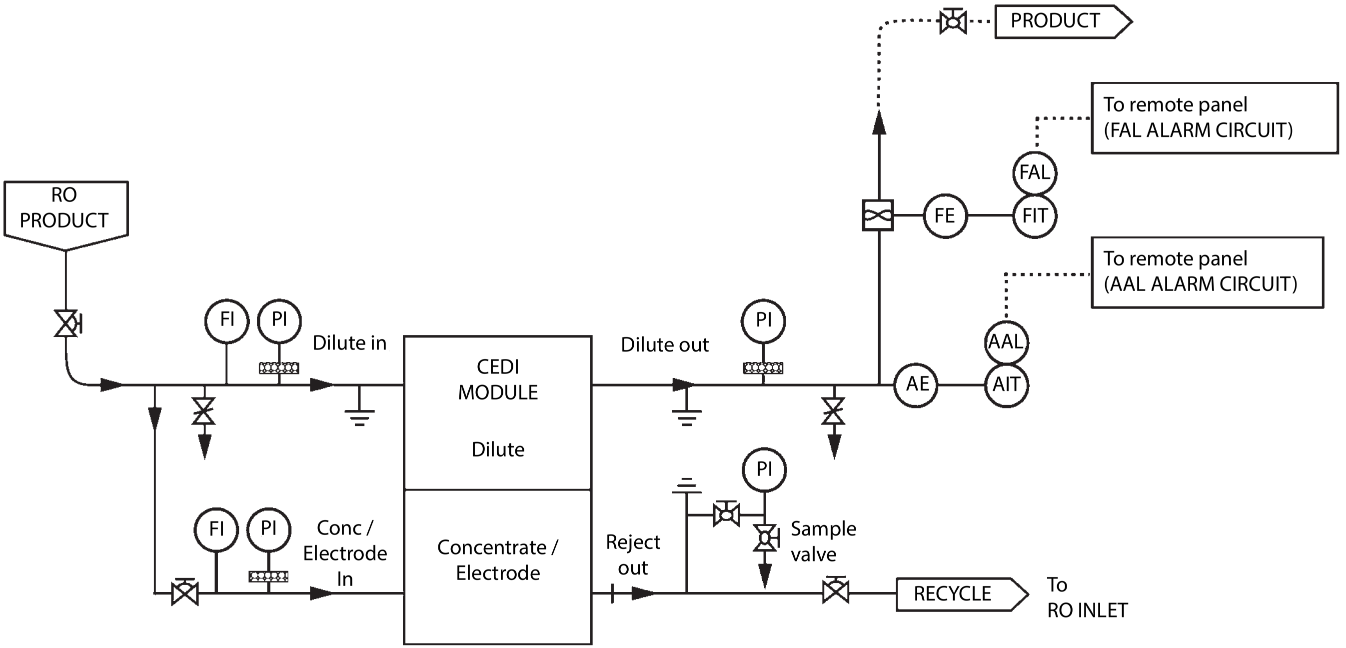


Figure 16.21 Typical process flow diagram for an all-filled CEDI configuration. *Courtesy of Evoqua—Ionpure Products.*

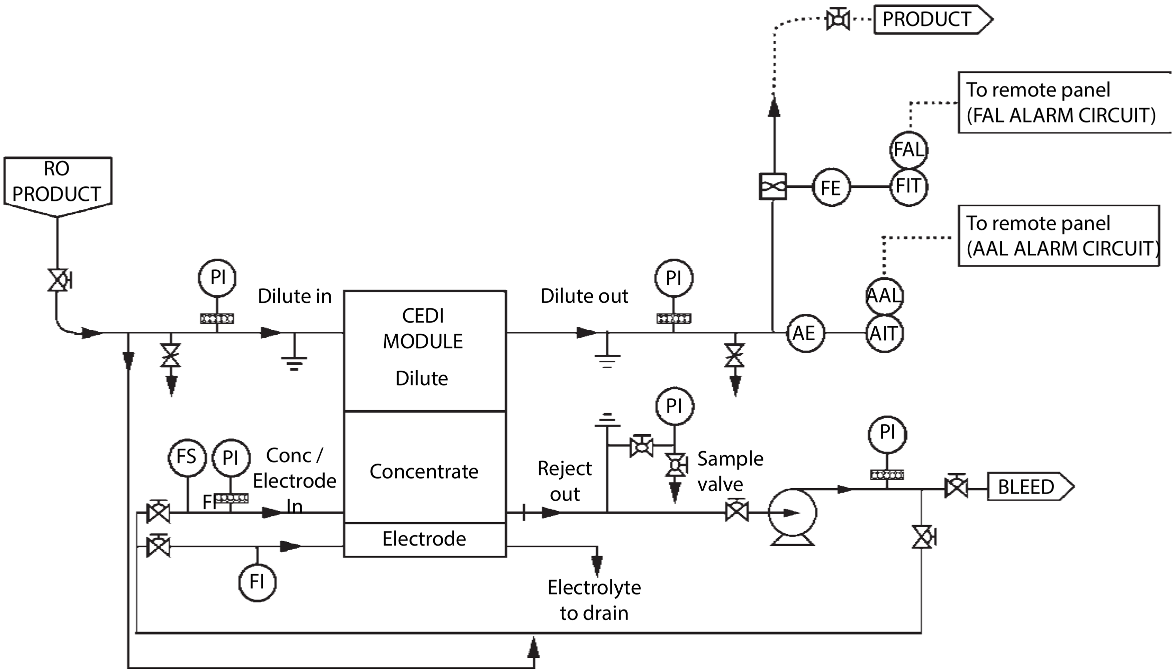


Figure 16.22 Typical process flow diagram for a CEDI configuration with unfilled concentrate spacers. *Courtesy of Evoqua—Ionpure Products.*

chlorine gas range from non-detectable up to 8 ppm, depending on the configuration of the CEDI module and whether or brine injection or concentrate recycle is employed.[26] Chlorine gas is more likely to be generated when more chloride is present in the concentrate compartment, as is the case when brine injection is used. These gases require removal that is usually accomplished using water passing over the electrodes and then venting the gases from this water flush stream.[26]

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \text{Cathode} \tag{16.1}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{Anode} \tag{16.2}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{Anode} \tag{16.3}$$

Some companies market spiral wound CEDI modules, such as the DOW™ EDI spiral wound module (formerly Omexell--DOW is a trademark of Dow Chemical Company, Inc., Midland, Michigan). Figure 16.23 shows the cross section of the Dow module.[27] As the figure shows, RO permeate enters the module on one end, while CEDI effluent exits the other end; concentrate is sent spiraling into the metal center tube of the module and exits out of this

