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Reverse Osmosis and Nanofiltration

AWWA MANUAL M46

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Science and Technology

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$Chapter$

Introduction

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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

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, polyethersulfone, 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 costprohibitive 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

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

Table 1-1 Membrane processes and target contaminants

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

* 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-µm 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 highquality 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 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 μ m thick on an otherwise spongy, porous film 80 to 100 μ m 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 triaetate, 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

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

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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-andframe 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 plateand-frame type of membrane arrangement.

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