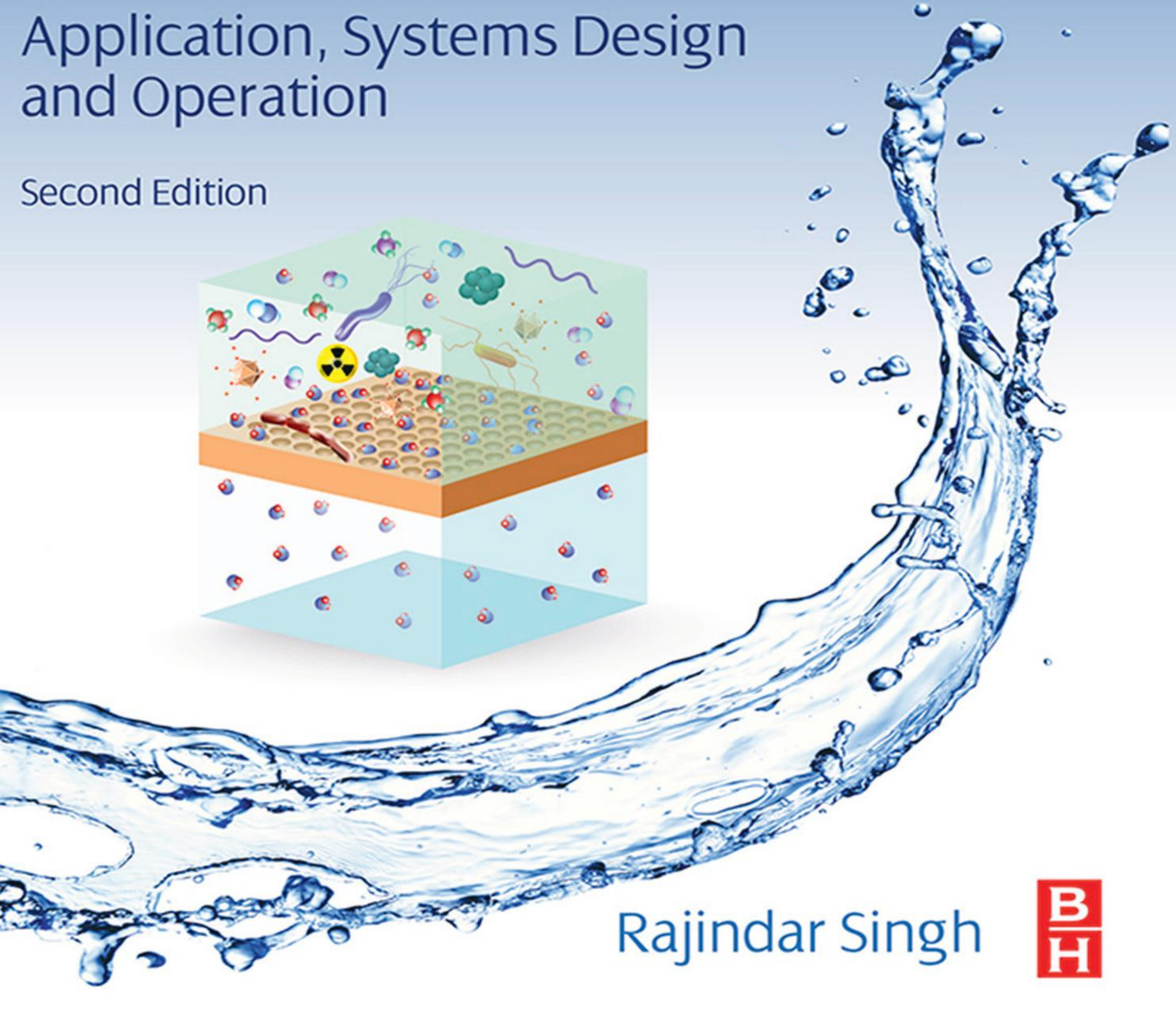
IChemE ADVANCING CHEMICAL ENGINEERING WORLDWIDE