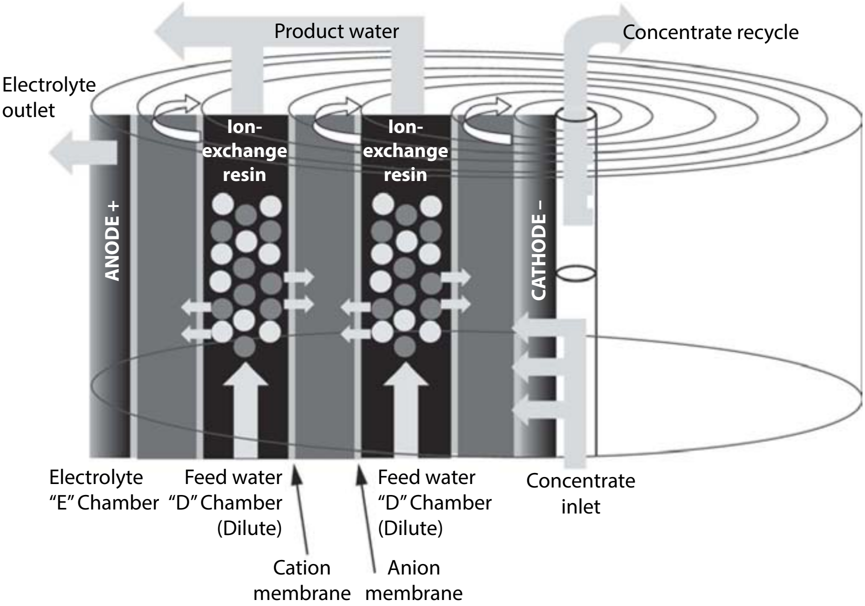


Figure 16.23 Cross-section of a DOW™ EDI—CEDI spiral wound module. *Courtesy of Dow Water and Process Solutions.*

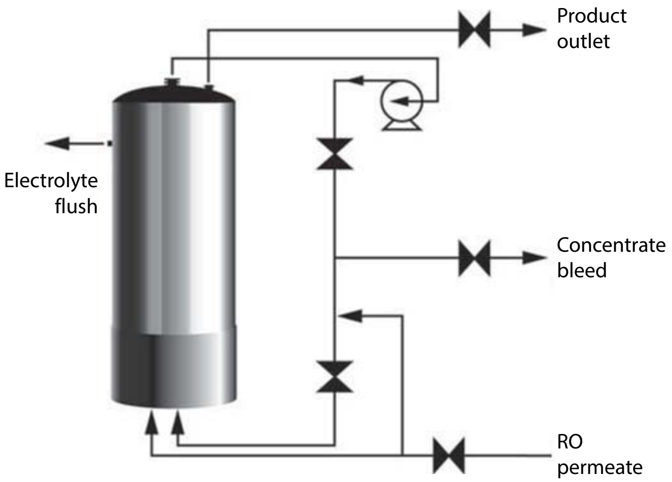


Figure 16.24 Process flow diagram of a spiral wound CEDI module. *Courtesy of Dow Water and Process Solutions.*

tube. A titanium cylinder is placed inside the fiberglass outer shell to act as the anode. The cathode is the metal center tube. In the case of this spiral module, only the diluting compartments are filled with ion exchange resin. Hence, a recycle of the concentrate solution is required. Figure 16.24 shows a process flow diagram of a spiral-wound CEDI module.

The major advantage of the spiral configuration over a plate-and-frame configuration is that there is minimal leakage associated with the spiral configuration. The spiral wound module does not require periodic tightening of nuts and bolts to prevent leaks, unlike plate-and-frame modules. Limitations of the spiral configuration include inferior current and flow distribution relative to plate-and-frame modules, as well as difficulty in assembly and field membrane replacement.[28]

A CEDI system can produce up to 18-megohm-cm water at 90–95% water recovery. Recovery by the CEDI system is a function of the total hardness in the feed water to the system. In general, 95% recovery can be realized at a feed water hardness of less than 0.1 ppm as calcium carbonate.[27]This is typically attained if the pretreatment to the CEDI consists of either 2-pass RO or sodium-cycle softening followed by RO. Recovery that is achievable is a function of the feed water hardness concentration and varies with manufacturer as well. Table 16.6 shows how recovery is a function of feed water hardness for a GE—E-Cell® module (E-Cell is a registered trademark of General Electric Company, Fairfield, Connecticut).[29]

Table 16.6 Continuous electrodeionization recovery as a function of feed water hardness for an E-Cell (GE) module.[28]

Feed Water Hardness (ppm as $CaCO_3$)	CEDI Recovery (%)
< 0.10	95
0.10–0.50	90
0.50–0.75	85
0.75–1.00	80

Continuous electrodeionization systems can achieve 95% rejection of boron and silica, and 99 +% rejection of sodium and chloride. This performance is possible due to voltage-induced dissociation of water that effectively regenerates a portion of the resin thereby allowing removal of weakly ionized species such as silica and boron.[30] In fact, the boron in the effluent from a CEDI system can be lower than that in the effluent from a mixed-bed ion exchange system.[24]

High feed water carbon dioxide is the leading cause of poor product quality in the effluent from a CEDI unit. This is because carbon dioxide is converted to carbonate and bicarbonate within the stack, and thus it contributes to total exchangeable anions. This must be taken into account when designing the system. Carbon dioxide concentrations below 5 ppm can reduce the removal of ions from the feed water, particularly weakly ionized species such as silica and boron.[24]In an effort to account for the carbon dioxide and its draw on the DC current, a "conversion factor" of 2.79 micro-Siemens per centimeter for every 1 ppm carbon dioxide is added to the measured conductivity of the feed water to the CEDI unit.[30] Carbon dioxide can be removed prior to the CEDI system using a membrane degasification system such as a Membrana Liqui-Cel® membrane contactor (Liqui-Cel is a registered trademark of Celgard LLC, Charlotte, NC) thereby minimizing the power required by the CEDI system and improving the removal efficiency of other ions.

Note that silica, is weakly ionized and will also contribute to the draw on DC current. A conversion-factor of 1.94 micro-Siemens per centimeter for every 1 ppm silica is added to the measured conductivity of the feed water to account for this. Although the conversion factor is greater for silica than for carbon dioxide, silica has much lesser effect on the DC current draw than carbon dioxide because of the relatively low concentration of silica in CEDI feed water as compared to carbon dioxide.

A significant amount of pretreatment is required to minimize fouling and scaling of the membranes in a CEDI system. Table 16.7 lists general feed water quality requirements for CEDI systems.[26,32] Due to the stringent feed water quality requirements, most CEDI systems are preceded by RO. Common configurations used to pretreat CEDI feed water include the following:[26] Note that 2-pass RO is preferred for pretreatment.

- Antiscalant → RO
- Softening → RO
- Antiscalant → RO → softening
- Antiscalant → RO → RO (preferred)

Table 16.7 General feed water quality requirements for CEDI systems. Adapted from specification sheets for various manufacturers.

Constituent	**Typical Feed Quality**	**Units**
Total Exchangeable Anions (TEA)	< 25	ppm
Total Hardness	< 0.5*	ppm $CaCO_3$
Iron, Manganese, Hydrogen Sulfide	< 0.01	ppm
Silica (soluble)	< 0.5 (some up to 1.0)	ppm
Conductivity	< 65	micro-S/cm
pH	5–9 (range 4–11)	
Free Chlorine	< 0.05	ppm
Other Oxidizing agents	ND**	ppm
Carbon Dioxide	< 10	ppm
Total Organic Carbon (TOC)	< 0.5	ppm
Oil & Grease	ND**	ppm
Color	< 5	APHA
SDI	< 1.0	
Turbidity	< 1.0	NTU
Temperature	35–113	°F
Pressure	25–100	psig

*See Table 16.6

**None detectable

Because of the high-quality feed water sent to a CEDI system, the concentrate from the CEDI is very low in dissolved solids and is often recycled to the influent of the RO system. This reduces the overall waste generated by the system and increases the water quality to the RO through dilution of the source water.

