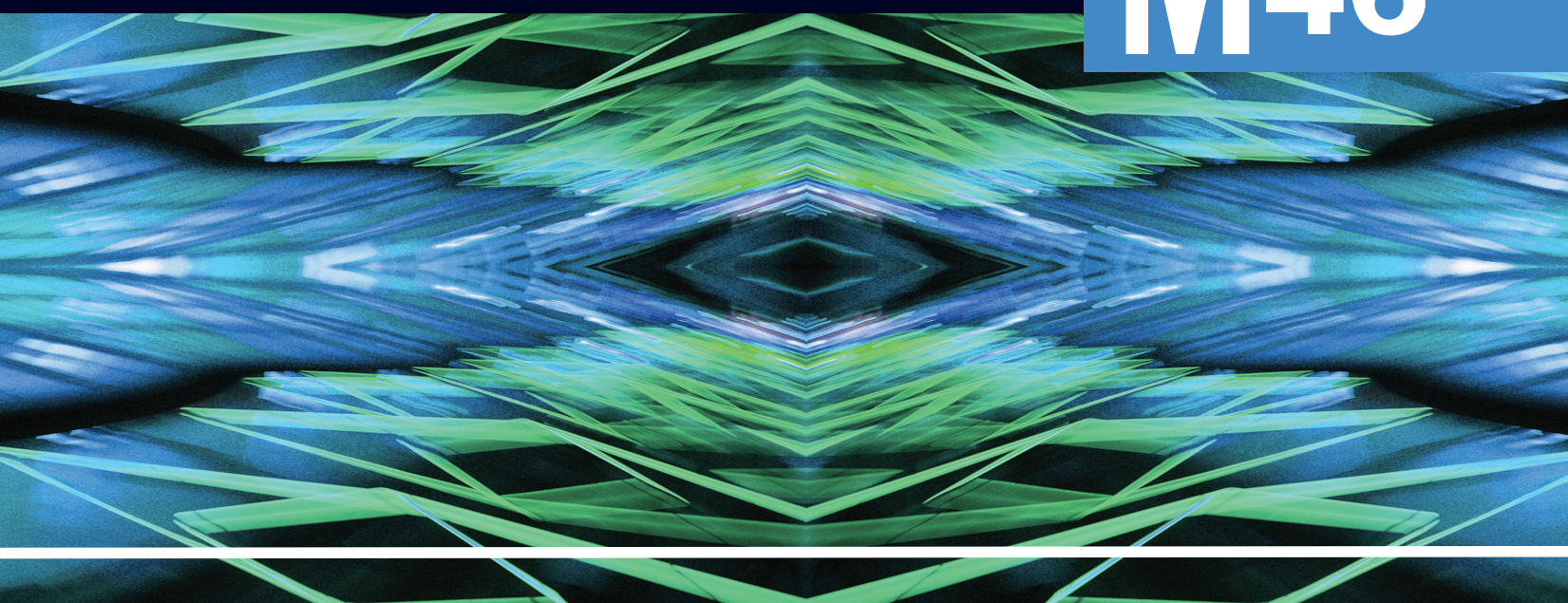


Reverse Osmosis and Nanofiltration

MANUAL OF WATER SUPPLY PRACTICES

M46



Second Edition



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MANUAL OF WATER SUPPLY PRACTICES—M46, Second Edition

Reverse Osmosis and Nanofiltration

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Contents

List of Figures, v

List of Tables, ix

Preface, xi

Acknowledgments, xiii

Chapter 1 Introduction 1

Overview, 1
RO and NF Membrane Applications, 7
Membrane Materials and Configurations, 12
References, 18

Chapter 2 Process Design 21

Source Water Supply, 21
Pretreatment, 26
Membrane Process Theory, 45
Rating RO and NF Elements, 51
Posttreatment, 59
References, 60

Chapter 3 Facility Design and Construction 63

Raw Water Intake Facilities, 63
Discharge, 77
Suspended Solids and Silt Removal Facilities, 80
RO and NF Systems, 92
Hydraulic Turbochargers, 95
Posttreatment Systems, 101
Ancillary Equipment and Facilities, 107
Instrumentation and Control Systems, 110
Waste Stream Management Facilities, 116
Other Concentrate Management Alternatives, 135
Disposal Alternatives for Waste Pretreatment Filter Backwash Water, 138
General Treatment Plant Design Fundamentals, 139
Plant Site Location and Layout, 139
General Plant Layout Considerations, 139
Membrane System Layout Considerations, 140
Facility Construction and Equipment Installation, 144
General Guidelines for Equipment Installation, 144
Treatment Costs, 151
References, 162

Chapter 4 Operations and Maintenance	165
Introduction, 165	
Process Monitoring, 168	
Biological Monitoring, 182	
Chemical Cleaning, 183	
Mechanical Integrity, 186	
Instrumentation Calibration, 188	
Safety, 190	
Appendix A SI Equivalent Units Conversion Tables	193
Appendix B Equations	195
Appendix C Silt Density Index Procedure	205
Appendix D Langelier Saturation Index and	
Stiff-and-Davis Stability Index	207
Appendix E Glossary and Acronyms	211
Index	217
Manuals List	225

Figures

- 1-1 Scottsdale Water Campus—10-mgd RO facility, 2
- 1-2 Membrane and conventional process overview, 4
- 1-3 Typical RO or NF membrane system, 7
- 1-4 Generalized membrane process selection chart, 8
- 1-5 Cross-section of an asymmetric membrane, 12
- 1-6 Effect of temperature and pH on hydrolysis of cellulose acetate, 13
- 1-7 Schematic cross-section of a thin-film composite RO membrane, 14
- 1-8 Spiral-wound module, 16
- 1-9 Pressure vessel assembly, 16
- 1-10 Membrane pressure vessel with eight elements, 17
- 1-11 Hollow fiber membrane module, 17
- 2-1 Feedwater flow rates for various permeate recovery rates, 24
- 2-2 Calcium sulfate solubility product versus ionic strength, 34
- 2-3 Barium sulfate and strontium sulfate solubility product versus ionic strength, 35
- 2-4 Calcium fluoride solubility product versus ionic strength, 36
- 2-5 Calcium phosphate solubility product versus pH, 36
- 2-6 Sample computerized evaluation of the supersaturation of sparingly soluble salts for a given source water, with polymeric scale-inhibitor dose projection, 37
- 2-7 Scale inhibition study, Sanibel, Fla., 39
- 2-8 Scale inhibition study, Venice, Fla., 40
- 2-9 Effect of temperature on theoretical SiO_2 solubility, pH 7.7, 41
- 2-10 SiO_2 pH correction factors, 41
- 2-11 Greensand horizontal filters, 42
- 2-12 Osmotic flow, 46
- 2-13 Osmotic equilibrium, 46
- 2-14 Reverse osmosis, 47
- 2-15 Schematic diagram of an RO membrane element, 48
- 2-16 Effect of increasing salt concentration on flux and salt rejection, 51
- 2-17 Effect of feedwater pressure on flux and salt rejection, 51
- 2-18 Effect of increased recovery on flux and salt rejection, 52
- 2-19 Effect of feedwater temperature on flux and salt rejection, 52
- 2-20 Schematic diagram of an RO membrane device, 54

- 2-21 Three-dimensional plot of permeate sodium concentration as a function of NAP and permeate recovery rate, 57
- 3-1 5,500 gpd RO system, 64
- 3-2 40,000 gpd RO system, 64
- 3-3 86,000,000 gpd RO system, 65
- 3-4 Vertical intake well, 68
- 3-5 Horizontal radial collector well, 69
- 3-6 Infiltration gallery, 70
- 3-7 Riverbed/seabed filtration system, 71
- 3-8 Seabed filtration system of Fukuoka District RO Facility, Japan, 72
- 3-9 Off-shore intake structure, Larnaca, Cyprus, 74
- 3-10 Microscreens, 76
- 3-11 500- μ m source water pretreatment strainers, 77
- 3-12 Desalination plant intake and discharge connection to power plant, 78
- 3-13 Cartridge filters located horizontally in vessel, 88
- 3-14 End-, side-, and multiport pressure vessels, 93
- 3-15 Integrated turbopump, 96
- 3-16 Integrated turbopump for feed pumping, 97
- 3-17 ER impulse turbine, 97
- 3-18 PEI hydraulic turbocharger, 98
- 3-19 Hydraulic turbocharger for interstage pressure boost, 98
- 3-20 Pressure/work exchangers, 100
- 3-21 RO system with isobaric pressure/work exchangers and boost pumps, 100
- 3-22 10.6 mgd Larnaca Seawater Desalination Plant—posttreatment system with limestone filters, 105
- 3-23 Typical membrane cleaning system, 109
- 3-24 Typical spent cleaning solution system, 109
- 3-25 Typical membrane control room, 111
- 3-26 Local control panel at a membrane process area, 113
- 3-27 Disposal methods for membrane desalination plants, 121
- 3-28 Disposal methods by membrane desalination plant capacity, 121
- 3-29 A majority of the membrane desalination water plants >0.025 mgd are located in four states, 122
- 3-30 Decision tree for disposal of desalination membrane residuals, 123
- 3-31 Deep injection well shaft, 130
- 3-32 Manual membrane element loading, 150

- 3-33 Machine-assisted membrane element loading, 151
- 3-34 Brackish groundwater reference design, 152
- 3-35 Seawater reference design, 153
- 3-36 Economy of scale for RO plant process equipment, 156
- 3-37 O&M cost breakdown for reference plants, 157
- 3-38 Relative capital cost of concentrate management options, 160
- 4-1 Operator collecting samples from RO unit at Dare County Utilities, Kill Devil Hills, North Carolina, 169
- 4-2 Example of an operating log, 172
- 4-3 RO or NF process diagram flow including reference values used in sample calculations, 176
- 4-4 Cleaning system flow diagram, 184
- 4-5 Sample conductivity profile data sheet, 187
- 4-6 Permeate probing apparatus for a spiral-wound membrane, 189
- 4-7 Probing a spiral-wound membrane, 189
- 4-8 Sample pressure vessel probing sheet, 190

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Tables

1-1	Membrane processes and target contaminants, 5
1-2	Comparison of three generations of brackish water RO membranes at Edgewood Water District, Fla., 6
1-3	Comparison of thin-film composite and cellulose acetate membranes, 15
2-1	Membrane system design factors and unit processes, 22
2-2	Suggested parameters for water quality analysis, 23
2-3	Feedwater flow rates based on permeate recovery rates, 24
2-4	Pretreatment techniques for reducing silt and colloidal material, 28
2-5	Common coagulant–flocculants, 30
2-6	Common limiting salts, 30
2-7	Common scales and other inorganic foulants and methods for controlling them, 32
2-8	Example of an ionic strength calculation, 33
2-9	Pretreatment for control of biological activity, 43
2-10	Factors influencing RO and NF performance, 52
2-11	Typical standardized test conditions for various RO devices, 53
2-12	Assumptions for the permeate solute concentration example, 56
2-13	Impact of varying permeate recovery rate, 56
2-14	Impact of varying NAP, 56
2-15	Impact of varying membrane characteristics on C_p , 57
2-16	Impact of varying NAP on water flux, 58
2-17	Impact of varying water permeation coefficient on water flux, 58
3-1	Advantages and disadvantages of co-location of desalination and power plants, 80
3-2	Surface water intake design elements and considerations, 81
3-3	Recommended pretreatment system configuration for suspended solids and silt removal based on source water SDI and turbidity, 82
3-4	Model water quality, 102
3-5	Model permeate and finished water quality following posttreatment, 107
3-6	Typical NF/RO plant concentrate quality, 118
3-7	Typical NF/RO cleaning solutions, 119
3-8	Plastic piping materials, 127
3-9	Disposal methods for chemical cleaning solutions at US RO/NF plants, 137
3-10	Summary of spent cleaning solution waste disposal methods, 137

- 3-11 Recommended pressure allowances, 143
- 3-12 Reference design parameters, 153
- 3-13 Construction cost for the reference designs, 154
- 3-14 O&M costs for the reference designs, 157
- 3-15 Total treated water costs for the reference designs, 158
- 3-16 Comparative capital costs for selected management options, 159
- 4-1 RO/NF troubleshooting ideas to correct problems, 166
- 4-2 RO/NF suggested proactive tasks to avoid problems, 168
- 4-3 Monitoring of RO and NF systems, 170
- 4-4 Typical TCF₇₇ values, 181
- 4-5 Chemical cleaning approaches for different problems, 185

Preface

Reverse osmosis (RO) and nanofiltration (NF) are membrane technologies that can be applied to the treatment of various water sources for the production of drinking water. Membrane technologies can remove organic and inorganic substances from water and can replace or be adjuncts to such traditional treatment methods as sand filtration, primary disinfection, lime and soda softening, ion exchange, and evaporative processes. RO and NF are both pressure-driven membrane processes with similar process configurations and equipment. The main differences between the processes are primary treatment focus (demineralization or salt reduction for RO and hardness and/or organics removal for NF) and the degree of necessary applied pressure (higher for RO). However, the two membrane processes exhibit far more similarities than differences, thus their inclusion in the same manual.

RO was commercialized in the United States in the 1960s and has been used for water desalting applications ever since. NF developed from research and development technology as a lower cost membrane process for softening water and removing organic color.

Membrane technology of all types became particularly applicable to drinking water production in the late 1980s when the amendments to the US Environmental Protection Agency's Safe Drinking Water Act (SDWA) required higher-quality drinking water. The amendments were based on health effects research and the ability to detect contaminants at increasingly lower detection limits using sensitive analytical techniques. Because of their ability to remove or reduce many of the substances addressed by SDWA, membranes will play an increasingly important role in enabling water utilities to meet these regulations.

This manual was developed to provide an overview of RO and NF technology for operators, administrators, engineers, scientists, educators, and anyone seeking an introduction to these processes. An introductory chapter, which discusses an overview of RO and NF processes and applications, is followed by chapters discussing RO and NF process design, facility design, and operations and maintenance. The information contained in these chapters includes history, regulations, theory, terminology, water resources, pretreatment, process technology, posttreatment, concentrate disposal, and membrane and system components, configuration, maintenance, chemistry, costing, and safety.

As this is the second edition of AWWA Manual M46, *Reverse Osmosis and Nanofiltration*, the Membrane Processes Committee and the American Water Works Association welcome comments and suggestions for improving future editions. Please send them as an e-mail attachment to the Water Quality Engineer at eharring@awwa.org or in hard copy to 6666 West Quincy Avenue, Denver, CO 80235.