Membrane Technology and Engineering for Water Purification

Application, Systems Design and Operation

Second Edition



Rajindar Singh

MEMBRANE TECHNOLOGY AND ENGINEERING FOR WATER PURIFICATION

MEMBRANE TECHNOLOGY AND ENGINEERING FOR WATER PURIFICATION

Application, Systems Design and Operation

SECOND EDITION

RAJINDAR SINGH
Membrane Ventures, LLC
Colorado Springs, CO, USA

ELSEVIER
AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO
Butterworth-Heinemann is an imprint of Elsevier

Butterworth-Heinemann is an imprint of Elsevier
The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK
225 Wyman Street, Waltham, MA 02451, USA

First edition 2006

Second edition 2015

Copyright © 2015 Elsevier Ltd. All rights reserved

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: www.elsevier.com/permissions.

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-444-63362-0

For information on all Butterworth-Heinemann publications
visit our website at http://store.elsevier.com/

ELSEVIER
Book Aid International
Working together
to grow libraries in
developing countries

www.elsevier.com • www.bookaid.org

"Water is the source of life, sap for all things."
— Guru Nanak Dev (1469-1539)

"Air is our guru, water our father,
And the great earth our mother. . . ."
— Guru Nanak Dev (1469-1539)

To the memory of my parents,
S. Niranjan Singh and Kuldip Kaur

CONTENTS

PREFACE TWO

"Overcoming the crisis in water and sanitation is one of the greatest human development challenges of the early 21st century," according to a recent U.N. report. About one in every six people today do not have sufficient access to clean drinking water. More than 1.2 billion people live in areas of water scarcity; rivers are drying up, groundwater levels are declining rapidly, freshwater fisheries are being damaged, and salinisation and water pollution are increasing (1). As a result, 2.2 million deaths per year are related to water/hygiene and public health; many of these are children. Such problems are forecast to grow worse, with more than half the world's population facing chronic to critical water shortages by 2050, limiting economic development and food supplies. Ensuring adequate water supplies, therefore, poses a major engineering challenge. Further, climate change means previously less water-stressed regions rely increasingly on brackish groundwater or seawater as the main source of water; alternatively, they must recycle and reuse wastewater. Global warming and rising oil prices imply increasing energy supply problems. This, in turn, implies further increases in the cost of water generally, and desalinated water in particular. Membrane-separation technology can dramatically improve the sustainability of our water resources. It is energy efficient with minimal or no chemical consumption, and capable of water recycling and reuse that minimises the direct disposal of wastewater to the aquatic environment.

The deployment of membrane technology in the water sector, especially since the first edition of the book was published in December 2005, is continuing to grow at a rapid rate. Overall, the market for membranes and membrane systems grew from $4.4 billion in 2000 to more $10 billion in 2010, and the sales of membrane equipment for water treatment may exceed $10.4 billion in 2014. In light of these developments, the first edition needed to be updated and revised. Although the major focus of the book is water treatment, membrane applications in other liquid processing areas, introduced in the first edition, are retained to familiarise the reader with the scope and extent of membrane technology. A chapter on membrane systems design, energy consumption, and costs is added to integrate membrane technology with systems engineering. The book title was revised at the recommendation of the reviewers.

The success of modern membrane science and technology was made possible by S. Sourirajan and S. Loeb in 1960, followed by enormous contributions by Sourirajan and his associates as well as many pioneers over the next 40 years, and the work continues to improve. Many of these brilliant researches assembled at the first Gordon Research Conference on Reverse Osmosis and Ultrafiltration held at Colby-Sawyer College in