Despite efforts to comply with the limitations on feed water quality, CEDI systems can still foul and scale with microbes, organics, iron and manganese, and calcium- and silica-based scales. This usually occurs due to upsets in the pretreatment system or a deficiency in the system design that result in excursion in feed water quality to the CEDI system. Organics, metals, hardness, and silica problems are usually found on the membranes and sometimes on the resin (as is the case with organics). Biofouling is typically found on the concentrate spacers outside of the electric field.[26] Systems with recirculating concentrate experience greater biofouling issues than the once-through (all-filled) systems.[26]

If the membranes do foul or scale, they can often be cleaned. A typical cleaning frequency is once per year. Cleaners include

- *Sodium chloride/sodium hydroxide mixture*: used for organic fouling in a manner similar to a "brine squeeze" of anion resin
- *Hydantoin (Halane)*: used for microbial fouling— should be used infrequently
- *Peracetic acid*: used as a sanitizing agent to prevent microbial fouling
- *Sodium carbonate/hydrogen peroxide mixture*: used for removal of biofilm
- *Hydrochloric acid*: used for scale
- *Sodium hydroxide*: used for microbial fouling and silica scale

Consult with the vendor for details on how to properly clean specific CEDI systems. Most CEDI systems can handle temperatures up to 45°C during cleaning (see Table 16.7). Some CEDI units may be heat sanitized at up to 80°C.

Continuous electrodeionization systems can also suffer mechanical failure, including salt bridging and electrical arcing. Salt bridging occurs when leaks, such as water wicking out of membrane edges that are left exposed to the environment, evaporate and leave behind salts. The amount of salt can build up until bridging occurs. This provides another path for the DC current, leading to arcing and module damage.[26]

The system can also degrade due to exposure to free chlorine. Note that this problem is usually encountered when chloramines are feed to the RO. In such cases, the amount of free chlorine in the RO product can be greater than that in the feed due to the equilibrium of chloramine with free chlorine- see equation 8.10. Hence, total chlorine must be removed prior to the RO membranes before it even gets to the CEDI system.

Continuous electrodeionization is primarily used as an alternative to ion exchange. Because of the extensive pretreatment required by CEDI systems, the technology has grown into a polisher for RO (see Figure 16.25). Continuous deionization can achieve mixed-bed water quality of RO permeate without the need to store and handle acid, caustic, and regeneration waste associated with conventional ion exchange. As a result, CEDI systems take up less space than traditional ion exchange that is equipped with regeneration equipment. Costs for CEDI systems have also decreased relative to mixed-bed ion exchange, as shown in Figure 16.26.

The pharmaceutical industry lead the way in adoption of CEDI for the production of ultrapure water. Since the early 1990's, the power industry has been employing CEDI as a polisher for RO effluent for steam generation. Other industries currently using CEDI include general industry for boiler make-up or high-purity process applications, including semiconductor manufacture. Commercially-available industrial CEDI modules range in size from less than 1 gpm to 80 gpm.

Manufacturers of CEDI modules include:

- Evoqua (Ionpure®)
- GE (E-Cell®)
- Dow Water and Process Solutions (Omexcell)
- Snowpure (Electropure™)
- Christ Water Technology Group (Septron®)
- Millipore (Elix®)
- Agape Water

16.5 HERO™ Process

High efficiency reverse osmosis (HERO) is a patented process (US Patent # 5925255, Debasish Mukhopadhyay, 1999) originally developed to treat high silica water for the microelectronics industry. Its use has expanded to power and zero liquid discharge applications (see Chapter 15.4.3). Features of the process include:

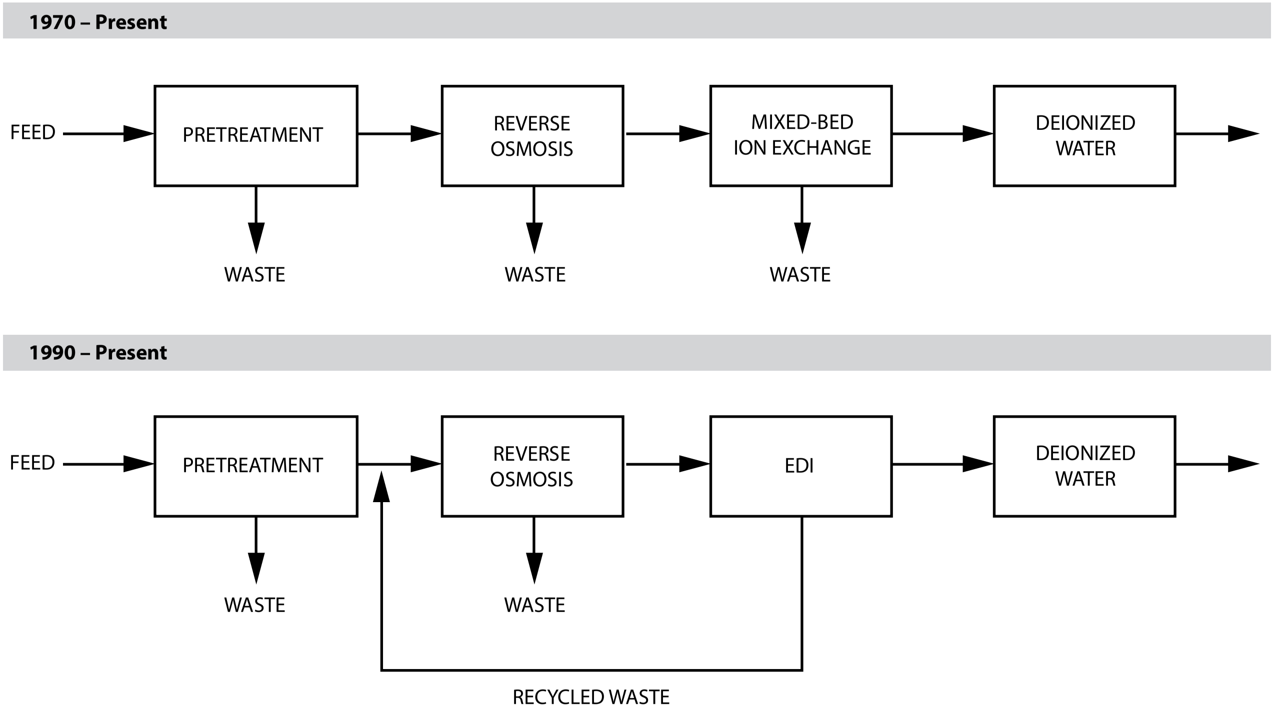


Figure 16.25 Evolution of membrane deionization.