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Chapter 1

Introduction

Brent Alspach

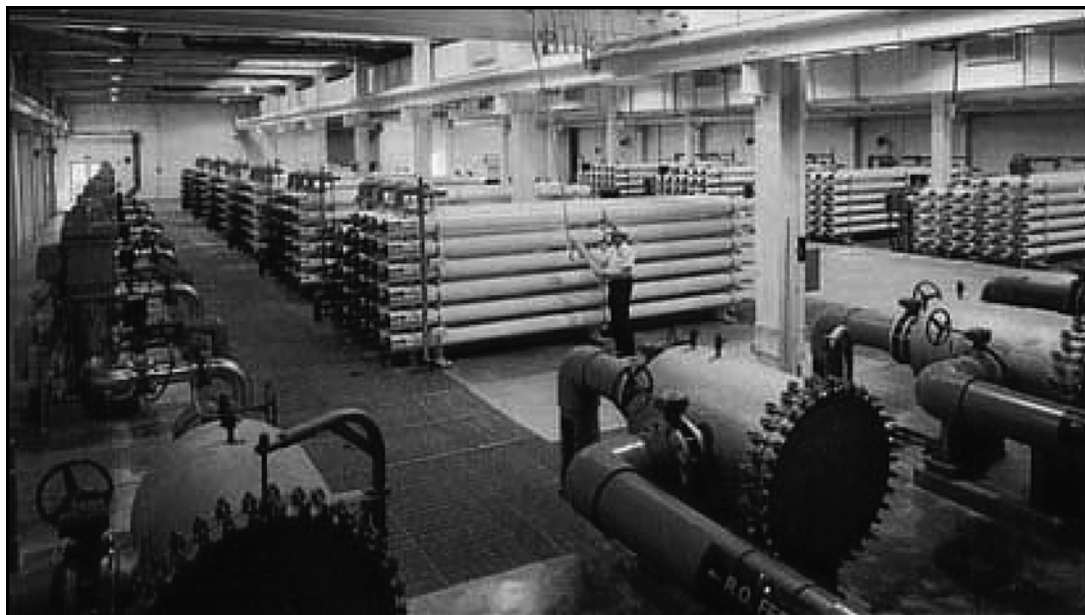
This first chapter provides a general introduction to the reverse osmosis (RO) and nanofiltration (NF) membrane treatment processes. The subjects addressed in this chapter should serve as the basic foundation for a broader understanding of RO and NF processes as applied to potable water, industrial process water, tertiary wastewater, and reclaimed water treatment, and include a general overview of the technology (i.e., types of processes, history of development, general RO/NF system description, and typical performance), specific applications, and membrane materials and configurations. Successive chapters will build on these concepts to provide more detailed information about process design (chapter 2), facility design and construction (chapter 3), and operations and maintenance (O&M) (chapter 4). For readers unfamiliar with RO and NF, a typical facility is shown in Figure 1-1. This picture shows the 10-mgd Scottsdale Water Campus, an RO system treating reclaimed water for aquifer recharge. The RO process itself consists of numerous skids with long horizontal pressure vessels containing the membrane elements, as shown in the center of the picture. The prefiltration (i.e., cartridge filters) to remove particulate matter upstream of the RO process is shown in the foreground at the bottom of the picture, and the high pressure pumps are aligned along the left side.

OVERVIEW

This section first provides a brief overview of the different types of membrane processes. The discussion subsequently narrows to RO and NF processes—the focus of this manual—presenting a brief history of the development of RO and NF membranes and the basics of RO and NF systems.

Types of Membrane Processes

The five membrane processes commonly used in the production of drinking water are RO, NF, ultrafiltration (UF), microfiltration (MF), and electrodialysis/electrodialysis reversal (ED/EDR). Although all five are classified as membrane processes, the technologies and applications are very different in some cases. In general, there are three groups of similar membrane processes: MF/UF, RO/NF, and ED/EDR. Four



Courtesy of Black & Veatch

Figure 1-1 Scottsdale Water Campus—10-mgd RO facility

primary factors distinguish these three groups of membrane processes from each other: the type of membrane, the mechanism of contaminant removal, the process driving force, and the primary application.

MF and UF are pressure-driven membrane processes that use microporous membranes to remove particulate matter (including turbidity and microorganisms), via a sieving mechanism, on the basis of size exclusion. These two processes do not remove ions or other dissolved constituents. Although there are some UF membranes that are used in industrial applications to separate high molecular weight organic molecules from solutions, these membranes are not commercially available for municipal drinking water treatment. In some cases, however, as with conventional media filters, MF and UF processes may be used to reduce levels of dissolved organic material (i.e., total organic carbon [TOC] when applied to coagulated water). MF and UF membranes may be manufactured from a number of different materials, including cellulose acetate and synthetic polymers such as polyvinylidene fluoride, polypropylene, polysulfone, polyether-sulfone, and polyacrylonitrile. For modern water treatment applications, these MF/UF membrane materials are commonly configured into hollow fibers, although other configurations may be available. MF and UF processes are discussed in detail in the American Water Works Association (AWWA) Manual of Practice M53: *Microfiltration and Ultrafiltration Membranes* (2005).

RO and NF are also pressure-driven processes; however, these technologies utilize semipermeable membranes to primarily target the removal of dissolved contaminants via a diffusion-controlled separation process. While RO and NF also remove particulate matter, the nonporous, semipermeable membranes can rapidly foul when subjected to significant particulate loading. When high pressure in excess of the natural osmotic gradient of the system is applied to the feed side of the membrane, water is forced through the molecular structure of the membrane surface

while the dissolved solids (i.e., the solutes) are largely rejected. Although solutes can also diffuse through the semipermeable membranes, the rate of mass transfer of these constituents is much slower than that of the water. Consequently, the water that passes through the membrane (i.e., the permeate) contains fewer dissolved solids than does water entering the system (i.e., the feed).

The amount of energy (hydraulic pressure) required to drive the feedwater across the membrane depends on the membrane material and thickness, as well as the osmotic pressure of the feed. The osmotic pressure is the pressure on the membrane created by the naturally occurring process of water flowing from a dilute solution (i.e., lower dissolved solids concentration) across a semipermeable membrane to a more concentrated solution (i.e., higher dissolved solids concentration). Thus, energy in the form of hydraulic pressure is required to overcome both the physical resistance of the membrane itself and the osmotic pressure of the system. Because this pressure is applied to force water against the natural osmotic gradient to produce less saline water from more concentrated water, the treatment process is called *reverse osmosis*.

The first RO membranes were developed at the University of California at Los Angeles in the early 1960s by Loeb and Sourirajan, who produced a membrane to generate drinking water from seawater (Buros 1980). This relatively thick membrane was made from cellulose acetate and required feed pressure in excess of 1,000 psi. Currently, RO membranes used to desalinate seawater require about 800 to 1,200 psi, while brackish water applications may necessitate feed pressure ranging from 100 to 600 psi. For a given membrane system and operating conditions, the feed pressure required depends primarily on the total dissolved solids (TDS) concentration and the temperature of the feedwater—lower TDS levels and warmer waters require lower feed pressure to produce similar quality and quantity of permeate.

NF membranes were developed in the late 1970s as a variant of RO membranes with reduced rejection characteristics for smaller, less charged ions, such as sodium and chloride. Because these membranes also required lower operating feed pressure, NF was well suited for applications such as softening and dissolved organic carbon (DOC)/disinfection by-product (DBP) precursor removal in which TDS was not a primary concern, because treatment objectives could be achieved at lower energy costs than with RO. Common applications for hardness and DOC removal may require only 70 to 120 psi using currently available NF membranes.

The two primary materials used to manufacture RO and NF membranes are cellulose acetate (and its derivatives) and various polyamides used in *thin-film composite* membrane construction. Although both RO and NF membranes are manufactured in several physical configurations, the spiral-wound configuration is the only one that is widely used in municipal treatment applications. (Membrane materials and configurations are discussed in more detail later in this chapter.)

ED/EDR are electrically driven membrane processes that remove dissolved solids using cation- and anion-selective membranes. However, unlike RO and NF, ED/EDR does not provide a barrier to pathogens and does not remove suspended solids or noncharged, nonionic constituents. In RO and NF processes, product water is filtered while passing through the membrane. By contrast, with ED/EDR the demineralized product water passes along the membrane surface in a tangential pattern while charged ions are transported through the membrane and concentrated into the brine stream; thus, the product water does not pass through a membrane barrier. ED/EDR has been used primarily to desalinate brackish waters and applied in specialty applications, such as the removal of fluoride or radionuclides. In addition, because ED/EDR does not affect silica concentrations, it may be advantageous in cases in which silica removal is not needed. Additional information about ED/EDR may be found in the AWWA Manual of Practice M38: *Electrodialysis and Electrodialysis Reversal* (1995).

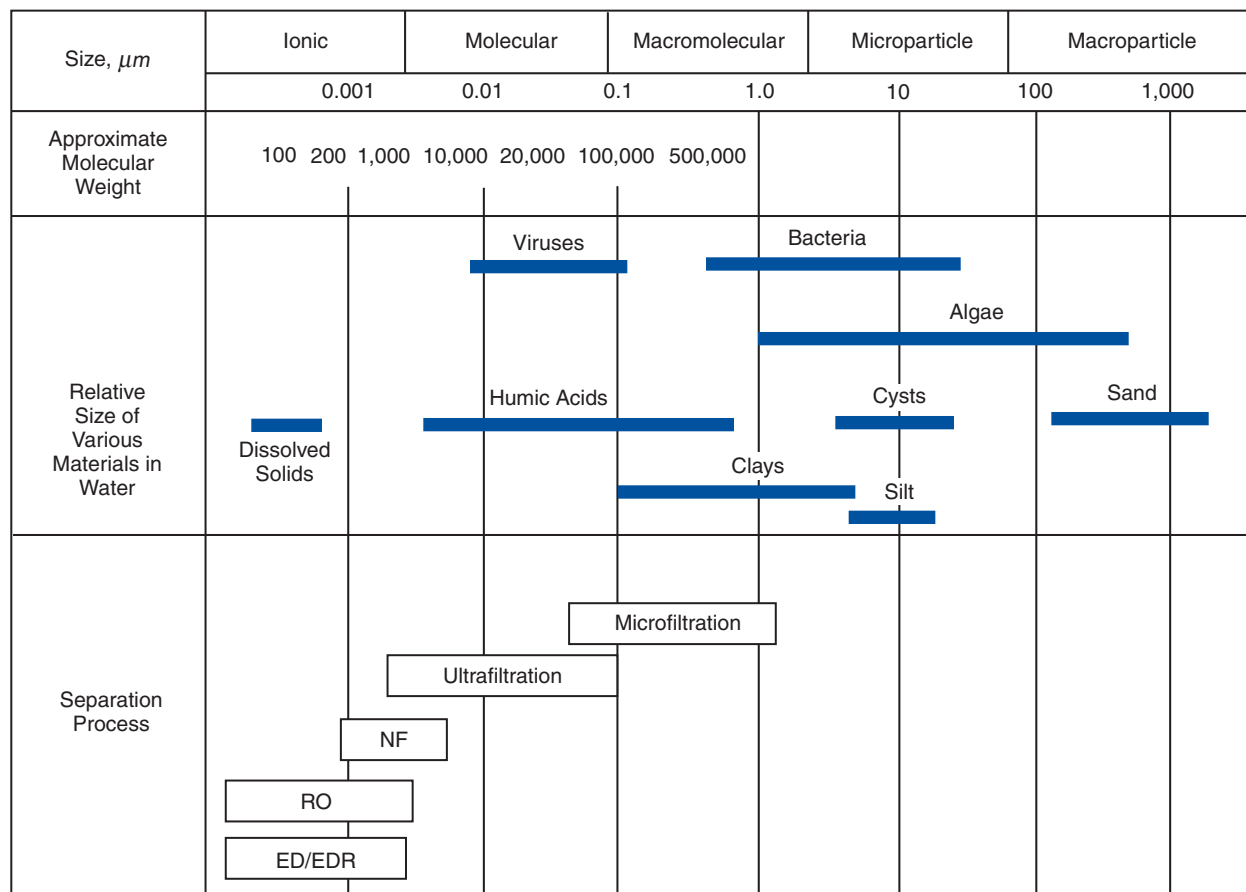


Figure 1-2 Membrane and conventional process overview

Figure 1-2 illustrates the removal abilities of the various types of membrane technology for their respective target drinking water contaminants, based on size of the removed compounds. Table 1-1 summarizes some of this same information in tabular form, including the various membrane process and target contaminants. Note that both Figure 1-2 and Table 1-1 focus on the *target* contaminants, not all the contaminants that the various membrane technologies are capable of removing. For example, while RO and NF processes will remove particulate matter, these technologies are generally not applied specifically for this purpose because the membranes will foul rapidly and in many cases irreversibly.

History of Development

One of the first applications for membrane technology was the conversion of seawater to drinking water through the use of the RO process. Early generation membranes were manufactured with cellulose acetate and were much less permeable than those currently used. The disadvantages of early membranes included the high pressure required and the low recovery rate—only 10 to 25 percent of the source water was converted to desalinated permeate. These factors resulted in extensive and cost-prohibitive energy requirements.

The first commercial application of RO membranes for brackish water desalting began in the early 1960s using the spiral-wound configuration developed in 1967, by General Atomics. In 1969, E.I. DuPont de Nemours, Inc. (DuPont) introduced the

Table 1-1 Membrane processes and target contaminants

Membrane Technology	Target Contaminants Removed
MF	• <i>Giardia</i> • <i>Cryptosporidium</i> • Bacteria • Turbidity/particulate matter • Coagulated organic matter • Inorganic precipitates
UF	• All contaminants removed by MF, <i>plus</i> • Viruses • Large organic macromolecules
NF	• Divalent ions/hardness • Limited monovalent ions • Dissolved organic carbon • Color
RO	• All contaminants removed by NF, <i>plus</i> • Monovalent ions
ED/EDR	• Dissolved ions

polyamide hollow fine-fiber membrane in the form of the B-9 permeator for brackish water desalting. These brackish water modules generally operated in the pressure range of 300 to 400 psi. The first municipal brackish water RO plant was located at Key Largo, Florida's, Ocean Reef Club. The plant began operation in October 1971 with an initial operating pressure of 600 psi and a capacity of 0.6 mgd, which was later expanded to 0.93 mgd.

In 1974, DuPont introduced the hollow fine-fiber B-10 permeator, the first RO membrane capable of producing potable water from typical seawater in a single pass at operating pressures of 800 to 1,000 psi. Spiral-wound, thin-film composite RO membranes developed for both seawater and brackish water desalting were introduced in the mid- to late 1970s. Feed pressures for the early composite membranes were approximately the same as for the cellulosic and polyamide hollow fine-fiber modules. Dow Chemical Company's introduction of the low-pressure Dowex™ hollow fine-fiber RO membrane led to a major reduction in the cost of brackish water RO facility operation. The first plant to use the new membrane began operation in 1981, at Venice, Fla., with a 1 mgd capacity. The Dowex™ membrane provided salt rejection and fluxes comparable to the standard pressure cellulosic and polyamide membranes at roughly one half the operating pressure (200 to 250 psi versus 400 to 600 psi).

Low-pressure, thin-film composite, spiral-wound modules were first introduced in the early 1980s by FilmTec Corporation (now part of Dow Chemical Company) and Fluid Systems (now part of Koch Membrane Systems). These composite membranes, currently available from a number of supplier firms, are now commonly used, except in applications in which the better chlorine tolerance of cellulosic membranes is desired.