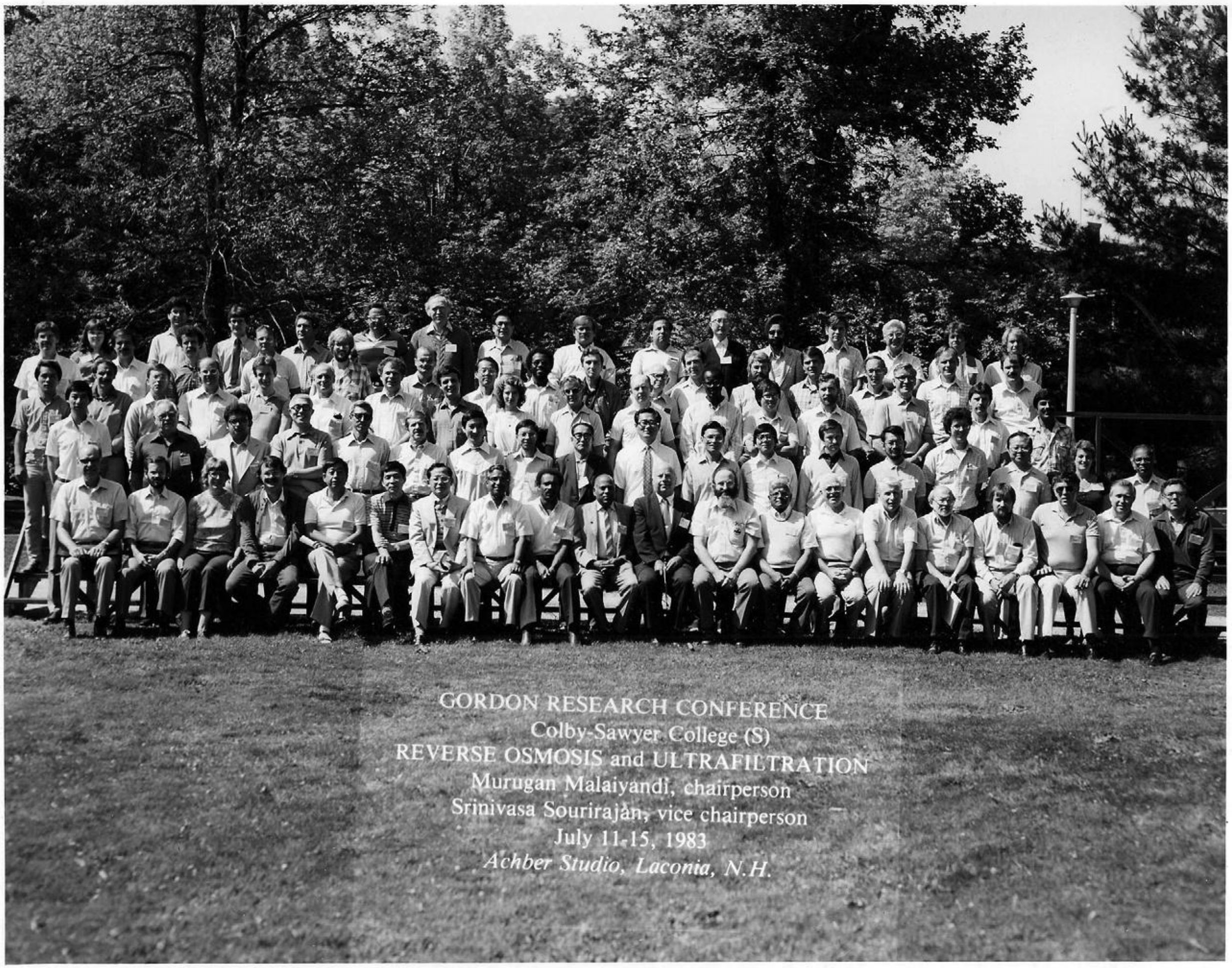
New Hampshire, USA, July 11–15, 1983, as shown in the photo. It was a time when membrane technology was still trying to establish itself as a viable process for water treatment on a large scale. Since then, and especially in the last 20 years, the technology has established itself as a reliable, superior, and indispensable process for desalination, industrial, municipal, and portable drinking water treatment. According to a recent market report, the sale of RO equipment is expected to reach \$8.1 billion by 2018 from \$4.9 billion in 2013 (2). Mega seawater reverse osmosis desalination plants as well as large membrane-filtration plants for water reuse around the world are becoming common. Besides covering these two topics in detail, the book also discusses other important membrane applications such as industrial wastewater, process water, high purity water, food and bioprocessing.