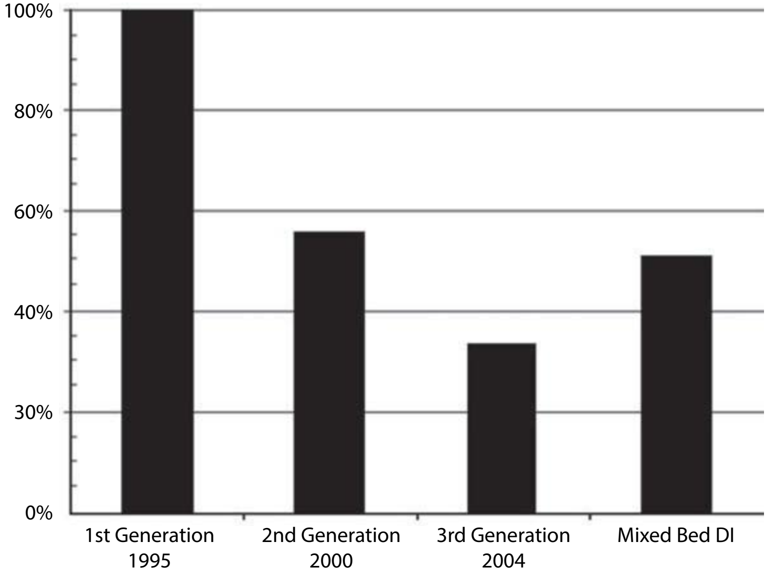


Figure 16.26 Costs of CEDI systems relative to mixed-bed ion exchange systems that follow improvements to CEDI technology. Assumes 120 gpm system. *Courtesy of Evoqua—Ionpure Proudcts.*

- High water recovery, typically 90–95%
- High rejections of species, including weakly ionized compounds such as boron and fluoride
- Significant reduction in membrane fouling from organics and microbes

The HERO process includes the following process steps:

- Hardness/bicarbonate alkalinity removal
- Dissolved carbon dioxide gas removal
- Caustic addition to pH 10–10.5

Figure 16.27 shows a simplified process flow diagram of a typical HERO process. The preferred method of hardness and bicarbonate alkalinity removal is simultaneous removal in a weak acid cation (WAC) ion exchange unit. Caustic is sometimes added prior to the WAC unit to improve the efficiency of the hardness/alkalinity removal process. Hardness removal via the WAC unit enables the RO system to operate at high recovery without fear of hardness scaling. The exchange of hardness for hydrogen ions in the WAC unit decreases the pH of the water, converting much of the alkalinity to carbonic acid and carbon dioxide. Additional acid is sometimes added

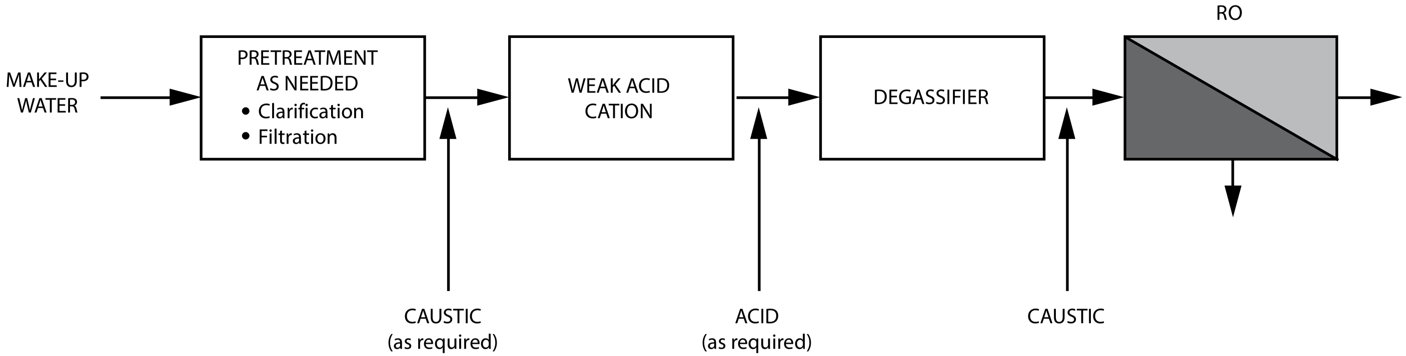


Figure 16.27 Process flow diagram of a typical HERO™ process.

after the WAC unit to complete the bicarbonate alkalinity conversion to carbon dioxide gas. Carbon dioxide is then removed in the degassifier (either conventional or membrane–based). Caustic is added after the degassifier to raise the pH to about 10–10.5 prior to the RO. Raising the pH to this high level does several things:

- Increases the solubility of silica, thereby reducing its tendency to scale. Solubility of silica at ambient temperature and pH 11 (typical reject pH in a HERO system) is greater then 1,500 ppm as compared to a solubility of about 120–160 ppm at pH 8 (see Chapter 7.7 and Figure 7.2, which shows how the silica solubility increases exponentially at concentrate pH greater than about 8).
- Increases the ionization of silica, thereby increasing its rejection by the RO membrane.
- Increases the ionization of weakly ionized species such as boron, fluoride, and organics as TOC, thereby increasing their rejection by the RO membrane.
- Destroys or disables the ability of biological organisms to propagate, thereby minimizing microbial growth on the RO membranes.
- Ionizes organics to organic salts, thereby increasing their rejection by the membrane and decreasing their tendency to foul the membrane.

In many cases, additional pretreatment is required prior to the HERO process. Additional pretreatment can include cold lime softening, sodium softening, and ultrafiltration or microfiltration. These pretreatment unit operations are required when the total hardness is very high and/or the concentration of suspended solids is high.

High efficiency RO is not practical for every-day RO applications due to the relative complexity and high capital and operating cost involved. However, for difficult feed streams that require high recovery, HERO is well suited. Advantages of HERO over conventional RO for these applications include:

- Very high recovery, including high silica feed water
- Less space required due to higher water flux and smaller RO (HERO systems typically operate at 25–30 gfd)[33]
- Reduced membrane cleaning due to the minimization of bacterial growth on the membranes and reduced silica scaling

- Reduced capital cost for larger (great than about 50 gpm) systems due to smaller RO (higher flux rates)[34]
- Lower operating costs due to lower operating energy and fewer specialty chemicals (e.g., antiscalants)

Limitations of HERO for ZLD include the number of unit operations required for treatment and the need for significant chemical application and sludge disposal. Other limitations with the HERO process revolve around the weak acid cation (WAC) unit that is used to remove hardness associated with alkalinity:

- The pH in the effluent from the WAC unit is typically about 4.5. At this pH, the organics in solution drop out of solution and it is difficult to re-solublize them when the pH is raised. This leads to higher-than expected organic fouling of the RO membranes.
- In many applications, single-stage solids contact clarifiers are used for bulk removal of hardness prior to the HERO process (via lime softening). For applications where cooling tower blowdown is being teated, the single stage softening does not allow sufficient time to break up dispersants used in the tower. Hence, the effluent from the unit is significantly higher than expected. This chelated hardness leaks through the WAC unit, and the RO experiences hardness scaling, particularly at the high recoveries and fluxes often used with HERO.