The expansion of the Englewood Water District's plant in southwestern Florida illustrates the evolution of spiral-wound brackish water RO membrane technology. The original RO process trains (1982) used standard brackish water cellulose acetate blend membranes operating at 400 to 600 psi. New RO trains installed during an initial expansion in 1986 employed the early generation polyurea composite membranes. During an additional expansion in 1989, the new trains and several of the older units were outfitted with more advanced, low-pressure, fully aromatic polyamide composite membranes. As shown in Table 1-2, the energy required for the RO process in 1989 was

Table 1-2 Comparison of three generations of brackish water RO membranes at Englewood Water District, Fla.

Parameter	RO Train			
	Train A (1982), Cellulose Acetate Blend	Train A (1986), Composite (Polyurea)	Trains B and C (1986), Composite (Polyurea)	Trains D and E (1989), Composite (Fully Aromatic Polyamide)
Design feedwater TDS, <i>mg/L</i>	4,700	6,000	6,000	7,000
Maximum design feed pressure, <i>psi</i> (stage 1)	600	420	*	335
Normalized specific flux, <i>gpd/psi</i> [†]	0.041	0.057	0.069	0.082
Relative membrane energy usage, % of initial plant design	100 [†]	72	59	50

* Trains include interstage booster pumps between the first and second stages.

[†] All RO trains have the following characteristics: 0.5-mgd permeate capacity at 65 percent minimum and 70 percent design recovery. All trains are normalized to 4,700 mg/L feedwater TDS to permit direct comparison of energy usage at initial plant feedwater conditions. After expansion and upgrade in 2005, a sixth RO train has been added and all trains now use polyamide membranes in single-stage train arrangements with 8 elements per pressure vessel designed to treat 7,000 mg/L TDS design groundwater quality.

50 percent less than the original 1982 plant design, a dramatic decrease made possible by rapid advances in the technology in less than a decade. Train F, installed in 2005, uses even less energy. Currently, all trains use polyamide composite RO membranes in a single-stage arrangement with energy recovery turbopumps that recover energy from the waste concentrate stream and transfer it to the feed. Chapter 3 discusses integrated turbopumps and other commercially available energy recovery devices.

The concept of membrane softening was introduced in 1976, and the following year a 0.25-mgd membrane softening plant was installed in Pelican Bay, Naples, Fla. The plant used a Fluid Systems hydrolyzed (i.e., “loose”) RO membrane and was later expanded to 0.5 mgd. Membrane softening was in limited use until 1984, when FilmTec Corporation introduced polyamide NF spiral-wound elements. Other manufacturers subsequently developed similar products.

RO and NF Membrane Systems

A typical RO or NF membrane system consists of three separate subsystems: pretreatment, the membrane process, and posttreatment. Figure 1-3 illustrates a typical system, including one influent stream (i.e., feed) and two effluent streams (i.e., permeate and concentrate). Essentially all sources of water to which RO and NF membrane systems are applied must undergo certain levels of pretreatment. Pretreatment processes usually involve adding acid, scale inhibitor, or both to prevent precipitation of sparingly soluble salts as the rejected ions become more concentrated, followed by 5- to 20- μ m cartridge filtration to protect the RO/NF membranes from particulate fouling. Additional pretreatment measures (typically upstream of the standard cartridge filter) may be necessary for water with higher fouling potential, such as most surface waters. Posttreatment may include many unit operations common to conventional drinking water treatment, such as aeration, degasification, pH adjustment, addition of corrosion control chemicals, fluoridation, and disinfection. The unit operations in each subsystem (i.e., pretreatment and posttreatment) are discussed in detail later in subsequent chapters. A thorough understanding of source water characteristics and product water quality goals is

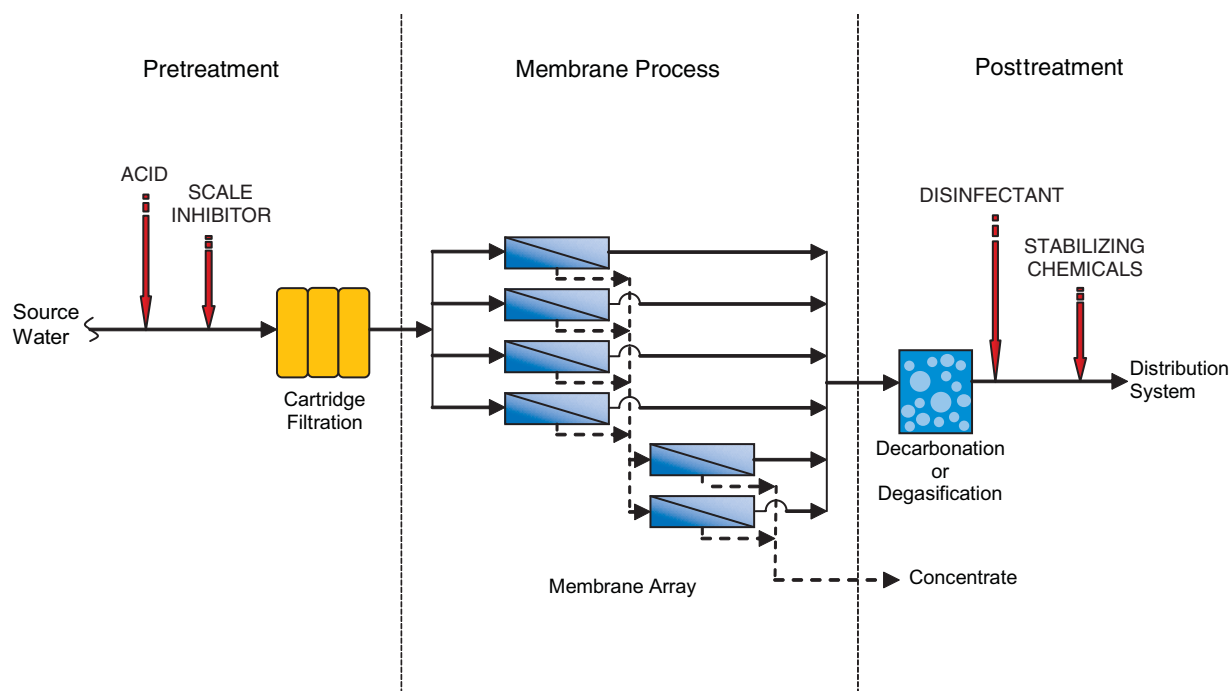


Figure 1-3 Typical RO or NF membrane system

essential to the successful design and operation of a RO or NF treatment plant, because the contaminants found in the source water determine which combination of pre- and posttreatment methods will be necessary.

RO AND NF MEMBRANE APPLICATIONS

This section describes the major current applications of RO and NF membrane processes, including: desalting, the removal/reduction of DBP precursors, hardness (i.e., softening), color, inorganic contaminants (e.g., nitrate, fluoride, arsenic, heavy metals, radionuclides, etc.), synthetic and volatile organic compounds, pathogens, and indirect potable reuse. A short discussion of emerging applications is also provided. Note that RO and NF can also remove suspended solids/particulate matter; however, because the semipermeable membranes are not porous (and therefore not able to be backwashed), any significant particulate loading can rapidly and sometimes irreversibly foul the membranes. Thus, although RO and NF will reduce particulate matter levels (i.e., turbidity, particle counts, etc.), the technology is not applied specifically for this purpose, and pretreatment to remove particulate matter upstream of the membranes is almost always employed.

A flowchart for selecting an appropriate membrane process (including MF, UF, and ED/EDR) is shown in Figure 1-4. Note that this is a very general guideline and does not take into account cost, site-, or application-specific considerations. The figure is primarily intended to serve as an illustrative tool to distinguish the various types of membrane processes on the basis of treatment application.

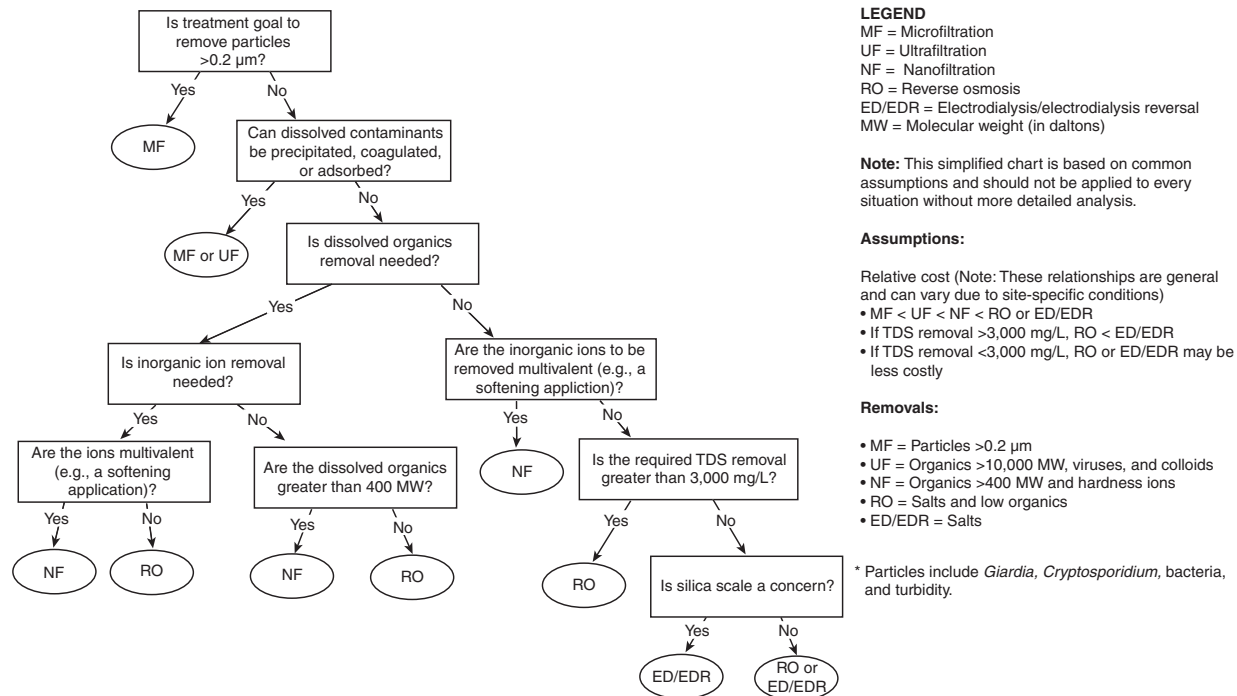


Figure 1-4 Generalized membrane process selection chart

Desalting (TDS Removal)

The primary application of RO and NF membranes is desalting (i.e., TDS removal) from saline surface water, brackish groundwater, seawater, tertiary treated wastewater, or industrial process water. The rejection capabilities of different commercially available products can vary significantly, and in many cases particular membranes are selected specifically for a target TDS range. Because incremental increases in TDS reduction boosts the required pressure, translating to higher energy costs, it can be significant in some cases to ensure that TDS is only reduced to the extent such that the desired treatment objective is satisfied. For example, for saline surface waters that may be relatively low in TDS but high enough to adversely impact the taste of the water for a utility's customers, a low-pressure/low-rejection RO membrane may be used with less efficient rejection characteristics. By contrast, in high purity applications that are common in industry or seawater desalination, RO membranes with much higher rejection of TDS are necessary. For potable water applications, the United States Environmental Protection Agency (USEPA) has established a secondary maximum contaminant level (SMCL) for TDS of 500 mg/L. While this federal SMCL is nonenforceable and established for aesthetic quality, this benchmark is often used as a target for treated water quality, particularly when it may be significantly more expensive to further reduce the TDS. (Note that water quality regulations can vary from state to state, and in some states, the federal SMCLs are enforceable by state mandate.)

Because the removal of TDS by RO and NF is nonselective and relatively high rejections are achieved, the permeate produced by these processes is typically very corrosive and characterized by low alkalinity and minimal buffering capacity. If acid

is used as pretreatment to control scaling, the pH may also be low, further compounding the aggressive nature of the permeate. However, RO and NF systems can be designed with appropriate posttreatment processes to produce water that is both low in TDS and well buffered with sufficient alkalinity to help reduce the potential for pipe corrosion in the distribution system.

DBP Precursors

Because DBPs are a significant regulatory concern, RO and NF membranes are increasingly applied to remove DBP precursors such as natural organic matter (NOM)/TOC, which can react with various disinfectants used in the water treatment process to form potential carcinogens. These DBPs include total trihalomethanes (TTHMs) and the sum of five haloacetic acids (HAA5), both of which are strictly regulated in the parts per billion range by the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules. As a result of these low maximum contaminant levels (MCLs), NOM removal is a significant water treatment objective for many utilities. RO or NF as a stand-alone process has been shown in many cases to reduce TOC to less than 0.5 mg/L. RO can also remove TTHMs and HAAs, albeit less efficiently than their precursor material; however, it is uncommon to apply these membranes for DBP reduction after the disinfection process in water treatment plants as a result of the susceptibility of most such membranes to damage from chemical disinfectants.

Hardness

NF has become a significant alternative to lime softening for reducing the level of calcium and magnesium ions in naturally hard waters where TDS reduction is not a primary treatment goal. Although RO membranes are also capable of reducing hardness, NF membranes have lower rejection characteristics for monovalent ions, allowing them to be operated at lower pressures while still efficiently removing the divalent ions that contribute to hardness, resulting in energy cost savings. Typically, NF membranes used for softening applications remove more than 95 percent of total hardness.

Color

NF is also more effective than lime softening in removing naturally occurring color and DBP precursors, both comprised primarily of organic carbon, and can often be operated more efficiently than RO. NF is generally capable of removing more than 95 percent of color.

Inorganic Contaminants

The USEPA currently recognizes RO as the best available technology (BAT) for removing most inorganic compounds (IOCs) regulated under the Safe Drinking Water Act (SDWA) (Clark and Parrotta 1991), including radionuclides and arsenic, among many others. This classification reflects the broad-spectrum removal capability of the RO process. The ability of NF to remove IOCs is determined to a large extent by the specific dissolved solids character of the water. NF rejection of specific multivalent cations is a function of solution pH and the speciation of other ionic constituents present to a greater degree than for the RO process.

One of the more common applications of RO for treating a specific inorganic contaminant is nitrate removal. RO is considered an effective nitrate removal process for groundwater supplies polluted by the agricultural use of nitrate-containing fertilizers or septic tank discharges. Rejection of nitrate by some RO membranes is significant; composite polyamide low-pressure brackish water membranes typically

exhibit sodium nitrate rejection in the range of 93 to 97 percent (FilmTec 1988; Toray 1989). Several RO plants are currently in operation in southern California treating groundwater contaminated with high concentrations of nitrate from past agricultural practices, including those in the cities of Riverside and Tustin, as well as several facilities operated by the Chino Basin Desalter Authority. Note that NF is generally not applied for nitrate removal as a result of its relatively low rejection of this anion compared to RO.