REFERENCES

[1] G. Conway, One Billion People Hungry. Can we feed the world?, Cornell University Press, Ithaca, NY 2012.
[2] Major Reverse Osmosis System Components for Water Treatment: The Global Market, Report MST049D, BCC Research, Wellesley, MA, June 2013.

ACKNOWLEDGEMENTS FOR THE SECOND EDITION

I would like to thank my family, foremost, for their love and support: my wife, Dr. Rashna Batliwala Singh, son, Dr. Samir Indar Singh, and daughter, Dr. Namrita Shirin Singh. I very much appreciate my book editors, Fiona Geraghty, Cari Owen and Nicky Carter for their cooperation and patience.



GORDON RESEARCH CONFERENCE
Colby-Sawyer College (S)
REVERSE OSMOSIS and ULTRAFILTRATION
Murugan Malaiyandi, chairperson
Srinivasa Sourirajan, vice chairperson
July 11-15, 1983
Achber Studio, Laconia, N.H.

GORDON RESEARCH CONFERENCES

REVERSE OSMOSIS & ULTRAFILTRATION

Colby-Sawyer College, New London, NH
July 11-15, 1983

Photo Identification

FIRST ROW: (Left to Right) J. Beasley, W. Light, S. Krause, G. Belfort, E. Chian, T. Matsuura, K. Kamide, D. Bhattacharya, R. Benson, S. Sourirajan (Vice-Chairman), R. Kesting, A. Zelman, M. Malaiyandi (Chairman), R. E. Probstein,W. Pusch, E. Klein, L. Zeman, A. Allegrezza, J. Smith, E. Casassa

SECOND ROW: (Left to Right) E. Lee, H. Hoehn, M. Cheryan, S. Chen, C. Lee, S. Rak, T. Nohmi, K. Chan, S. Suzuki, T. Chu, V. Lin, C. Lee, C. Reineke, M. Fushijima, J. Zupancic, D. Chan, M. Bitritto, V. Sastri

THIRD ROW: (Left to Right) M. Tsukano, J. Berger, P. Blais, T. Waarvik, D. R. Lloyd, L. A. Errede, T. Suffet, F. Fiessinger, A. M. Wowk, W. K. Wilkinson, R. Petersen, W. Klagba, B. Wong, B. Farnand, J. Cadotte, R. Beaver, L. Wadhwa

FOURTH ROW: (Left to Right) D. Kubek, T. I1cCollough, R. Sullivan, C. Walker, J. Dickson, A. Benedek, R. Yang, R. Goffe, B. Bikson, L. Meriwether, D. Setti, R. Rice, A. Cantwell, H. Steadly, W. Eykamp, W. Robertson

FIFTH ROW: (Left to Right) J. Otis, J. Niculetti, R. Weigand, A. Zampini, J. Henis, J. Burke, P. Kabasalalian, J. Schaefer, G. Freedland, Y. V. Wu, R. Singh, P. Edwards, C.B. Lundsager, A. Herczeg, F. Larimore

CHAPTER 1

Introduction to Membrane Technology

> *"No power on earth can stop an idea whose time has come."*
>
> ***— Victor Hugo***

1.1 TECHNOLOGY OVERVIEW

Synthetic membrane processes perform versatile functions with the membrane acting as a barrier interface between feed and product. In liquid separations, for example, they are used to separate particles that span four orders of magnitude from dissolved ions to bacteria (Figure 1.1). Virtually all membrane processes are pressure driven, do not involve a phase change, and consume much less energy than alternate separation processes.

Since 1960, membrane technology has transformed from laboratory development to proven industrial applications. More than 95% of applications are for liquid separations. Membranes are used for desalination of seawater and brackish water, potable water production and for treating industrial effluents, and water reclamation and reuse. Membranes are used for the concentration of and purification of food and pharmaceutical products, in the production of base chemicals and energy conversion devices such as fuel cells. Membranes are also used in medical devices such as haemodialysis, blood oxygenators, and controlled drug delivery products. Membrane-separation processes are being increasingly integrated with conventional technologies as hybrid membrane systems to reduce energy consumption and minimise environmental impact.