High efficiency RO is often used in zero liquid discharge (ZLD) applications. The HERO process is used prior to the thermal equipment to reduce the size and energy required by the thermal system. In many cases, the brine concentrator can be eliminated entirely, such that the concentrate from the HERO process feeds directly to the crystallizer.

Suppliers of the HERO process under license include GE and AquaTech.

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7

FREQUENTLY ASKED QUESTIONS

17

Frequently Asked Questions

This chapters answers some common questions about RO in general as well as operational and equipment-related questions.

17.1 General

17.1.1 What Is Reverse Osmosis Used For?

An RO system is designed to remove ions from solution. Rejection of most ions ranges from about 96% to 99+%, depending of the nature of the ion and the type of membrane used (see Chapter 4.2).

Although RO membranes also act as barriers to suspended solids, it is not recommended that they be used for this purpose. The membranes will foul with suspended solids, resulting in higher operating pressure, frequent membrane cleaning, and shorter membrane life. To avoid fouling, pretreatment is required to remove suspended solids from the RO feed water (see Chapter 8).

The most common uses of RO are for desalination of seawater and brackish water for potable and industrial applications. However, as demand for fresh water grows, RO is being pressed into service for wastewater and reuse applications. These will require extensive pretreatment, sometimes involving other membrane technologies such as micro- or ultrafiltration, to minimize fouling of the RO membranes (see Chapter 16.1).

17.1.2 What is the Difference Between Nanofiltration and Reverse Osmosis?

Nanofiltration (NF) and RO are closely related in that both share the same composite membrane structure and are generally used to remove ions from solution. However, NF membranes use both size and charge of the ion to remove it from solution whereas RO membranes rely only on "solution-diffusion" transport to affect a separation (see Chapters 16.2 and 4.1, respectively). Nanofiltration membranes have pore sizes ranging from about 0.001 to 0.01 microns, and therefore, the rejection of ions in solution by an NF membrane is not a good as that by an RO membrane (see Figure 1.1). Because NF is similar to RO, but with lower rejection, NF is sometimes called "loose" or "leaky" RO.[1] Nanofiltration is commonly used to "soften" potable water or to remove color and organics from RO feed water.

17.1.3 What is the Difference Between Forward Osmosis (FO) and Reverse Osmosis (RO)?

Forward osmosis relies on the *osmotic* pressure differential across a membrane to drive water through the membrane; RO relies on the *hydraulic* pressure differential to drive water through the membrane. A draw solution is used on the permeate side of the membrane to osmotically drive water from the feed side of the membrane into the draw solution, which becomes more dilute. The draw solution is then treated (sometimes by heating followed by membrane distillation or by RO) to recover the water and to regenerate the draw solution for reuse.

17.1.4 What is Data Normalization?

Data normalization is a method used to understand the performance of the membranes in an RO system (see Chapters 11.3 and 12). Performance, namely permeate flux, salt rejection, and pressure drop, are all functions of operating conditions, such as temperature and pressure, and functions of the degree of membrane fouling, scaling, and degradation. Since these conditions are always changing, comparison of actual data is difficult, as there are no common reference conditions. Normalizing data takes out the changes in operating conditions (temperature, pressure, and concentration), such that the only changes in normalized performance are due to membrane fouling, scaling, and degradation. Normalization provides a common reference point, start-up conditions, that all data is compared to. Hence, normalizing data allows the user to determine the condition of the membranes, be they fouled, scaled, or degraded.

17.1.5 How do SDI and Turbidity Correlate?

Silt density index (SDI) and turbidity are only loosely related. In general, the higher the feed water turbidity, the higher the SDI. However, the converse is not always true. Low turbidity, less than 1 NTU, can still correspond to high (greater than 5) SDI. This is particularly important to consider when using potable water as the feed source, especially if the ultimate source is surface water. City water generally has a turbidity less than 1 NTU, but will often have SDI greater than 5. Hence, it is not uncommon to install multimedia filters as RO pretreatment on city water sources.

17.1.6 Why Does the pH Drop from the RO Feed to the RO Permeate?

This phenomenon is a function of the carbon dioxide present in the RO feed water. Because carbon dioxide is a gas, it is not rejected by an RO membrane. Hence, the permeate will contain carbon dioxide if the feed water contains it. However, the membrane rejects carbonate and bicarbonate which are in equilibrium with carbondioxide in the feed water. Because carbonate and bicarbonate are rejected by the membrane, a new equilibrium occurs in the RO permeate, reducing the pH (see Chapter 9.8 and equation 9.3).

17.2 Operational

17.2.1 When is it Time to Clean an RO Membrane?

Cleaning an RO membrane is generally based on the normalized permeate flow or the pressure drop (see Chapter 13.2.1). When the normalized permeate flow drops by 10%–15% or the pressure drop increases by 10%–15% from start up, it is time to clean. Waiting too long to clean membranes will most certainly result in some permanent fouling. Cleaning too often (when it's not yet time to clean) will result in shorter membrane life, due to the destruction of the membrane by the cleaning conditions (pH and temperature) and chemicals. Thus, cleaning based on a calendar schedule rather than based on performance is not recommended, because inevitably, the membranes will either be cleaned too often or not often enough.

17.2.2 How Long does it Take to Clean an RO System?

A typical two-stage RO skids can take 10–12 hours to clean, depending on the time it takes to heat up the cleaning chemical solutions. If an extended soak time is required, it can take even longer, up to 24 hours, including the soak period (see Chapter 13.2.2). Each stage in a skid should be cleaned independently of the other (s) so as not to contaminate one stage with foulants or scale from another, which is why it may take a day or so to clear an entire system.

17.2.3 What Temperature Cleaning Solution Should Be Used to Clean Membranes?

Membranes should be cleaned at as high a temperature and at pH extremes as recommended by the manufacturer (see Chapter 13.2.2). Studies have indicated that cleaning under these conditions removes more scale and foulants than cleaning at ambient temperature and neutral pH (see Chapters 13.2.3.1 and 13.2.3.2). However, cleaning outside the recommended temperature and pH parameters leads to membrane degradation, will void the membrane warranty, and should not be attempted without prior approval from the manufacturer.

17.2.4 Can Extended Soak Time Compensate for Cleaning at Lower Temperature, for Example, When the Heater is Not Working?

Cleaning at lower temperatures is not recommended. Cleaning solutions are typically not effective at ambient temperatures and some components of the solution may even precipitate at these temperatures. Longer soaks will not compensate for cleaning at lower temperatures. In fact, during extended soak periods at higher temperatures, a slow recirculation is recommended to maintain temperature.

17.2.5 Should the Low or High pH Cleaning Be Conducted First?

It is strongly recommended that the high pH cleaning be conducted first. Acid cleaners will generally react with silica, organics, and bio- film on the membranes, making these fouling and scaling problems worse. Acid cleaning should only be used first if it is known that only calcium carbonate or iron oxides are present on the membrane, and no biofouling is present.