Another inorganic contaminant to which RO is often applied is fluoride. Many groundwater sources in the United States contain elevated levels of naturally occurring fluoride. The USEPA has established a fluoride MCL of 4 mg/L to protect against skeletal fluorosis and a recommended SMCL of 2 mg/L to prevent tooth discoloration. Because levels of naturally occurring fluoride are about the same order of magnitude as the MCL, it is generally not necessary to achieve extremely high rejection, particularly considering that 0.8 to 1.2 mg/L of fluoride in drinking water is recommended for dental health. As a result, in many cases treatment costs can be reduced through the use of split treatment, in which a portion of adequately treated source water is bypassed around the membrane system and blended with the RO permeate.

In general, for water quality constituents or specific inorganic contaminants that are relatively common, RO/NF membrane manufacturers have modeling software that can predict permeate quality fairly accurately. However, for the removal of less common inorganic contaminants for which RO and NF have not been as frequently utilized, rejections are typically based on manufacturer, utility, or independent, third party experience and research. Although increasingly uncommon for many well-known inorganic contaminants, pilot testing can be conducted to quantify or verify rejection levels, if desired.

Synthetic and Volatile Organic Chemicals

Many of the synthetic organic compounds (SOCs) regulated by the USEPA in drinking water supplies are pesticide residuals. Pilot testing has been conducted in a municipality–USEPA partnership to evaluate the pesticide removal efficiency of a number of different types of RO membranes for treatment of groundwater contaminated by various agricultural chemicals (Bailer et al. 1987). This study found that removals were greatest for the polyamide thin-film composite membranes (67 to 95 percent), and it concluded that RO should be considered as a water treatment process for this application (Lykins et al. 1988). Other studies have assessed the capability of a wide range of NF membranes to remove commonly occurring pesticides to below the 0.1 µg/L (Côté et al. 1993; Hofman et al. 1993). Theoretically, specific SOC rejection is primarily a function of molecular size and degree of ionization. This theory was corroborated by a pilot study demonstrating that the degree of rejection is proportional to the molecular weight. Synthetic organic chemicals with a molecular weight greater than 300 Daltons were completely rejected by one type of NF membrane, while those with molecular weights less than 300 Daltons were only partially rejected. For these studies, the degree of rejection was proportional to the molecular weight (Taylor et al. 1989b).

It is less common for RO and NF to be applied for the removal of volatile organic compounds (VOCs), such as trichloroethylene and tetrachloroethylene, among others, because rejection is generally inefficient (albeit varying by specific compound). In addition, many VOCs are solvents that at higher concentrations may dissolve the glue lines on the membrane elements or damage the membranes themselves. It has also been reported that some VOCs may adsorb onto the membrane, potentially

reducing permeability or desorbing into the permeate in concentrations higher than the feed until steady state is achieved (Lenz et al. 2005).

Pathogens

Because semipermeable RO and NF membranes are not porous, they have the ability to screen microorganisms and particulate matter in the feedwater. This ability has been verified in a number of studies, such as one that demonstrated that RO membranes provide between 4- and 5-log (i.e., 99.99 to 99.999 percent) removal of viruses normally associated with waterborne disease (Lozier et al. 1994). According to the *Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources* (commonly referenced as the *Surface Water Treatment Rule [SWTR] Guidance Manual*), RO is listed as an alternate filtration technology that is effective for the removal of *Giardia* and viruses (USEPA 1990), such that unlike many other alternate technologies, no piloting or other studies are necessary to demonstrate that the RO process can achieve 3.0-log (i.e., 99.9 percent) *Giardia* and 4.0-log virus removal when combined with disinfection. The proposed Ground Water Rule also notes the demonstrated ability of RO and NF to achieve 4.0-log virus removal. In addition, under the Long Term 2 Enhanced Surface Water Treatment Rule, both NF and RO are specifically listed as *membrane filtration* technologies that can be applied to achieve significant *Cryptosporidium* removal credit (USEPA 2006).

However, it is important to note that RO and NF are not necessarily absolute barriers. RO and NF membranes are primarily designed for the removal of TDS rather than particulate matter, and thus the elimination of all small seal leaks that have only a nominal impact on the salt rejection characteristics is not the primary focus of the manufacturing process. Consequently, RO and NF spiral-wound elements are not intended to be sterilizing membranes and some passage of particulate matter, including pathogens, may occur despite the absence of pores in the membrane.

Indirect Potable Reuse

Both RO and NF are being increasingly used in the reclamation of municipal wastewaters serving indirectly as future potable water supplies and other reuse applications. In some of these applications, RO and NF remove many contaminants, including nitrogen, heavy metals, TOC, and pathogens, and subsequently the high-quality permeate is injected into groundwater aquifers for recharge. The underground strata serve as an additional filtration step to achieve natural attenuation of the groundwater supply, in some cases over many years, before it is pumped to the surface again for further treatment and distribution. RO technology is often a critical component for groundwater recharge with reclaimed water. The state of California, for example, currently requires all recycled water to be treated via RO prior to injection. The oldest and most widely known groundwater recharge project is the Orange County Water District's Ground Water Replenishment System in Fountain Valley, Calif., which originated as Water Factory 21, and has been in service since 1976. Numerous other utilities in California, Arizona, and other states are also practicing, planning, or studying indirect potable reuse using RO.

Emerging Applications

Because RO and NF achieve significant rejection/removal of a wide assortment of potable water contaminants, these processes are often among the first treatment technologies considered for a variety of emerging applications. For example, perchlorate—an inorganic anion—is one such emerging contaminant that is only

effectively removed by a limited range of technologies, such as RO and ion exchange. RO and NF are also likely to be among the BATs for removing contaminants such as endocrine disruptors and pharmaceutically active compounds, two broad classes of contaminants that are just beginning to be studied and quantified in drinking water sources. As improved analytical techniques continue to reveal previously unknown contaminants, it is likely that the number of applications for RO and NF will likewise increase.

MEMBRANE MATERIALS AND CONFIGURATIONS

The fundamental components of an RO/NF system are the membrane material and the configuration into which the material is manufactured. This section describes both of these components, elaborating on the different types of materials and configurations used in drinking water applications.

Membrane Materials

The two basic types of membranes currently used are asymmetric homogeneous and composite. A wide variety of materials are used, including cellulose acetate and polymers such as aromatic polyamides. The first commercial membranes were asymmetric (i.e., nonuniform density) brackish water RO membranes with a thin, dense surface, 0.1 to 1.0 μm thick on an otherwise spongy, porous film 80 to 100 μm thick, as illustrated in Figure 1-5. The surface or skin gives the membrane its rejection characteristics, and the porous substrate supports this skin to withstand pressure differentials of over 1,000 psi in some seawater RO applications. These first

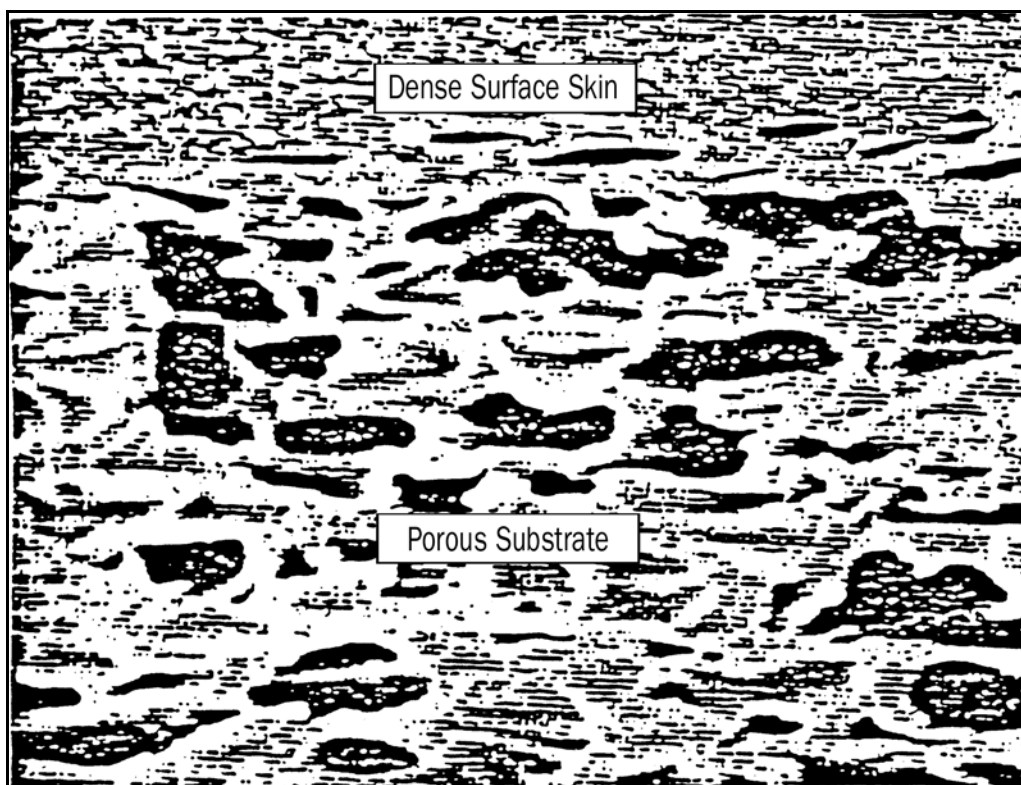


Figure 1-5 Cross-section of an asymmetric membrane

commercial asymmetric RO membranes were made of cellulose acetate material, with the dense skin obtained through an annealing process. Modified cellulosic membranes, including cellulose diacetate and cellulose triacetate, are less expensive than noncellulosic membranes and are thus still used in some applications.

Membranes made from cellulosic materials have some significant limitations. First, cellulose acetate hydrolyzes back to cellulose over a period of time, resulting in a loss of salt rejection even under ideal conditions. As shown in Figure 1-6 the hydrolysis of cellulose acetate is influenced by both pH and temperature. In particular, hydrolysis is accelerated at warmer water temperatures. The optimal feed water pH is approximately 5 for cellulosic membranes, and the pH must be maintained between 4.5 and 6.5 to maximize the membrane's useful life. Accordingly, chemical cleaning must be performed within a relatively narrow pH range (4 to 8), which can limit the effectiveness of the cleaning process in some cases. Cellulosic membranes are also subject to deterioration in the presence of microorganisms capable of cellulose enzyme production. However, because of the material's substantial oxidant tolerance, this risk can be avoided by source water chlorination to 1 mg/L. This same oxidant tolerance is one of the primary advantages of cellulosic membranes.

Asymmetrical membranes, whether manufactured from cellulosic or other materials, are subject to compaction. Compaction occurs mainly in the porous spongy substrate and results in the loss of productivity (i.e., flux) over time. Because the degree of compaction is influenced by the applied pressure, this phenomenon is more pronounced in high-pressure seawater RO applications. However, some degree of compaction also occurs in brackish water applications operating at much lower pressures.

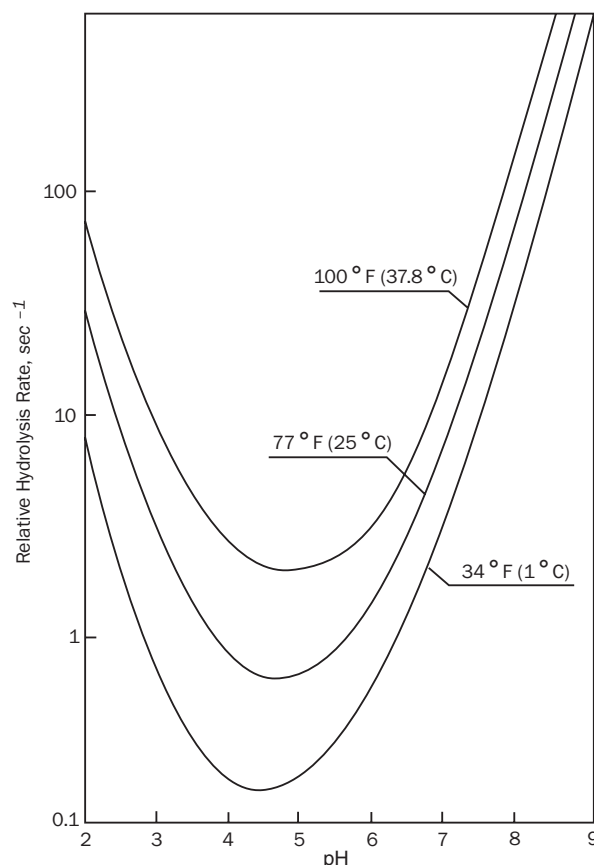


Figure 1-6 Effect of temperature and pH on hydrolysis of cellulose acetate

More recently developed types of membranes are composites of various polymers. Composite membranes are formed by interfacial polymerization on a separate microporous layer, usually polysulfone, which replaces the conventional substrate to support the ultrathin (i.e., 250 to 2,000 Å) salt barrier, as shown in Figure 1-7. A variety of polymers are used for the barrier layer, including the most common fully aromatic polyamides: aryl-alkyl polyamides and polyurea. The initial thin-film composites used aryl-alkyl polyamides as the salt barrier and were extremely sensitive to oxidants, which adversely affected long-term performance. Composites are also made with a salt barrier of fully aromatic cross-linked polyamides that feature more of the desirable characteristics than any other membrane to date. NF employs another type of composite membrane using modified polyamides and piperazinamides for the barrier layer.

Aromatic polyamide membranes, which can tolerate pH levels from 2 to 12 without hydrolysis, can operate over a wider pH range than cellulosic membranes. These membranes are also not susceptible to biological attack. However, because the material is sensitive to oxidants, which can degrade the membrane and result in the loss of salt rejection capabilities, chlorinated water supplies must be dechlorinated prior to the membrane process.

Table 1-3 provides a general summary of key advantages and disadvantages of cellulose acetate and thin-film composite membranes. (It should be noted that properties and characteristics vary somewhat by manufacturers and specific membrane products.)

Primarily due to higher rejection characteristics and lower operating pressures, thin-film composite membranes are most commonly used in water treatment applications. One general exception is the use of membranes in applications in which the source water is higher in organic material. In these cases, the cellulose acetate membranes may offer benefits in terms of more limited membrane biofouling, less frequent cleaning, and potentially reduced pretreatment.