Four developments are widely considered to be responsible for transferring membrane science from the laboratory to commercial reality:

1. development of high-efficiency membrane elements (modules) with large surface areas;
2. creation of advanced materials with controllable capabilities to separate molecularly similar components (e.g., gases, salts, colloids, proteins);
3. tailoring membrane morphology for controlling microscopic transport phenomena; and
4. manufacturing membrane elements economically and reliably [1].

Continuing advances in development of new membranes with better thermal, chemical, and improved transport properties have led to many new possible applications. Development of newer membrane modules and operating procedures in recent years has provided a key stimulus for the growth of the membrane industry such as submerged membrane filtration for treating municipal water.

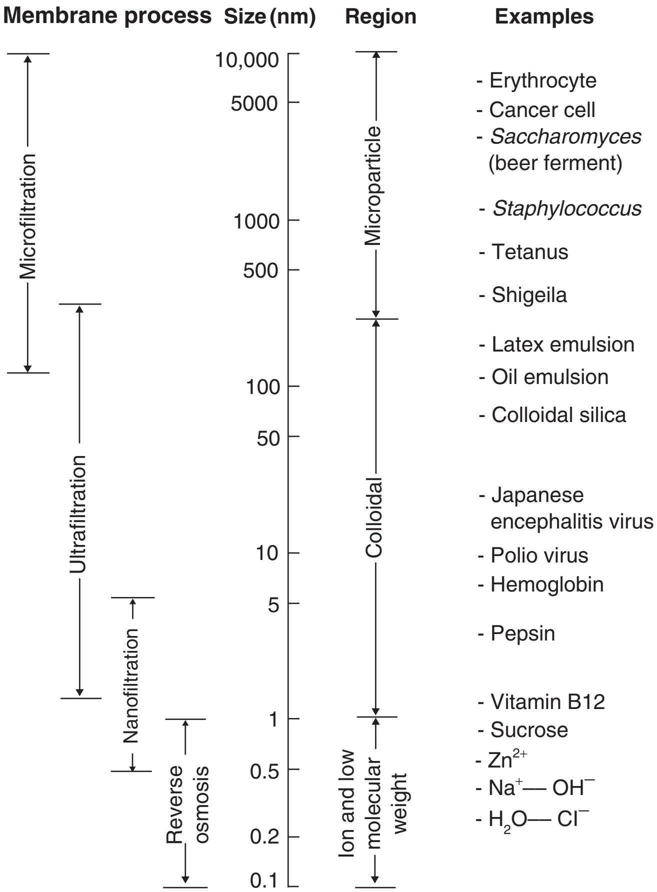


Figure 1.1 Membrane process designation by solute size.

The market for membrane applications is determined by product quality and by the availability of new and better membranes and membrane processes; for example, heterogeneous membranes made from polymers and ceramics are being developed for handling non-aqueous feed streams [1]. The first significant application for membranes was in the testing of drinking water at the end of World War II. Total annual sales in 1960 was $20 million in 2012 dollars. Overall market for membranes and membrane systems grew from $4.4 billion in 2000 to more $10 billion in 2010. The largest market segment for membrane technology in 2000 was in the biomedical sector with sales of haemodialysis equipment about $2.2 billion [2]. The sales of gas separation (GS), pervaporation (PV), membrane reactors and bipolar membranes were substantially smaller. According to a report published in 2013 by McIlvane Company, the sales of membranes and equipment for water treatment could exceed $10.4 billion in 2014 with one-third for desalination.