17.2.6 What Should Be Done if Cleaning Does Not Return Performance to Baseline?

It is acceptable if performance returns to within a couple of percent of baseline. However, if performance falls short of baseline by more than 2–3%, additional cleaning is recommended. Refer to Table 13.3 for specific foulants and scale removal cleaning solutions. Should these additional cleaning solutions fail to return performance, off-site cleaning is suggested (see Chapter 15.3). Vendors of off-site cleaning services have access to several cleaning solutions and can try different variations to find one that is effective. If off-site cleaning is ineffective, the fouling, scaling, or degradation problem is probably irreversible. Improvements to the pretreatment system as well as cleaning when normalized data indicate it is time to do so, will reduce the potential for irreversible fouling or scaling, or membrane degradation in the future.

17.2.7 If the Clean-in-Place Pump cannot Provide the Required Flow Rate, Can the Pump be Run at Higher Pressure to Compensate?

The CIP pump should provide 45–50 gpm at less than 50–60 psi per pressure vessel being cleaned (see Chapter 13.2.4.2). If the pump cannot supply this flow rate, operating at higher pressure will not help; it will make the fouling or scaling situation worse. This is because the higher pressure will force particles and cleaning solution irreversibly into the membrane. Cleaning should be conducted at pressures less than 60 psig. A good indicator of pressure is that little or no permeate should be generated during cleaning.

17.2.8 What Should Be Done With Permeate That is Generated During Membrane Cleaning?

The RO membranes should be cleaned at pressures low enough to prevent generation of permeate during the cleaning process. If permeate is generated, the risk is that the high pressure is forcing cleaning solution and foulants or scale into the irreversibly into the membrane (see Question 17.2.7). If any permeate is generated, reduce the pressure (while maintaining flow rate) and send the permeate back to the CIP tank.

17.2.9 Why is the Permeate Conductivity High after Cleaning the Membranes?

Permeate conductivity is typically higher the nominal after a high pH cleaning of membranes. High pH used during cleaning "loosen" the membrane polymer, making it more permeable to dissolved solids. This is a temporary condition; conductivity should return to nominal within a few hours to a few days. The converse is true for low pH cleaning; the permeate conductivity will be lower than nominal after low pH cleaning.

17.2.10 Why is Chlorine Both Added and then Removed Prior to the RO?

Chlorine (or other disinfectant) is required to minimize the potential for fouling the membranes with microbes (see Chapters 8.2.1, 8.2.2, and 8.5.2.1). Once membranes are fouled with microbes, it is very difficult to remove them. A free chlorine residual of about 0.5 to 1.0 ppm in the pretreatment system is desirable. Feed water to the RO must be dechlorinated prior to the membranes because the membranes are sensitive to oxidizers, which will degrade the membrane. Sodium bisulfite is the preferred method to dechlorinate unless the RO feed water has a high organic concentration, in which case, carbon filtration at a flow rate of 2 gpm/ft^3 is recommended. (see Chapters 8.1.4 and 8.2.3) Sodium metabisulfite is typically about 33% active, and the stoichiometic dosage of sodium metabisulfite is about 1.8 ppm per ppm free chlorine. So, the stoichiometric dosage of 33% active sodium metabisulfite is 5.4 ppm. For safety, a factor of 1.5 is used to increase the dosage of sodium metabisulfite to ensure complete elimination of free chlorine.

17.2.11 What Chemicals Can be Used to Disinfect RO Membranes Directly?

For biocide treatment directly on the membranes, DBNPA is a good non-oxidizing biocide (see Chapter 8.2.2.2 and 8.5.2.2.1). For clean membranes, a dosage of 30–50 ppm for 30 minutes 2 to 3 times per week is recommended. For heavier fouling, 100 ppm for 60 minutes 2 to 3 times per week should be fed. Alternatively, DBNPA can be fed continuously at about 2–3 ppm. Note that once biofouling gets out of control, it will be very difficult for DBNPA to work, because it is a non-oxidizer and cannot penetrate biofilm. DBNPA works best as a preventative treatment.

Isothiazolone can be used as a cleaner, but not for slug treatment, as it requires a longer contact time than DBNPA (see Chapter 8.2.2.3 and 8.5.2.2.2). When cleaning with isothiazolone, it should be allowed to contact the membrane for at least 4 hours.

Isothiazolone can also be fed on a continuous basis[2] and is an excellent method to keep membrane free of microbial growth. The recommended methods of using isothiazolone are the direct method and the post-cleaning method[2]:

1. Direct method:
   a. Operate with a continuous feed of isothiazolone of 100 ppm for one week for maximum kill.
   b. Drop the dosage to about 10 ppm continuous for one week.
   c. Drop the dosage again to a maintenance dosage of 3–5 ppm. The microbial population should be carefully monitored during the maintenance dosing to ensure that the dosage is high enough to control growth.
2. Post-cleaning method:
   a. Thoroughly clean the membranes to kill and remove bacteria from the membranes. Use standard cleaners followed by DBNPA.
   b. Feed isothiazolone at about 5 ppm for one week.
   c. Drop the dosage to a maintenance feed rate of about 1–3 ppm, again with careful monitoring of the biological activity.

17.2.12 Why does the RO Trip Off on Low Suction Pressure?

Low suction pressure is typically a result of inadequate water supply to the RO feed pump caused by upstream demand starving the RO system. Upstream demands include filter backwash water and water diverted for other applications within the facility. Starving of the RO due to equipment backwashing upstream is a system design flaw. Diversion of feed water usually occurs during installation or even after, as the need for fresh make-up water grows for other applications within the facility. These issues should be considered during the design phase and/or prior to installation of the RO system.

17.2.13 Should RO Feed Water be Heated?

There are advantages and concerns with heating RO feed water. Heating the water, particularly in the winter time when surface waters tend to be cooler than in the summer months, will reduce the energy required to pressurize the water (see Chapter 9.2). On the other hand, heating water will encourage microbial growth and perhaps microbiological fouling of the RO membranes. These two conditions should be carefully evaluated before heating water is considered. A variable frequency drive or VFD is recommended for applications where there is a significant temperature difference from summer to winter such that heating of the feed water is not required. (see Chapters 6.2 and 9.2)

17.2.14 What Limits Recovery by an RO?

The recovery of feed water as product water is a function of several factors. These factors include the concentration of scale formers in the feed water and the design of the RO array (see Chapter 5.1):

- Scale formers limit recovery to the saturation concentration(s) . Projections using ion product, solubility products, and LSI should be prepared prior to completing design of the RO system to determine the likelihood for scaling (see Chapter 3.8). Antiscalants can be used to delay or even eliminate scaling so that higher recoveries can be achieved (see Chapter 8.2.4).
- System design plays a role in determining acceptable recovery by an RO. Flow rates per pressure vessel, recovery per module, and BETA values must all be taken into account when considering acceptable recovery by the RO system (see Chapters 9.4, 9.5, and 9.6). The higher the recovery of the RO system, the closer concentrate flow rates and individual module recoveries come to reaching limits recommended by membrane manufacturers.