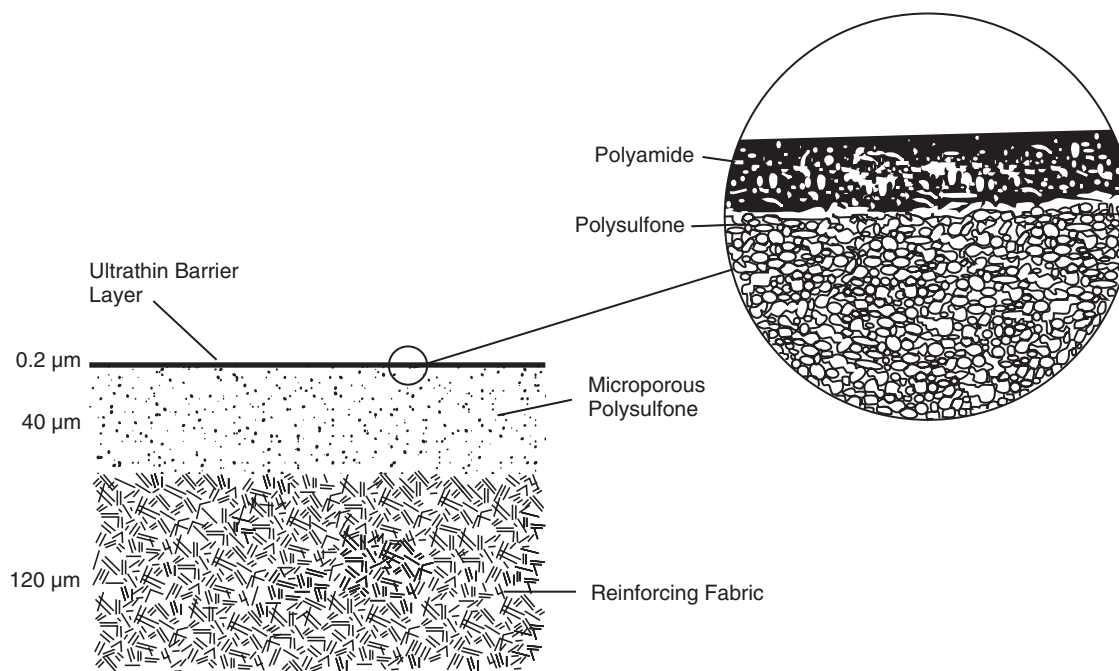


Figure 1-7 Schematic cross-section of a thin-film composite RO membrane

Table 1-3 Comparison of thin-film composite and cellulose acetate membranes

Parameter	Thin-Film Composite Polymer Membranes	Cellulose Acetate Membranes
Salt rejection	Higher (>99.5%)	Lower (up to 95%)
Net driving pressure	Lower	Higher
Surface charge	More negative	Less negative
Chlorine tolerance	Poor	Fair
Cleaning frequency	Higher	Lower
Organics removal	Higher	Lower
Biofouling	More susceptible	Less susceptible
Biodegradation	None	Higher
pH tolerance	High (2–13)	Limited (4–8)

Membrane Element Configurations

A membrane by itself is fragile and must be carefully supported and packaged so that it can be integrated into a unit process. In addition, features are added that enhance permeation of water through the membrane (i.e., flux) and which increase salt rejection. The membrane is generally packaged to minimize hydraulic pressure losses and yet allow sufficient velocities to keep the surface of the membrane flushed clean of concentrated salts and particulate matter. The mechanical design of a membrane element also allows for passage of colloidal and particulate matter through to the concentrate to the extent possible in order to minimize particulate fouling. All of these features are combined with the membrane material itself into a membrane element, which is the smallest discrete unit of an RO or NF system. There are four basic element configurations that have been utilized to at least some extent in commercial applications: tubular, plate-and-frame, hollow fine-fiber, and spiral-wound. Although each of these configurations is described briefly as follows, only the spiral-wound configuration is widely used in modern municipal water treatment applications.

Spiral-wound elements. A membrane utilized in a spiral-wound configuration, as illustrated in Figure 1-8, is manufactured or cast in sheet form on a backing material such as sail cloth (for cellulosic membranes) or a nonwoven polyester web (for the newer composite membranes). Two of these sheets are placed back to back, separated by a spacing fabric/screen that acts as a permeate channel or carrier. Two sides and one end of this sandwich assembly are glued together along the edges to form an envelope or leaf. The open end of the leaf is connected to the permeate tube, around which the leaf is wrapped to form the spiral. An additional sheet of plastic netting (i.e., the feed spacer) is wrapped with each of the numerous leaves to separate the membrane surfaces, maintain the feed channel height, and create turbulence. The spiral assembly, or element, is secured to prevent unraveling by an outer wrap, and a concentrate (i.e., brine) seal is fixed to one end. An antitelescoping device is attached to both ends of the membrane element to maintain a fixed space between elements and facilitate flow from one element to the next. Multiple elements are housed in a series in a cylindrical vessel, as illustrated in Figures 1-9 and 1-10, with the feed and concentrate flowing through the feed-side channels in a straight line along the axis of the element. Some of the water penetrates the membrane and spirals its way to the center, collecting in the central permeate tube. The remaining water passes from the element and out the concentrate port of the pressure vessel. For most applications, several elements, usually six to eight, are housed in a series within the pressure vessel. The concentrate from one element serves as the feed for

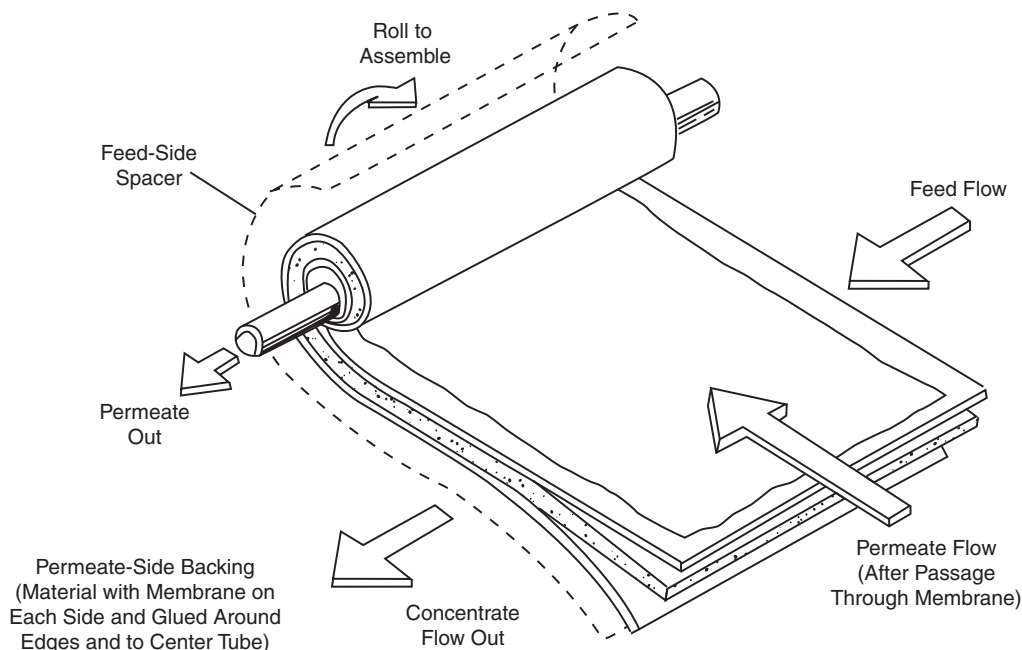


Figure 1-8 Spiral-wound module

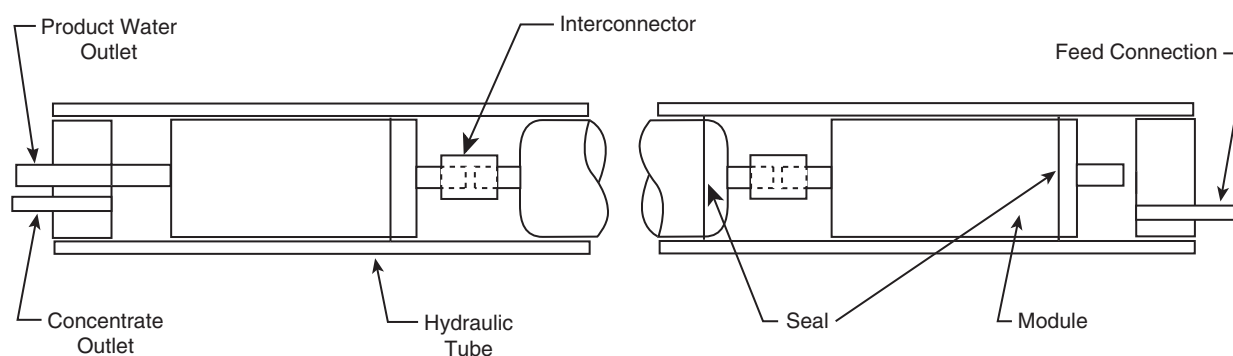


Figure 1-9 Pressure vessel assembly

the next in a series. Permeate can be collected from the back end or both ends of the membrane pressure vessel

Hollow fine-fiber elements. Sometimes called *hollow fiber membranes*, the additional term *fine* is often used to distinguish this membrane configuration from larger diameter hollow fiber membranes, such as those employed with MF and UF. A hollow fine-fiber membrane is spun with its own support structure. A diagram of a hollow fiber dual-module product is shown in Figure 1-11. The fibers are bundled together as U-shaped tubes with the open ends potted in a tube sheet. The other end of the fiber bundle is also sealed to prevent short-circuiting of the feed stream to the concentrate (i.e., brine) outlet. The bundle is cased in a pressure vessel with the pressurized feed distributed from a tube in the center of the bundle. As it flows radially through the bundle and over the fibers, some of the water penetrates the fibers, flows down the bore, and is collected at the end of the vessel. The remainder

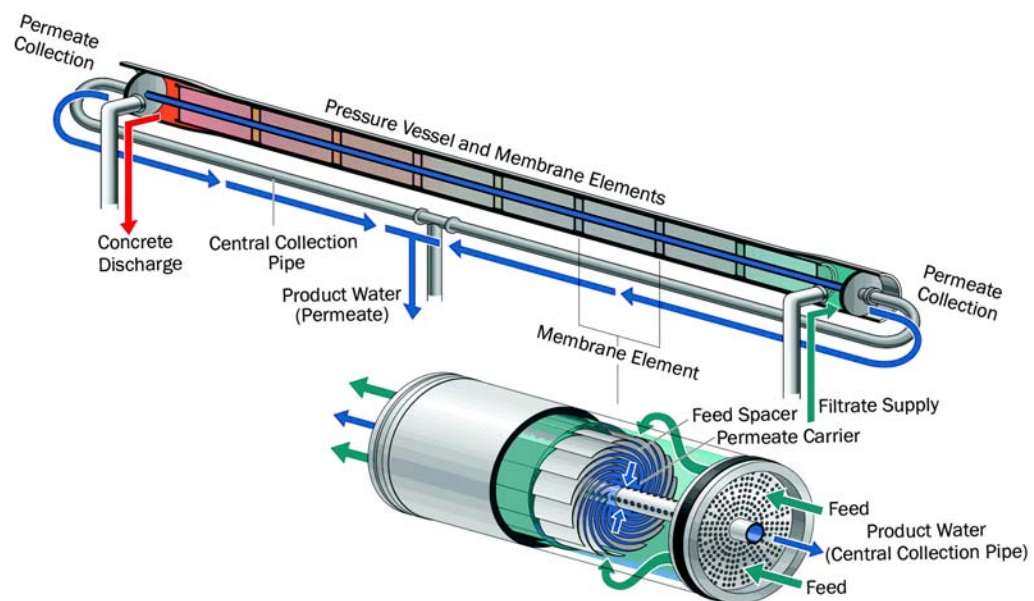
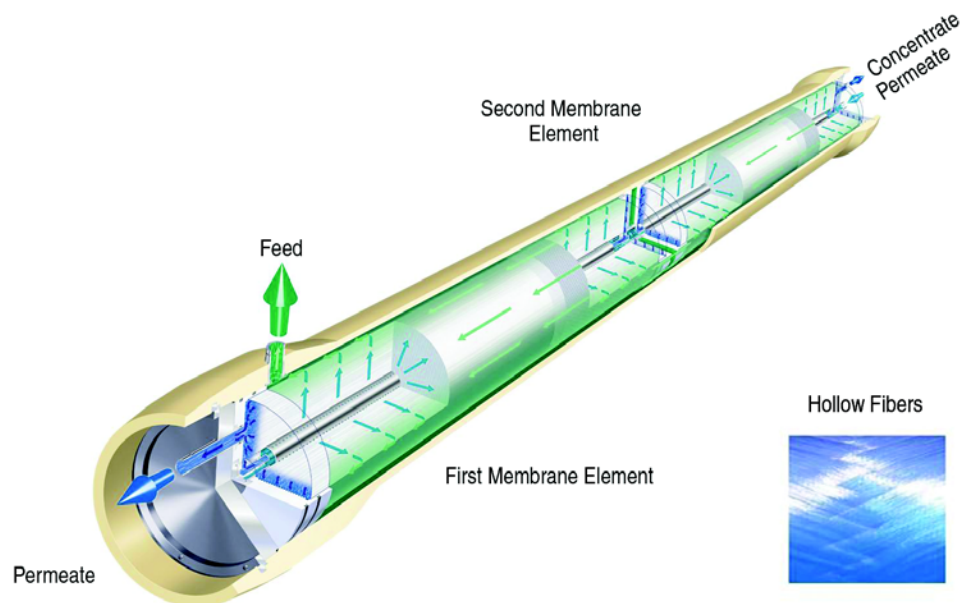


Figure 1-10 Membrane pressure vessel with eight elements



Courtesy of Toyobo, Co., LTD.

Figure 1-11 Hollow fiber membrane module

of the water carries concentrated salts to the concentrate port of the vessel. Because the membrane packaging density is so high, this device has the highest ratio of membrane area to treatment process footprint. The very small diameter fibers dictate lower fluxes with the hollow fine-fiber membrane configuration, but this offers the advantage of minimizing the problem of concentration polarization. The high-density packaging also leaves very little space between the fibers, making it even more critical to remove suspended solids and colloidal matter in order to avoid fouling.

Tubular and plate-and-frame elements. The use of tubular and plate-and-frame membrane configurations dates back to the beginning of membrane technology. Tubular membranes are essentially a larger, more rigid version of hollow fine-fiber membranes that are not as prone to clogging and that are comparatively easy to clean. The plate-and-frame configuration, one of the earliest membrane designs developed, is simply a series of flat sheet membranes separated by alternating filtrate spacers and feed-concentrate spacers. Both the tubular and plate-and-frame designs have a low membrane-packing density, resulting in a higher capital cost and larger footprint than for spiral-wound or hollow fine-fiber configurations. These designs are used in the food industry (e.g., whey concentration in cheese production and tomato juice concentration) and in some wastewater treatment applications, but seldom compete with spiral-wound and hollow fine-fiber devices in potable applications of brackish water or seawater desalination. One notable exception is in the case of ED/EDR systems, which utilize a design that lends itself well to the use of a plate-and-frame type of membrane arrangement.