1.2 HISTORICAL DEVELOPMENT

The first recorded study of membrane phenomena appears to have been by the French Abbe Nollet in 1748. He placed spirit of wine in a vessel, the mouth of which was closed with an animal bladder and immersed in water. Because it was more permeable to water than to wine, the bladder swelled and sometimes even burst, demonstrating semipermeability for the first time. Dutrechet introduced the term "osmosis" in the 1820s to characterise the spontaneous flow of liquid across a permeable barrier. The first synthetic membrane was prepared by Fick in 1855, made from nitrocellulose. In 1861 Graham reported the first dialysis experiments with synthetic membranes. He also demonstrated that rubber films exhibited different permeabilities to different gases. During the next 30 years, Traube and Pfeffer prepared artificial membranes, and their work with osmotic phenomena led to the well-known van't Hoff osmotic pressure relationship [3]. Bechold coined the term "ultrafiltration" in 1906, and Michaels pioneered modern ultrafiltration (UF) in the 1960s. Many of these membranes could be used as very fine particle or molecular filters. The microporous filters developed by Zigmondy and others around 1910 were asymmetric with a finely porous skin on the feed side and open structure on the permeate side. The tightest of the UF membranes were made from cellophane or regenerated cellulose.

Membrane filters were first commercialised in 1927 by the Sartorius Company in Germany using the Zigmondy process. Reverse osmosis (RO) was first observed and studied in the 1920s. However, it remained unnoticed until rediscovered by Reid and his co-workers 30 years later. The first practical phenomenon of haemodialysis was demonstrated by Kolff in the 1940s. Membrane milestones are given in Table 1.1.

Table 1.1 Membrane milestones

Event	Scientist	Year
Osmosis	Abbe Nollet	1748
Laws of diffusion	Fick	1855
Dialysis, gas permeation	Graham	1861, 1866
Osmotic pressure	Traube, Pfeffer, Van't Hoff	1860–1887
Microporous membranes	Zsigmondy	1907–1918
Distribution law	Donnan	1911
Membrane potential	Teorell, Meyer, Sievers	1930s
Hemodialysis	Kolff	1944
Skinned membrane	Sourirajan and Loeb	1959
Membrane-transport models	Kedem, Katachalsky, Lonsdale, Merten, Pusch, Sourirajan	1960–1970
Spiral-wound membrane element	Westmoreland, Bray	1965–1970
Hollow-fibre RO membrane	Mahon, Hoehn and Milford	1965–1970
Thin-film composite membrane	Cadotte and Rozelle	1972

Source: [3].

Until 1945, microporous membranes were used primarily for removing microorganisms and particulate matter from gaseous and liquid streams, for diffusion studies and for estimating the size of macromolecules (or particle) and shape (spherical or linear). In the period after World War II, Juda and McRae pioneered electrodialysis (ED) using ion-exchange membranes. Soon after, ED systems were commercialised for brackish water desalination. In the early 1950s, investigation of RO (also called "hyperfiltration") for desalinating seawater was initiated by the Office of Saline Water to meet future water demands since microporous membranes were not suitable for desalination because of their large pore size. In the mid-1950s, Reid and Berton discovered polymeric membranes that exhibited high salt rejections, but they could not cast thin membranes without imperfections. The membranes were too thick (about 6.0 μm), and exhibited water fluxes that were too low to be practical; the flux through a semipermeable membrane is inversely proportional to the thickness of the membrane.

The first breakthrough came in 1959 when Sourirajan and Loeb discovered a method to make a very thin cellulose acetate (CA) membrane using the phase inversion method [4]. This technique produces homogenous membranes with an asymmetric (or anisotropic) structure. The membranes were subsequently found to be "skinned" when examined under an electron microscope by Riley in 1964 [3]. The membranes consisted of a very thin, porous salt-rejecting barrier of CA, integrally supported by a fine CA porous substrate. Pictures of asymmetric membranes are shown in Figures 1.2 and 1.3. These early Loeb–Sourirajan (L–S) membranes exhibited water fluxes that were 10 times higher than those observed by Reid, and with comparable salt rejection [5]. The membrane flux was 8–18 l/m^2/h (lmh) with 0.05% NaCl product water from a 5.25% NaCl feed water