17.2.15 How do I Start Up an RO?

Starting up an RO, particularly when new membranes have been installed, needs to be done carefully to prevent water hammer from crushing the membrane modules (see Chapter 6.2) First, before anything is started, the start-up procedures provided by the equipment vendor should be read completely and understood. Then, to prevent water-hammer damage to the membranes, the concentrate and permeate valves should be wide open at start-up. *Never start the RO system with the concentrate valve closed and then opening it until the desired recovery is reached*. The RO feed pump should be started slowly, increasing the pressure at a rate no greater than 10 psi per second. If a variable frequency drive (VFD) is used, it can be adjusted to start up slowly. If not VFD is installed, and a centrifugal pump is being used, the concentrate valve should start open and then be closed down slowly until the desired recovery and feed pressure is reached, making sure that the pressure increases at an acceptable rate. The use of older, positive displacement pumps requires a pulsation dampener and a slow start, using the concentrate and pump recycle valves (both of which are to start wide open) to adjust the recovery and feed pressure.

To prevent damage to the membranes, they should be properly shimmed and the thrust ring correctly installed (see Chapter 4.3.3 and Question 17.3.4). The shims and thrust ring will minimize or prevent movement of the modules during start-up and shut-down of the RO system.

17.2.16 Do RO Membranes Need to be Preserved When Taken Off Line?

First, when membranes come off line, they should be flushed with either permeate water or low-pressure feed water (see Chapter 13.1.1). This will reduce the concentration of ions and any suspended solids on the feed side of the membrane, thereby minimizing the potential for fouling or scaling the membrane while idle. The next step (s) depends on how long the membranes will be off line.

- Short-term idling: Short-term idling includes membranes that are off line for no more than 48 hours. An automatic flush event should occur at least once every 24 hours (more frequently in warm weather). No other steps need to be taken to preserve the membranes.

- Short-term storage: Short-term *in situ* storage includes membranes that are off line for longer than 48 hours but less than 2 weeks (see Chapter 13.3).
  - Membranes should be flushed as described above. All air should be vented from the system while flushing. This can be accomplished by overflowing the flushing solution through the utmost point of the highest pressure vessel.
  - Once the vessels are filled, all valves should be closed to prevent air from entering the membranes.

These steps should be repeated every 5–7 days.[3]

- Long-term storage: Long-term in situ storage includes membranes that are off line for longer than two weeks (see Chapter 13.3.2). It is necessary to clean the membranes prior to storage. Standard cleaning techniques should be applied (see Chapter 13.2). After cleaning, the following preservations procedures should be conducted:
  - Circulate a 1 to 1.5% solution of sodium metabisulfite through the membranes, completely filling the pressure vessels. To ensure that the vessel are completely filled, the solution should be allowed to overflow through an opening located at the utmost point of the highest pressure vessel being filled.
  - Once the pressure vessels are filled with the bisulfite solution, all valves should be closed to prevent the oxygen in the ambient air from oxidizing the sodium metabisulfite.
  - The pH of the preservative solution should be checked once a week. The solution should be changed out when the pH reaches 3 or lower.
  - The preservative solution should be changed at least once per month during colder weather (less than 80°F), regardless of its pH. During warmer weather, the solution should be changed every two weeks. Under *ideal* conditions, the solution can last up to 6 months.

During long-term *in situ* storage, the following precautions should be taken:

  - Membranes should not be allowed to dry out. Dry membranes irreversibly lose flux.
  - Temperature extremes should be avoided. The system must be kept free of frost (typically greater than 5°C) and

should not be allowed to exceed 45ºC (consult with membrane manufacturer for temperature ranges for specific membranes). Cooler temperatures are preferred, as lower temperatures minimize microbial growth.

17.2.17 Is there a Shelf Life for Reverse Osmosis Membranes?

Shelf life depends on the condition of the membrane when they were stored. New membranes that are stored in their original, unopened bags have a shelf life of about 1 year.[4,5] Membrane warranties typically start at system start-up or 1 year after shipment, whichever comes first.[4] Membranes that were wet tested prior to shipment from the factory should be inspected every three months for biological growth and for pH. If biological activity is found (the preservative solution is not clear), after six months of storage, or if the pH of the preservative solution drops below 3, the modules should be stored in fresh preservative solution, as described below. Membranes that were not wet tested ("dry" membranes) should also be inspected regularly for biological growth. If growth is found, they should be soaked in a preservative solution as described below.

Membranes that have been used can be removed from the RO skid and stored. They should be cleaned prior to storage. Once removed from the pressure vessel, each membrane module should be soaked in a 1% solution of non-cobalt activated sodium metabisulfite solution mixed with deionized water such as RO permeate. For greater disinfection and protection, Toray recommends soaking on a 0.2 to 0.3% solution of formaldehyde for membranes that have been in operation for more than 72 hours.[6] (Note that storage in formaldehyde may result in permanent flux loss. Formaldehyde is a poison to humans, and, therefore, is not recommended for food-related applications. Consult with the membrane manufacturer before using preservatives other than sodium metabisulfite.) The modules should be soaked in the vertical position for one hour. After soaking, allow the module to drip and then storage it in an oxygen-barrier plastic bag. There is no need to fill the bag with the preservative solution, as the moisture in the module is adequate. Modules can be stored for six months using this method. Stored membranes should be inspected every three months for biological growth and for pH. If biological activity is found, after six months of storage, or if the pH of the preservative solution drops below 3, the modules should be soaked in fresh preservative solution and sealed in a new oxygen-barrier bag. Membrane should be cleaned in a high-pH solution when it comes time to return them to service.

Membrane modules should always be stored in a cool, dark place out of direct sunlight and kept from freezing. Wet-tested membranes should be stored at no lower than about 5°C to prevent freezing of the sodium metabisulfite preservative solution (FilmTec membranes can go to –4°C).[7] Dry membranes will not be affected by freezing temperatures. (Note that once wetted, membranes should not be allowed to dry out, as irreversible loss of flux may occur.)

17.2.18 What is the Difference Between Membranes that Have Been Wet Tested and those that are Dry?

Brackish water membranes can be shipped from the manufacturer wet or dry. Wet membranes have been performance tested at the factory. However, testing is usually conducted for shorter (hours) versus longer (days) periods. As noted in Figure 14.2, there is a period of time after start up during which membrane performance is not stable due to compaction. Flux and salt passage both decrease during this period. Unless a membrane is wet tested until stable performance is achieved, the performance specifications for that membranes based on the wet test are not accurate.[8]

Dry membranes may have been leak tested with air or they may not have been tested at all.

17.2.19 What is the Impact on the RO If the Pretreatment System Fails, for Example, If the Softener Leaks Hardness?

Any failure in the pretreatment syst em will be registered on the RO membranes as fouling or scaling or degradation (see Chapter 12). Failures include:

- Malfunction of chemical pretreatments, including chlorine, sodium bisulfite, and antiscalant leading to biofouling, degradation, and scaling, respectively
- Channeling through multimedia filters leading to fouling of the membranes
- Hardness leaking from softeners leading to scaling of the membranes
- Particle unloading from cartridge filters due to high pressure drop leading to fouling of the membranes

Fouling will usually affect the first membranes in the first stage of the RO system. Pressure drop will increase across this stage and operating pressure will increase. Normalized permeate flow will decrease over the first stage. Degradation will also primarily affect the first stage. Salt passage will increase and operating pressure will decrease. Normalized permeate flow will increase over the first stage. Scaling will affect the last stage of the RO system. Salt passage and operating pressure will both increase. Normalized permeate flow will decrease over the last stage. Refer to Chapters 3.7, 3.8, and 12 for additional information.