REFERENCES

- AWWA. 1995. *M38—Electrodialysis and Electrodialysis Reversal*. Denver, Colo.: American Water Works Association.
- AWWA. 2005. *M53—Microfiltration and Ultrafiltration Membranes*. Denver, Colo.: American Water Works Association.
- Bailer, J.H., B.W. Lykins Jr., C.A. Fronk, and S.J. Kramer. 1987. Using reverse osmosis to remove agricultural chemicals from groundwater. *Jour. AWWA*, 79(8): 55–60.
- Bergman, R.A., and J.C. Lozier. 1990. Expanding Applications for Membrane Processes in Water Treatment. In *Proc. of the National Water Supply Improvement Association Biennial Conference*. August 19–23. Lake Buena Vista, Fla.: National Water Supply Improvement Association.
- Brunswick, R.J., W. Suratt, and J.E. Burke. 1993. Pilot Testing RO Membranes for Nitrate Removal. In *Proc. of the AWWA Membrane Technology Conference*. Denver, Colo.: American Water Works Association.
- Buros, O. 1980. *The USAID desalination manual*. Englewood, N.J.: IDEA Publications.
- Clark, S.W., and M.J. Parrotta. 1991. Membrane Technologies and Drinking Water Regulations. In *Proc. of the AWWA Membrane Technologies in the Water Industry Conference*. Denver, Colo.: American Water Works Association.
- Côté, P., M.M. Bourbigot, and K. Agbekodo. 1993. Nanofiltration: An Advanced Process for the Production of High Quality Drinking Water. In *Proc. of the AWWA Membrane Technology Conference*. Denver, Colo.: American Water Works Association.
- Filmtec Corporation. 1988. *FT-30 Reverse Osmosis Membrane Specifications*. Technical Bulletin. Midland, Mich.: Dow Chemical Company.
- Hofman, J.A.M.H., Th.H.M. Noij, J.C. Kruithof, and J.C. Schippers. 1993. Removal of Pesticides with Nanofiltration. In *Proc. of the AWWA Membrane Technology Conference*. Denver, Colo.: American Water Works Association.
- Lenz, M., M. Bell, C. Spangenberg, G. Filteau, and E. Owens. 2005. Performance of NF and RO Membranes on VOC Contaminated Groundwaters: Literature Summary and Pilot Test Results. In *Proc. of the AWWA Membrane Technology Conference*. Denver, Colo.: American Water Works Association.
- Lozier, J.C., T. McKim, and J. Rose. 1994. *Meeting Stringent Surface Water Discharge Requirements for Reclaimed Water with Membrane Processes*. Paper presented at the ASCE/NCEE Conference July 11–13 at Boulder, Colo.

- Lykins, B.W., et al. 1988. *Reverse Osmosis for Removing Organics from Drinking Water: A Cost and Performance Evaluation*. USEPA Publication PB88-225016. Cincinnati, Ohio: US Environmental Protection Agency.
- Mickley, M., R. Hamilton, L. Gallegos, and J. Truesdall. 1994. *Membrane Concentrate Disposal*. Denver, Colo.: Awwa Research Foundation and American Water Works Association.
- Taylor, J.S., S.J. Duranceau, W.M. Barrett, and J.F. Goigel. 1989a. *Assessment of Potable Water Membrane Applications and Research Needs*. Denver, Colo.: Awwa Research Foundation and American Water Works Association.
- Taylor, J.S., L.A. Mulford, S.J. Duranceau, and W.M. Barrett. 1989b. Cost and performance of a membrane pilot plant. *Jour. AWWA*, 81(11): 52-60.
- Toray Industries. 1989. *Toray "Romembra" UTC Membrane Reverse Osmosis Module (SU-Series, SU-710L/720L)*. Technical Bulletin Series. China 279, Japan: Toray Industries.
- USEPA. 2006. *Membrane filtration guidance manual*. Washington, D.C.: USEPA.
- USEPA. 1990. *Guidance manual for compliance with the filtration and disinfection requirements for public water systems using surface water sources*. Washington, D.C.: USEPA.

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Chapter 2

Process Design

Revision Authors: Rob Huehmer and Nikolay Voutchkov (for intakes)

This chapter discusses the general process design principles of RO and NF membrane systems, including the following topics:

- source water
- process design of membrane unit
- posttreatment

Process design fundamentals for selecting and sizing pretreatment, membrane, and posttreatment components of an RO or NF system are discussed in this chapter, as are source water quality and quantity factors. Refer to Figure 1-3 for a schematic view of the typical membrane system used in the subsequent discussions. Table 2-1 summarizes the typical design factors and related unit processes.

This chapter is intended to introduce readers to basic RO and NF design considerations. Reference sources are available for further study in the Additional Sources of Information section at the end of the chapter.

SOURCE WATER SUPPLY

An accurate source water quality analysis of parameters, such as those listed in Table 2-2, is required for NF and RO design. The water quality analysis allows the designer to correctly design the pretreatment and membrane components. The analysis is also used to predict membrane permeate quality. Samples should be split among several certified laboratories with experience in analyzing source water for membrane process treatment as part of the quality assurance and control program. Critical parameters, such as barium, strontium, sulfate, fluoride, and silica, must be accurately analyzed at appropriate detection levels to evaluate scaling potential, particularly for RO and NF applications. For many applications, fouling potential is

Table 2-1 Membrane system design factors and unit processes

Design Factors	Related Unit Processes
Source water supply	
Water quality	Intake, pretreatment, membrane bypass/blending
Water quantity	Pumping, unit operation sizing
Pretreatment	
Fouling potential	
Particulate	Coagulation, flocculation, sedimentation, filtration, MF, UF
Organic	Coagulation, flocculation, sedimentation, filtration, MF, UF
Biological	Coagulation, flocculation, sedimentation, filtration, MF, UF, chlorination, dechlorination
Scaling potential	pH adjustment and scale inhibitor addition
Membrane process	
Feed pressure	Membrane treatment
Permeate recovery rate	Membrane treatment
Permeate flux	Membrane treatment
Permeate quality	Membrane treatment
Posttreatment	
Stabilization	Recarbonation, aeration–degasification, pH adjustment, alkalinity recovery, potential corrosion inhibitor addition
Disinfection	Disinfection
Finished water quality	Membrane bypass and product water blending

also generally predicted by the concentration of DOC, turbidity, and/or biological activity indicators such as heterotrophic plate count (HPC). The reader is cautioned that fouling rates should be determined based on pilot-plant tests for the most accurate indication of fouling potential.

Contaminants of primary concern are:

- Cations that may form scales when concentrated in the membrane system (e.g., calcium, strontium, barium); that may precipitate as hydroxides and foul the membrane elements (e.g., iron, manganese); or are important to meet product water quality objectives (e.g., hardness ions, sodium, boron [for seawater applications])
- Anions that may form scales (e.g., alkalinity ions, sulfate, fluoride, phosphate [water reclamation and reuse application]) and are important for meeting product water quality criteria (e.g., chloride)
- Silica, a nonionic constituent that may precipitate when concentrated, especially in the presence of multivalent cations
- Potential foulants, including bacteria and colloidal material
- Hydrogen sulfide

One of the most important components of any membrane treatment system is a reliable source water supply (Missimer 1994). Even the most sophisticated, well-designed membrane treatment facility has limitations in its ability to treat highly contaminated or varying quality source water.

The required feedwater flow rate will exceed the permeate production because of the limitations in permeate recovery. Assuming permeate recovery rates ranging from 50 to 90 percent, the ratio of required source water to permeate could range from 1.11 to 2.00, as shown in Table 2-3. Figure 2-1 shows the required feedwater flow rates for facilities with capacities of 1 to 40 mgd at various permeate recovery rates. The impact of raw water flow versus system recovery should be considered in the design of wells, pumps, and delivery piping. Also, if two or more water sources of different quality are available, it may be more economical to use one source water over another. Therefore, an analysis of membrane process costs versus source water supply costs should be performed. It is also very important to assess the chemical stability of the source water.

Table 2-2 Suggested parameters for water quality analysis*

Cations		
Aluminum	Ammonium	Barium
Boron	Calcium	Chromium
Copper	Iron (ferrous and ferric)	Lead
Magnesium	Manganese	Potassium
Sodium	Strontium	Zinc
Anions		
Bicarbonate	Carbonate	Chloride
Fluoride	Nitrate	Nitrite
Phosphate (total and ortho)	Sulfate	
Other		
Algae	Alkalinity	Assimilable organic carbon (AOC)
Color	Conductivity	Dissolved oxygen
HPC	Hydrogen sulfide	Ionic strength and ion balance (calculated from analysis)
Oil and grease	Organic carbon (total and dissolved)	pH
Silica (total and reactive)	Silt density index (SDI)	Sulfide-generating bacteria
Temperature	TDS	Total coliform
Total hardness	Total suspended solids	Turbidity
Yeast and mold		

*Not all of these analyses are required for all membrane design efforts. Membrane manufacturers and consultants with expertise in RO/NF design should be consulted for a recommended list of water quality parameters to be tested.

Table 2-3 Feedwater flow rates based on permeate recovery rates

Permeate Flow Rate, <i>mgd</i>	Product Recovery Rate, %	Feedwater Flow Rate, <i>mgd</i>	Concentrate Water Flow Rate, <i>mgd</i>
1.00	50	2.00	1.00
1.00	60	1.67	0.67
1.00	70	1.43	0.43
1.00	75	1.33	0.33
1.00	80	1.25	0.25
1.00	85	1.18	0.18
1.00	90	1.11	0.11

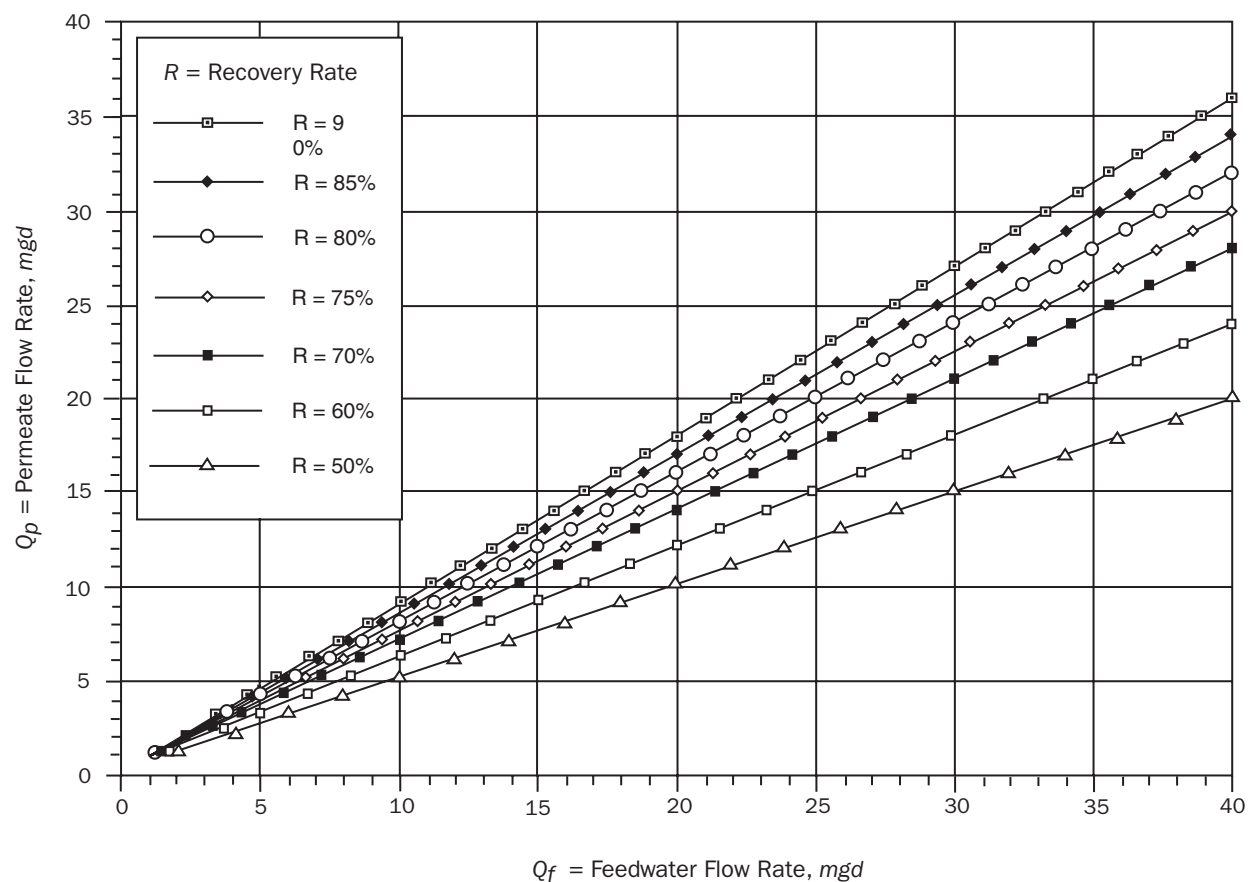


Figure 2-1 Feedwater flow rates for various permeate recovery rates

The following section discusses the development of source water supply and maintenance of water quality. Chapter 3, Facility Design and Construction, presents a discussion of intake design for surface and groundwater sources.

Surface Water

Surface waters present numerous technical problems for pretreatment systems for membrane treatment processes. RO and NF membranes are very sensitive to the concentration of particulates in the water. A surface water source may require construction of comprehensive pretreatment facilities to prevent particulate material from plugging the membranes. Facilities for the coagulation/removal of organic compounds, such as humic acids, may also be required to mitigate membrane fouling.

Beach or shallow wells are sometimes used to avoid direct intakes of surface water. The quality of the surface water supply source can be monitored for many years to assess needed changes in a treatment facility's design.

Fresh water. Intakes for most fresh surface water treatment facilities, regardless of the treatment process, are submerged pipes in rivers, lakes, or reservoirs. A fixed-position intake pipe is commonly found where sufficient data are available to determine that the pipe will always be submerged regardless of climatic conditions. However, many utilities prefer multiple-depth openings to optimize source water quality.

The elevation of the intake pipe should be at least a few feet below the water surface to avoid inflow of floating debris and higher concentrations of aquatic plants, which tend to stay in the photic zone (i.e., those areas of water that are penetrated by light). The intake pipe must also be placed as far from the bottom as possible to avoid collection of sediments. Intakes possessing the ability to withdraw water from multiple depths are recommended in waterways that experience seasonal anaerobic conditions in the benthic region to avoid membrane fouling resulting from increased manganese and iron concentrations. Additional details are contained in *Water Treatment Plant Design* 4th ed. (AWWA/ASCE 2005) and *Water Quality and Treatment* (AWWA 1999).

The end of the intake should be screened to avoid the entrainment of large debris. The diameter of the intake pipe should be sized to adequately permit the required flow, while maintaining acceptable approach velocities to prevent sediment entrainment and the scouring of vegetative growth from the pipe. The presence of zebra mussels in many waterways in North America also requires additional considerations in the design of intake systems. Provision must be provided for the maintenance of the intake screens and pipe work, including disinfection (zebra mussel kill) and physical removal of zebra mussels from the facilities. In many cases, provision of two parallel intake facilities is recommended.

Seawater or brackish water. Intakes from tidal surface water bodies feeding RO water treatment facilities share many common problems with freshwater systems. However, a number of other issues, such as the susceptibility of a facility to corrosion, storm damage, and marine organism growth, must be considered.

A number of existing seawater membrane treatment facilities use surface intake systems. Many of these systems are located in the Middle East or on islands, both natural and artificial (i.e., oil platforms). Most large-scale membrane facilities using direct surface water intakes are located adjacent to large tidal water bodies, such as the Atlantic Ocean or the Arabian (Persian) Gulf. Some critical problems in the design of intakes in these areas are how far offshore and how deep the intake should be placed and what type of terminal should be used.