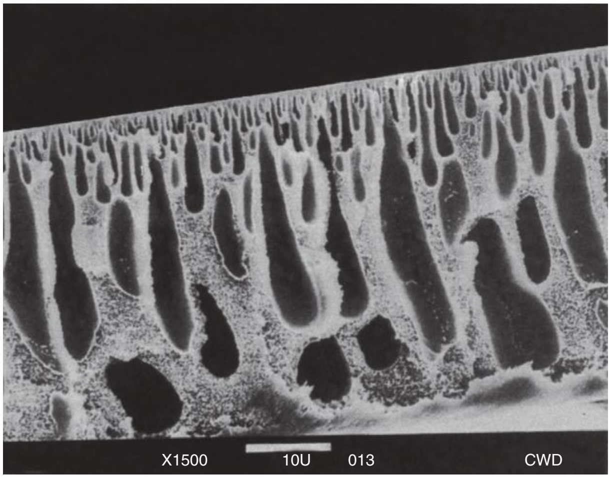


Figure 1.2 Electron micrograph of a UF asymmetric membrane showing the skin layer on the top (feed side) and macrovoids in the interior.

Figure 1.3 Cross-section photograph of a UF hollow fibre asymmetric membrane with the skin layer on the tube side. *Source:* [3].

under a pressure of 100–135 bar g. The high flux of these asymmetric membranes is due largely to their extreme thinness and porosity. The entire thickness of the membrane is about 0.1 mm, while the thickness of the active surface layer is only 30–100 nm.

Within a few years of the invention of the L–S membrane, development of the RO membrane modules technique was realised. Haven and Guy developed tubular RO membranes in the mid-1960s. In the late 1960s, Westmoreland and later Bray invented the spiral-wound module, which was more efficient than the tube-in-shell module. The spiral-wound membrane can be viewed as a plate-and-frame (PAF) arrangement that has been rolled up. The original module had a single leaf of membrane whereas modern spiral-wound modules contain multi-leaf membranes.

At the same time scientists and engineers at Dow and DuPont were examining new RO membrane materials and module designs. Mahon and others at Dow developed cellulose triacetate (CTA) hollow-fibre (HF) membranes. Although technically successful, this approach was not competitive commercially. The first non-cellulosic asymmetric membrane was the HF polyamide (PA) membrane developed by Henry Hoehn and George Milford at DuPont in the late 1960s [3]. It turned out to be quite competitive with the L–S type CA spiral-wound membrane. The PA fibres are solution-spun into very fine hollow fibres. The fibre inside diameter was 42 μm and the outside diameter was 85 μm. The fibres had a skinned (asymmetric) structure on the shell side. The water flux was well below that exhibited by CA membranes; the aromatic PA membrane was less water-permeable but more salt-retentive than the CA membrane. However, this low flux was compensated by several hundred thousand of these fibres incorporated into modules containing several thousand square feet of membrane area. The development of skinned hollow-fibre RO membranes led to the development of hollow-fibre UF and microfiltration (MF) membranes shown in Figure 1.3.

Cadotte and Rozelle developed the so-called thin-film composite (TFC) RO membrane from a new class of membrane materials in the early 1970s [6]. It was made by depositing a very thin layer of a salt-rejecting PA polymer onto the surface of a suitable finely porous substrate such as polysulphone UF membrane by an interfacial polymerisation reaction. In 1976, Cadotte also developed TFC membranes that showed high flux and high rejection of divalent ions but high permeability to aqueous chloride solutions. These loose RO membranes were given the name “nanofiltration” by Petersen in 1984. Thus emerged another membrane process that is “a most fascinating extension of reverse osmosis technology” in the words of Petersen [7]. The TFC polyamide membrane is now the state-of-the-art membrane and dominates the current RO and NF market. Although TFC membranes are more expensive than CA membranes, they have a higher flux and, hence operate at a lower feed pressure than CA membranes. Further, TFC membranes are not biodegradable, and have a higher rejection of silica, boron, nitrates and organic compounds than CA membranes.

The invention of the RO membrane stimulated both commercial and academic interest in other membrane processes and applications. For example, Henis and Tripodi, the co-inventors of hollow-fibre GS membranes, made industrial GS economical by drawing on the experience of developments in RO membranes and modules [3]. Technical milestones for the commercial development of various membrane processes are given in Table 1.2.