To prevent these failures, constant monitoring of the pretreatment system is necessary. Alarms should be installed on critical systems, such as the ORP associated with the sodium bisulfite feed. Particle monitors could be used to detect channeling or carry over through filters. Hardness analyzers with alarm should be installed on the effluent from softeners.

17.2.20 Can Different Types of Membranes Be Used in a single RO Unit?

Different membranes can be mixed in a single RO unit, but is usually not recommended. One case where membranes are mixed is in low-pressure systems. In a low-pressure system, the water flux can drop off significantly through the last few membrane modules as the osmotic pressure of the feed approaches the difference between the applied pressure and the pressure drop (driving force) in the pressure vessel. This situation is common in low-pressure municipal applications where many systems have 7 membrane modules in series in a pressure vessel.[9] In this case, the last 2 or 3 membranes in the last stage can be replaced with low-energy (high flow) membranes (see Chapter 4.4.2.1). Theses low-pressure membranes usually sacrifice rejection, but high rejection is not as critical for municipal applications where 80–90 ppm TDS product water is acceptable. Note that low-pressure membranes should never precede standard- pressure membranes in an RO system. This is because water will follow the path of least resistance and a disproportional amount of water will flow through the lead membranes, in effect “starving” the later, standard-pressure membranes.

The other case where membranes are sometimes mixed is during emergency situations where some but not all membranes have been damaged in some way and need replacing. In this case, it is not uncommon for membranes from different manufacturers to be combined in a single RO unit. If this is a necessity, the interconnectors should be compatible with each membrane (see Chapter 4.3.3). Because of the variations among interconnections, membranes from different manufacturers are generally not combined in the same stage of a single RO system. Also, performance specifications should be similar for all the different membranes used in a single RO system.

17.2.21 What Species Should Be Included in an RO Feed Water Analysis?

The species listed in Table 17.1 are recommend for inclusion in an RO feed water analysis. These same species also can be included in permeate and concentrate analyses so that a mass balance can be conducted around the RO membranes. In some cases, filtered and total analyses of cations are useful; but in other cases, a total analysis is sufficient. Typically, waters that include iron, manganese, fluoride, and silica benefit from both the total and filtered analyses.

Table 17.1 Recommended species to include in an RO analysis.

Cations*	Anions	Alkalinity	Other	On-Site Tests
Aluminum	Chloride	Bicarbonate	Ortho-Phosphate	pH
Barium	Fluoride	Carbonate	Non-Purgeable organic carbon (TOC)	Silt Density Index
Boron	Nitrite		True Color	
Calcium	Nitrate		Conductivity	
Iron	Sulfate		Total Dissolved Solids	
Magnesium			Total Suspended Solids	
Manganese			Turbidity	
Phosphorous			Silica**	
Sodium				
Strontium				

*In some cases, filtered and total cation analyses are importnat.

**Reactive and total silica can sometimes be of value.

17.3 Equipment

17.3.1 What is the Footprint For an RO System?

While the footprint of an RO system will obviously very with size of the system, there are some generalities that can be made. The length of the RO system depends on how many membrane modules are in series in the pressure vessels. Table 17.2 lists the approximate size of an RO skid as a function of the number of modules in the pressure vessels. Note that sizes may vary depending on the manufacturer.

Additionally, there are "work zone" areas that should be allowed for in the plant layout of the RO skid. At each end of the RO skid, a zone of a minimum of 4 feet (6 feet is best) should be allotted for loading and unloading membrane modules. The front side of the skid should have about 4 feet allotted for pump maintenance and access to the controls and instruments. The backside of the skid requires no access and the skids can be placed 1 to 2 feet away from the backside of adjacent equipment.

17.3.2 What is a Variable Frequency Drive Used For?

A variable frequency drive (VFD) adjusts the speed of a motor to alter the discharge pressure (see Chapter 6.2). This is useful when there are significant variations in feed water temperature with changes of seasons.

Table 17.2 Approximate RO skid size as a function of number of modules per pressure vessel.

Number of Modules in Series	Length, inches	Width, inches	Height, inches	Array	Capacity, gpm
3	168	32	77–89	3:2:1	30–100
4	226	57	80–91	4:3:2 3:2:1 6:4:2	100–200
6	280	66	115	8:4 10:5	320–400
6	280	94	128	14:7 18:9	560–720

Because an RO membrane requires lower pressure at higher temperature to force water through the membrane, energy can be saved during the summer months if a VFD is employed (see Chapter 9.2). Thus, during the warmer months, the VFD can be used to "dial back" the discharge pressure, reducing the energy required to operate the system.

17.3.3 What is the Difference Between Pleated, String-Wound, and Melt-Blown Cartridge Filters?

All three types of cartridge filters are acceptable for pretreatment to RO membranes (see Chapter 6.1). Pleated cartridge filters are typically used in higher-purity applications such as pharmaceuticals and microelectronics. String-wound filters are just as they sound; material such as polypropylene in string form is wound around a central core. These filters suffer from particle unloading at higher pressure drops and require a slower velocity through them than other types of cartridge filters, typically 2–3 gpm per 10-inch equivalent (TIE) rather than 5 gpm per TIE for pleated and melt-blown filters. The melt-blown variety is thermally bonded polypropylene microfibers and is typically denser near the core than at the outside. This allows for particles to be trapped throughout the cross section of the filter similar to a depth filter.

17.3.4 What is the Correct Way to Install Shims and the Thrust Ring?

Shims and the thrust ring are used to protect the membrane modules from moving around in the pressure vessel during start-up and shut-down of the RO system (see Chapter 4.3.3).

The thrust ring is installed at the concentrate end of the pressure vessel before any membranes are installed. Consult with the manufacturer of the pressure vess el for correct orientation of the ring.

Shims are installed at the feed end of the module/pressure vessel assembly (refer to Fgures 6.16). Because pressure vessels are constructed with slight variations in length (known as "freeboard"), membrane modules can slide during pressurization and depressurization. Shims are installed between the face of the lead module and the adapter hub to prevent this motion. Membrane modules should be pushed completely against the thrust ring prior to installation of the shims. Shims are washer-like plastic rings that may be purchased from the pressure vessel manufacturer or fashioned out of PVC (must be free of burrs and be cut parallel to work properly).

17.3.5 How Should the Cleaning Pump be Sized?

The cleaning pump should be sized to handle 45–50 gpm per 8-inch pressure vessel to be cleaned at a pressure less than a 50–60 psig (see Chapter 13.2.4.2). For example, given an 8:4-6M array, the pump would have to provide cleaning solution for a maximum of 8 pressure vessel at one time. At 45 gpm per pressure vessel, the pump needs a discharge flow of 360 gpm.

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