Oceanographic investigations for intakes are required to assess storm impact potential, potential growth rates of attaching benthic marine organisms (such as corals and sponges), and near-shore water quality fluctuations. The terminal must be below a water depth affected by damaging orbital storm wave motion and yet far enough offshore to avoid the near-shore sediment transport area where storms can

cause suspension of large quantities of sediment. Water quality changes must also be considered in the establishment of the intake point. In the Arabian Gulf, water quality and temperature vary significantly. In some instances, the final intake point may lie several miles offshore. Alternative designs should be considered before a surface intake is installed into any tidal water body.

Similar to fresh water surface sources, the end of the intake should be designed to limit entrainment and impingement. Marine growth may also require additional considerations in the design of the intake system. Provisions for intake screen and pipework must be provided, including disinfection and physical removal of marine growth from the facilities. In many cases, provision of two parallel intake facilities is recommended.

Groundwater

Under steady-state conditions, groundwater normally provides a chemically stable, low turbidity source of water over a long time. However, in coastal areas with high groundwater withdrawal quantities, groundwater quality can vary dramatically. Overpumping can cause saltwater intrusion, which in turn may cause a membrane treatment plant to have problems unless it is designed to accommodate the increased concentration of dissolved solids.

In the development of a groundwater source, the aquifer must be carefully tested and modeled to determine the anticipated short- and long-term changes in water quality. Groundwater quality can change depending on the nature of the aquifer used or the presence of overpumping. The potential for significant water quality changes over time should be considered in the design of the membrane treatment system.

PRETREATMENT

Preserving membrane integrity through proper pretreatment of source water is essential to maximize the efficiency and longevity of an RO or NF membrane system. This section provides a discussion of the various methods of pretreatment that prevent chemical alteration of the membrane polymer and foulant accumulation and scaling on the membrane surface.

Prevent Membrane Damage

If an RO or NF membrane is chemically altered by substances in the source water, the membrane performance efficiency will decrease (such as a decline in salt rejection or loss of productivity). Chemical attacks on membranes generally occur via oxidation or hydrolysis, both of which are easily controlled. The susceptibility to chemical attack is a function of the chemical composition of the membrane polymer.

Cellulose acetate polymers are subject to a loss of rejection properties because of a gradual hydrolysis of the acetyl groups on the polysaccharide backbone. The rate of hydrolysis is a function of pH. Mineral acid is generally required to adjust the pH of most source waters into the 5.5 to 6 range to maximize cellulosic membrane life. Polyamide membranes are capable of operating over a rather broad pH range: from pH 2 to 11 on a continuous basis and up to pH 12 for short-term cleaning. When a polyamide membrane is used for processing water at the higher pH (>8) range, careful consideration must be given to controlling calcium carbonate scaling, as discussed in greater detail in this section.

Although polyamide membranes are not particularly pH sensitive, all varieties of these membranes are intolerant of chlorine and certain other strong oxidizing agents to some extent. Dechlorination through the addition of sodium metabisulfite in excess of stoichiometric requirements should protect the more tolerant polyamide

membranes from chlorine attack. For the most susceptible polyamide compositions, chlorine should be totally avoided as a part of pretreatment. Cellulosic membranes, on the other hand, will tolerate chlorine at levels used to provide disinfection of potable water supplies, typically 1 mg/L Cl_2 or less. However, over long membrane service life, the chlorine will facilitate oxidation of the membrane material. In some cases, such as municipal wastewater tertiary treatment, chloramines have been successfully used with composite polyamide membranes for biological control.

Mitigate Membrane Fouling

An accumulation of one or more foreign substances on the surface of a membrane will result in a loss of productivity. Higher operating pressures will then be required to maintain water production (flux) and quality. Membrane fouling generally occurs by one of the following mechanisms:

- Deposition of silt or other suspended solids that were inadequately removed by the pretreatment
- Inorganic scale deposits formed because of precipitation of sparingly soluble salts or silica
- Biological fouling caused by excessive microbial growth
- Interaction of organics with the membrane

In some instances, pretreatment is required to remove algae; certain metals, such as iron and manganese; or other particulate matter. The need for such treatment is dictated by the source water quality, the permeate standards, and the need to protect the membranes. Only the most commonly encountered contaminants are discussed in this manual.

Particulate removal. Designers must take great care to minimize the amount of suspended solids fed to the membrane systems. Most RO and NF membranes used today are spiral-wound elements. Suspended solids can negatively impact a spiral-wound membrane in several ways. As discussed in chapter 1, spiral-wound membranes are fabricated with a feed spacer separating the individual membrane leaves. Suspended solids will plug the feed spacer, resulting in increased pressure drop. The increased feed–concentrate flow stream pressure drop necessitates increased feed pressure to maintain permeate flow rate and, if the pressure drop is too great, the membrane element can be physically damaged. Ensuring adequate removal of suspended solids is a top priority of membrane system designers.

The performance of pretreatment system particle removal is characterized using turbidity and SDI. In some surface water applications, zeta potential is also measured. It is recommended that the zeta potential be greater than -30 mV.

Membrane manufacturers of spiral-wound elements require the feedwater turbidity to not exceed 1 ntu and the SDI to not exceed 4 or 5. However, it is recommended the following guidelines for suspended solids be met:

- Turbidity less than 0.3 ntu
- SDI of 3 (hollow fiber) and 4 or 5 (spiral-wound)

Turbidity is best measured by an in-line continuous monitor. SDI, as described in ASTM method D4189, is based on the rate of plugging a standard $0.45\text{-}\mu\text{m}$ membrane filter. The procedure is shown in appendix C. Zeta potential, used for fresh and brackish surface water, measures a colloid's electrical stability with a meter that can also be installed for continuous monitoring.

SDI values of 3 for hollow fiber membranes and 4 or 5 (depending on manufacturer) for spiral-wound membranes are upper limits recommended by various manufacturers. If these levels are exceeded, pretreatment is required; at lower levels, pretreatment may be recommended to reduce cleaning cycles. The minimum

Table 2-4 Pretreatment techniques (listed in decreasing order of effectiveness) for reducing silt and colloidal material

Method	Comments
Low-pressure membrane filtration (MF or UF)	Operates at low pressures and requires periodic chemical cleaning and frequent backwashing. Removes particulates but essential no organics (unless a precoagulant is fed). High solids loads may require additional pretreatment to be cost effective.
Precoat filtration	Precoat media must be added to replace losses in the backwash step. Does not remove dissolved organics. High solids loads may require additional pretreatment to be cost effective.
Coagulation/flocculation/sedimentation/filtration	Provides the most process flexibility of all methods. Process is able to remove appreciable organics using coagulation. Highly tolerant of variable suspended solids loads.
Multimedia and pressure filtration	Pilot testing may be required to determine the best media for SDI reduction. May be used in conjunction with coagulants–flocclulants, with and without settling.
Rapid sand filters and ultrahigh-rate filters	Coagulants are generally required to achieve acceptable SDI reduction, most through inline coagulation. Can handle limited high turbidity events.

pretreatment for suspended solids, regardless of the SDI, typically is a 5- μ m cartridge filter located immediately upstream of the membrane feed pump. If the SDI exceeds the manufacturer's recommendations, it may be possible to achieve sufficient reductions by other treatment techniques listed in Table 2-4. The treatment techniques include a wide range of processes, depending on the concentrations of various contaminants.

For those cases where contaminant particle size is so small that filtration alone is not sufficient, or the suspended solids load exceeds the ability of filtration to operate effectively, adding chemicals to coagulate the colloidal particles is necessary. These chemicals destabilize the colloidal particles by neutralizing the electrostatic charge that surrounds the particles. Once neutralized, the particles are readily agglomerated and removed by sedimentation and/or filtration. Pretreatment techniques can involve relatively complex systems, such as coagulation/flocculation/sedimentation/filtration, for applications where high concentrations of suspended solids occur in the source water. *AWWA Water Quality and Treatment* and *AWWA/ASCE Water Treatment Plant Design* describe conventional treatment processes.

The use of coagulation in a pretreatment system prior to RO or NF must be approached with caution. Properly applied, these chemicals are very effective. When overdosed or dosed at the wrong pH, their use can cause more problems than it solves. It is not possible to predict the feed rate based on chemical or physical parameters of the source water. Jar testing or pilot plants are essential to determine the optimal chemical treatment and level of application. With surface waters, the level of suspended solids can vary widely depending on a host of environmental factors. This necessitates frequent checks to determine the proper feed rate to

maintain the required turbidity and SDI. Online instruments, such as streaming current detectors, can be applied to control chemical dosing rates.

Common coagulant–flocculant chemicals are listed in Table 2-5. Ferric and aluminum salts can be used effectively provided the pH is properly controlled, sufficient time is allowed to fully precipitate the metallic hydroxide, and the precipitates are completely removed by the media filter. Otherwise, the downstream membrane system can be fouled by aluminum or iron hydroxides. In case of an upset, both of these inorganic coagulants can be removed from the membrane by cleaning, with iron being somewhat easier to dissolve than aluminum. Cationic polyelectrolytes are excellent coagulants but, if overdosed, will foul membranes rapidly and sometimes irreversibly. Polymer use should be approached with caution; the least likely to react with the membrane are the anionic or nonionic polymers. Cationic polymers can also react with anionic scale inhibitors to form insoluble organic deposits that can be very difficult to remove by cleaning. Many RO and NF membrane manufacturers state that cationic polymers should not be used in membrane pretreatment processes and essentially all manufacturers prefer no polymer be used in pretreatment as long as turbidity and SDI criteria are met.

Although the cautionary information in the preceding discussion is important, silt or colloidal fouling is not an issue with most groundwater sources. Most plants drawing water from brackish aquifers or hard groundwaters in Florida operate successfully using only a 5- μ m filter for protection against particulate fouling. Certain large seawater RO plants have been able to avoid pretreatment for colloidal fouling problems by drawing the water from a beach well rather than from a surface intake.

Scale control. As product water that is relatively low in solutes passes through the membrane, the remaining feedwater becomes increasingly concentrated in dissolved solids. At certain degrees of concentration, the solubility of various salts can be exceeded, which causes salts to precipitate onto the membrane surface. This process is called *scaling*. Scaling can severely reduce the flow or flux of permeate and can irreversibly damage the membrane. Calcium sulfate is particularly notorious for its ability to damage membranes.

For a large proportion of mineralized source waters, the concentration of salts in the concentrate stream (and conversely the degree of permeate recovery) is limited to the point at which the membrane process becomes uneconomical without pretreatment. This situation is particularly true for water with high concentrations of calcium, barium, strontium, sulfates, or carbonates. With silica precipitation, however, a certain degree of oversaturation is generally tolerated because the chemical reaction is relatively slow and feedwater leaves the system before the precipitate forms. However, membrane manufacturers or system suppliers should always be consulted before silica oversaturation is allowed for a membrane system, particularly when multivalent cations such as iron are present. Lime softening at a pH greater than 11 can be used to reduce silica. Inhibitors to prevent silica deposition also are used to address this problem. Table 2-6 provides a list of common limiting salts or compounds.

Limiting salt calculations are normally performed with computer software. Appendix C illustrates the general steps used to determine the limiting salt and calculate allowable permeate recoveries. The results of those calculations show that, for the hypothetical feedwater, the solubility of calcium carbonate is exceeded and calcium carbonate will precipitate. The results also show that a recovery rate of 84 percent is possible before the solubility limit of strontium sulfate is exceeded. The examples in appendix C are illustrative and do not take the ionic strength of the solution into account.

Table 2-5 Common coagulant–flocclulants

Chemical	Comments
Inorganics	
Aluminum sulfate or alum, $[\text{Al}_2(\text{SO}_4)_3]$	Minimum solubility is achieved at pH 5.7 to 6.5 in freshwater and brackish water applications. Lower values are reported for seawater. Must allow sufficient time for complete precipitation or aluminum salts may deposit on membrane.
Aluminum chlorohydrate (ACH) and Polyaluminum chloride (PACl)	Highly effective coagulant results in minimal membrane fouling, effective over wide pH range (pH 5 to 8).
Ferrous sulfate, (FeSO_4)	Oxidation to ferric form of iron is required to be effective. Optimal pH is >8.4 for freshwater for particulate removal. Lower pH is optimal for organics reduction.
Ferric sulfate, $[\text{Fe}_2(\text{SO}_4)_3]$	Works best at ambient pH in freshwater for particulate removal. Lower pH is optimal for organics reduction.
Ferric chloride, (FeCl_3)	Works best at pH 6.0 to 7.0 for freshwater. Chemical is widely used for membrane pretreatment of surface water.
Organic polyelectrolytes	
Cationic	Will interact with many scale inhibitors. Can irreversibly foul many spiral-wound membranes. Consult manufacturer.
Anionic and nonionic	Will not react with most scale inhibitors. May foul certain membranes. Consult manufacturer. Generally less effective than cationic as a coagulant–flocclulant.

Table 2-6 Common limiting salts

Salt	Solubility Product of Salt, pK_{sp} at 25°C
Calcium carbonate (CaCO_3)	8.30
Calcium fluoride (CaF_2)	8.27
Calcium phosphate (CaPO_4)	25.00
Calcium sulfate (CaSO_4)	4.70
Barium sulfate (BaSO_4)	9.70
Strontium sulfate (SrSO_4)	6.20
Silica (SiO_2)	2.70

An increase up to a certain point in ionic strength of the solution will make the salt more soluble and, in effect, increase the allowable permeate recovery rate. Design software that membrane manufacturers use takes into account the impacts of ionic strength in determining allowable recovery rates.

To increase the permeate recovery rate, feedwater may be chemically altered to reduce the concentration of cations or anions of the limiting salt. One method to

prevent the formation of calcium carbonate scales is to add an acid to convert carbonate ions (CO_3^{2-}) to bicarbonate ions (HCO_3^-). Bicarbonate ions can also be converted to carbonic acid (H_2CO_3) and subsequently carbon dioxide during acidification. Appendix C gives an example of adding sulfuric acid to control calcium carbonate scaling.

Scale inhibitors are often added to the feedwater stream to allow the membrane system to operate at permeate recovery rates in excess of limiting salt constraints. Scale inhibitors work by one of several mechanisms including mitigation of scale formation by inhibiting the rate of formation of crystalline precipitates under supersaturated conditions, chelation of metal ions permitting them to stay in solution at higher concentrations, or dispersion, which maintains colloids in suspension until discharged from the membranes in the concentrate stream.

Several different chemicals have been historically used as scale inhibitors including polyphosphates (potassium pyrophosphate and sodium hexametaphosphate). Sodium hexametaphosphate, used in conjunction with acid, was the scale inhibitor of choice for many years in RO systems. One disadvantage of sodium hexametaphosphate is the tendency of the polyphosphates to hydrolyze over time, reducing its effectiveness. Another disadvantage of sodium hexametaphosphate is its ineffectiveness in inhibiting the precipitation of other sparingly soluble salts.

The development of synthetic polymers (polyacrylates) in the 1970s provided significant progress in scale control. The synthetic polymers provided good calcium carbonate and calcium sulfate control while providing limited metal ion stabilization and dispersant activity. Scale inhibitors currently utilized evolved from these early synthetic polymers with the development of proprietary copolymers that provide excellent scale inhibition, enhanced metal ion stabilization, and colloidal dispersant properties. Many scale inhibitors marketed are formulated to provide optimum performance on one or more sparingly soluble salt.

Scale inhibitor dosage calculations are too complex to be presented in this manual. There exist issues regarding compatibility with coagulant and flocculant aids, and membrane materials that must be considered. Chemical dosage and efficacy information for specific membranes is available from scale inhibitor manufacturers, and membrane manufacturers provide information on the compatibility of scale inhibitors with their membranes.

Methods other than acids or scale inhibitors used to control scaling or colloidal fouling include:

- Ion exchange softening to reduce multivalent cations (Ca^{2+} , Mg^{2+})
- Lime softening to reduce multivalent cations and silica
- Aeration and chemical oxidation and filtration to reduce iron and manganese
- *Greensand* or oxidation filtration to reduce iron and manganese
- Coagulation and filtration to reduce colloidal and particulate matter

Scale with crystalline morphology. Scale forms on a membrane surface when naturally occurring, sparingly soluble salts are concentrated beyond their solubility limit by the membrane process. Table 2-7 lists the commonly encountered scales and the methods for preventing precipitation on a membrane. The methods will be discussed in greater detail later in this chapter.

The solubility limit of a sparingly soluble salt is defined by the salt's solubility product constant K_{sp} , which is discussed in more detail in appendix C. Membrane manufacturers have design software that performs complex calculations to yield values of K_{sp} . For ease of discussion and preliminary analysis, most chemists and

engineers prefer to simplify the mathematics by defining a conditional solubility product constant (K_{sp}) that specifies solubility as a function of ionic strength (I). The ionic strength of a solution may be defined as follows:

$$I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \dots + m_n z_n^2) \quad (\text{Eq 2-1})$$

Where:

- m_i = molar concentration of the i th species
- Z_i = ionic charge of the i th species
- n = total number of ionic species in the solution

An example of an ionic strength calculation is given in Table 2-8. In addition, Figures 2-2 and 2-3 illustrate how the solubility product of the sulfate salts of calcium, barium, and strontium vary with the ionic strength of the solution. Figure 2-4 illustrates how the solubility product of calcium fluoride salts vary with the ionic strength of the solution. Figure 2-5 illustrates how the solubility of calcium phosphate varies with respect to pH.

Whenever the ratio of the ion product to the K'_{sp} exceeds 1.0, there is a potential for scale deposition on the RO or NF membrane and pretreatment is essential. Calculation of an ion product is also discussed in appendix C. For spiral-wound

Table 2-7 Common scales and other inorganic foulants and methods for controlling them

Species	Method of Control	
	Primary	Secondary
Calcium carbonate (CaCO_3)	Mineral acid Threshold inhibitor	Soften
Calcium sulfate (CaSO_4)	Threshold inhibitor Soften	Limit recovery
Barium sulfate (BaSO_4)	Threshold inhibitor Soften	Limit recovery
Strontium sulfate (SrSO_4)	Threshold inhibitor Soften	Limit recovery
Calcium fluoride (CaF_2)	Threshold inhibitor Soften	Limit recovery
Calcium phosphate (CaPO_4)	Mineral acid Threshold inhibitor	Limit recovery
Silica (SiO_2)	Threshold inhibitor Limit recovery	Raise pH to greater than 8.5 (if carbonate scale is not an issue) or increase temperature
Ferric hydroxide [$\text{Fe}(\text{OH})_3$]	Precipitation and filtration Chelating agent	Soften
Aluminum hydroxide [$\text{Al}(\text{OH})_3$]	Precipitation and filtration at pH of minimum solubility Chelating agent	—
Sulfur (S) (from hydrogen sulfide)	Exclude air and other oxidants prior to membranes	—

Table 2-8 Example of an ionic strength calculation

Species	Assumed Concentration, <i>mg/L</i>	Number of Milligrams per Mole	m_i^*	z_i^2	$m_i z_i^3$
Calcium (Ca^{2+})	409	40,000	0.0102	4	0.0408
Magnesium (Mg^{2+})	169	24,300	0.00695	4	0.0278
Sodium (Na^+)	314	23,000	0.0137	1	0.0137
Bicarbonate (HCO_3^-)	150	61,000	0.00246	1	0.00246
Sulfate (SO_4^{2-})	1,510	96,100	0.0157	4	0.0628
Chloride (Cl^-)	500	35,500	0.0141	1	0.0141
$\sum m_i z_i^2$					= 0.1617
$I = \frac{1}{2} \sum m_i z_i^2$					= 0.0808

*Determined by dividing the value in column 2 by the value in column 3.

membranes, because of concentration polarization at the membrane surface and occasional water quality variation, pretreatment is recommended whenever the ratio of the ion product to K'_{sp} is greater than 0.8.

In theory, supersaturation of all insoluble salts can be evaluated in this manner. However, when examining calcium carbonate solubility, engineers prefer to evaluate scaling potential in terms of either the Langelier saturation index (LSI) or, in the case of seawater, the Stiff-and-Davis stability index (S&DSI). Both indexes are explained further in appendix D. For either index, a positive value indicates a scale-forming condition. For most brackish waters, the LSI has proven to be an adequate predictor. For seawater, which has a much higher ionic strength, the S&DSI has become the preferred index. Nomographs have been widely published to allow one to calculate either index without having access to logarithm tables or a calculator that has scientific functions. Membrane manufacturers, consulting engineers, and technical service departments of chemical suppliers have computer programs that can either be made available or accessed on request to evaluate the supersaturation of sparingly soluble salts at various levels of recovery from a source water of known composition. Results from one such program are given in Figure 2-6.

The following are some methods for preventing scale (as briefly mentioned in Table 2-7):

- Acidify to remove carbonate or bicarbonate ions
- Limit recovery to prevent salts and/or silica from concentrating in excess of solubility limits
- Soften the source water to remove calcium ions
- Use threshold scale inhibitors, which are effective for calcium sulfate and calcium carbonate

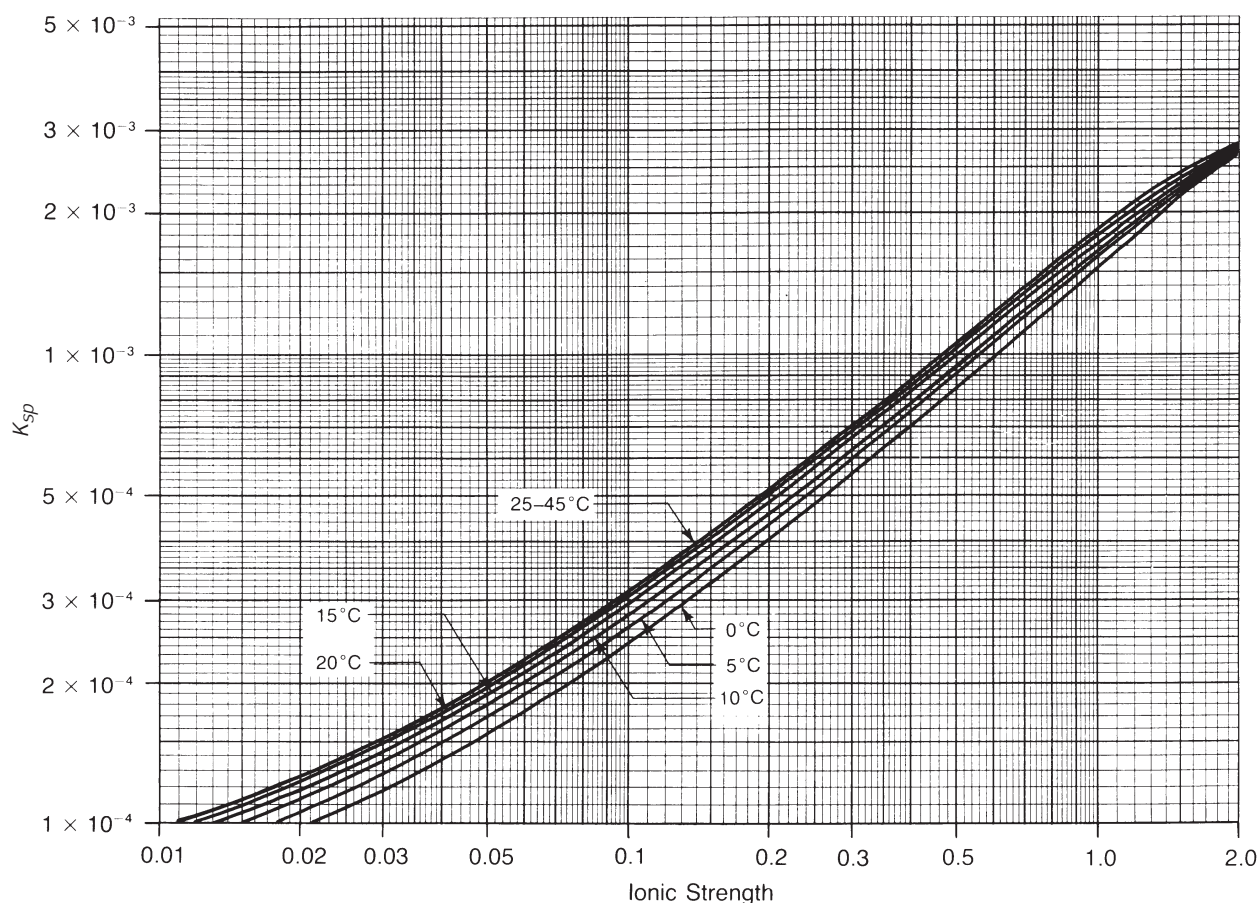


Figure 2-2 Calcium sulfate solubility product versus ionic strength

Acidification is effective in preventing calcium carbonate scaling, provides a small benefit in terms of increased silica solubility, and is usually required to prevent hydrolysis of cellulose acetate membranes. The obvious safety hazards associated with handling strong mineral acids necessitate appropriate operator training and conscientious attention to safe handling practices. Cation exchange softening is impractical on most brackish waters because of the high levels of hardness in the water; it is not feasible with seawater. Lime softening is practiced occasionally for brackish waters with exceptionally high hardness, but the costs of capital, labor, chemicals, and sludge disposal are high. Limiting recovery to ensure solubility limits are not exceeded should be viewed as a last-resort method for dealing with crystalline scales because the practice wastes a substantial portion of the source water resource. The addition of a threshold scale inhibitor is the most practical and widely used method to prevent crystalline scale from forming on membranes.

Threshold scale inhibitors have often been incorrectly referred to in desalination literature as sequestrants. These chemicals do not sequester by being in exact proportions for interaction with calcium, barium, or strontium. Instead, they react with the surfaces of ion clusters to prevent the orderly growth needed to form the scale crystal or allow it to grow to a harmful size. Because of this unique property,

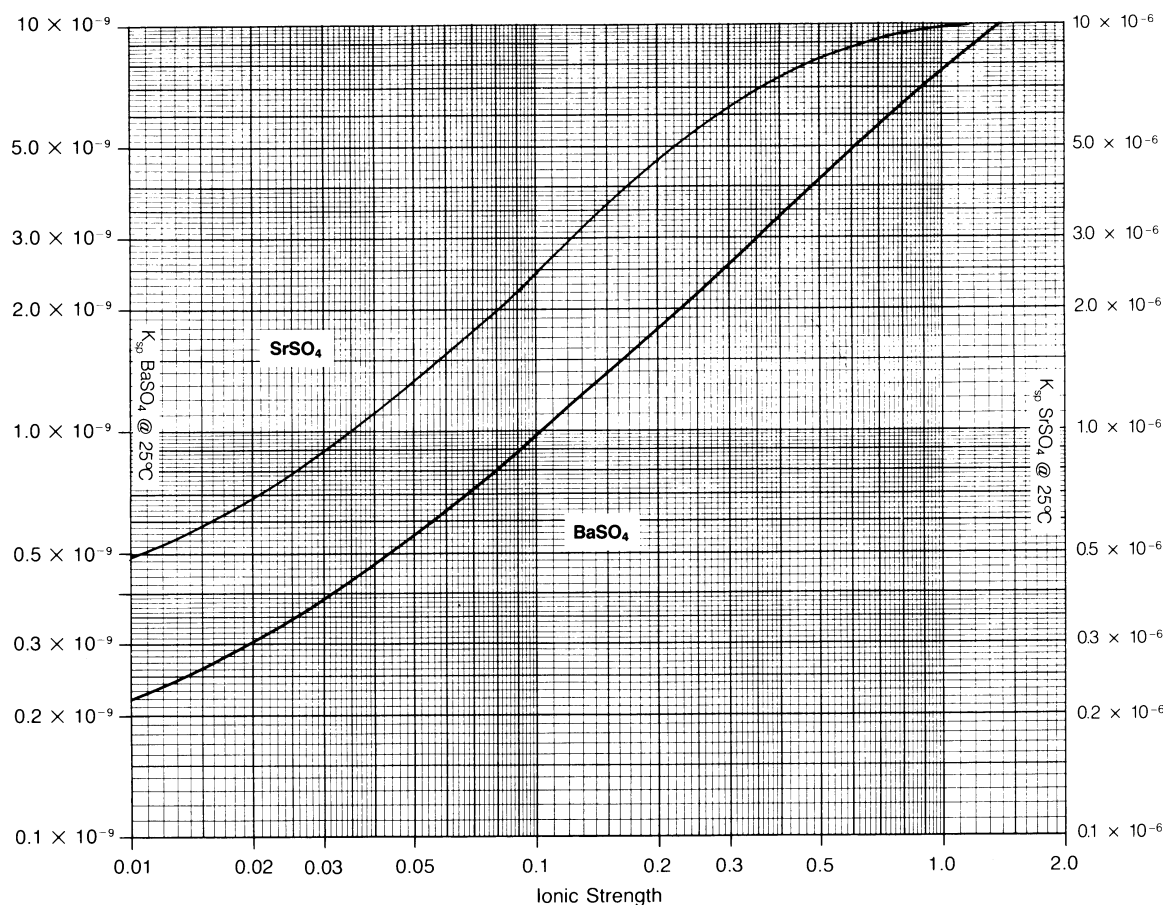


Figure 2-3 Barium sulfate and strontium sulfate solubility product versus ionic strength

scale inhibitors can be added at very low levels, usually less than 5 mg/L, into the membrane source water to prevent scale from forming at multiple levels of supersaturation. Two types of chemical scale inhibitors that have achieved widespread usage in the production of potable water are polyphosphates and high-performance polymeric scale inhibitors, most typically polyacrylates.

Before the development of polymeric scale inhibitors, sodium hexametaphosphate (SHMP) was widely used in membrane systems to prevent sulfate scales from precipitating in a membrane system. However, SHMP has several potential drawbacks:

- It is less effective than the new polymeric scale inhibitors, so higher doses of SHMP are normally required.
- The solid form of SHMP has to be diluted for injection. Once diluted in water, it starts to hydrolyze to the orthophosphate, which is ineffective as a scale inhibitor and contributes to calcium phosphate scaling.
- Discharging the concentrate stream, which contains phosphates, can contribute to environmental problems.
- It can contribute to biological growth within the membrane element.