Packaging of membranes in suitable element or modules that began in the 1960s resulted in several membrane modules by the 1980s: spiral-wound modules with CA and TFC polyamide membranes, PA and CTA hollow-fibre membranes, and UF polysulphone hollow-fibre membranes. These membranes and modules found their own niches in the marketplace in the 1980s; broadly speaking, CA spiral-wound membranes for industrial and municipal water treatment, TFC spiral-wound RO membranes for water desalination and high-purity water production, hollow-fibre RO membranes for seawater desalination, and hollow-fibre UF and MF membranes for industrial

Table 1.2 Commercial development of membrane processes

Membrane process	Country	Year	Application
Microfiltration	Germany	1920	Laboratory use
Ultrafiltration	Germany	1930	Laboratory use
Hemodialysis	Holland	1950	Artificial kidney
Electrodialysis	USA	1955	Desalination
Reverse osmosis	USA	1965	Desalination
X-flow ultrafiltration	USA	1971	Concentration of macromolecules
Gas separation	USA	1979	Hydrogen recovery
X-flow microfiltration	Australia, USA	1980	Water treatment
Pervaporation	Germany, Holland	1982	Dehydration of organic solvents
Nanofiltration	USA	1986	Water softening
Electrodeionisation	USA	1987	Demineralisation
Submerged membrane filtration/bioreactor	Japan	1987	Water reclamation/sewage water treatment

applications. In the last 20 years, spiral-wound NF and submerged hollow-fibre and flat-sheet UF/MF membranes have evolved as important technologies for municipal and industrial water treatment.

A historical review of membrane technology would be incomplete without a brief discussion of the subject of mechanism of water transport through RO membranes [3, 5, 8]. The two leading transport mechanisms are the solution-diffusion (SD) model and the preferentially sorption-capillary flow (PSCF) model. The PSCF model [5, 8] was developed in the 1960s by Sourirajan and co-workers based on the assumption that the RO membrane surface has pores whereas the SD model assumes the membrane surface is pore-free. Subsequently, it was shown that RO membranes have a two-size (bi-modal) distribution of pores in the RO membrane surface; predominantly small pores (≤ 10 Å) thought to exist in perfect or ideal membranes; and occasional large (≥ 100 Å) pores that are attributable to the inevitable existence of defects in the skin layer [8]. According to the PSCF model, "pore" or "capillary" refers to any connecting void space whatever its origin or size. Preferential sorption, positive or negative, takes place at the pore wall–fluid interface and the desalted layer is removed under pressure continually. The interfacial fluid – the composition of which is different from the bulk fluid – is forced through channels, however small, penetrating across the membrane. Thus, both pore size and interaction force govern the separation of the solute molecules from the solvent. The strength of the PSCF model is its ability to encompass solution properties as well as the chemical and physical properties of the membranes.

The SD model was originally employed to explain the permeation of gases, vapours and organic liquids through dense (non-porous, homogeneous) but defect-free membranes by Ferry [9]. The SD mechanism involves molecular-scale interactions of the permeating solutes (dissolved species) with the membrane. The model assumes that each component is sorbed by the membrane at one interface, transported by diffusion across the membrane through the voids between the polymeric chains (the so-called free volume), and desorbed at the other interface. The voids are tiny spaces between polymer chains caused by thermal motion of the polymer molecule. The transition in pore size between the porous and pore-free membranes is believed to be in the range of 5–10 Å (0.5–1.0 nm).

To summarise, the development and remarkable success of commercial membrane processes for liquid separations – RO, nanofiltration (NF), UF, and MF – would not have been possible without the discovery and subsequent development of high-flux, extremely thin (skinned) CA membranes by Srinivas Sourirajan and Sidney Loeb at UCLA, culminating in the development of TFC PA membranes by John Cadotte. Membrane technologies such as NF, PV and GS got the impetus from the work on RO in the 1950s and 1960s. These successes have led to the development of newer membrane processes such as membrane distillation (MD) and forward osmosis (FO).

1.3 MEMBRANE-SEPARATION CHARACTERISTICS

Membrane-separation is characterised by simultaneous retention of species and product flow through the semipermeable membrane. Membrane performance is based on its high selectivity and flux; good mechanical, chemical and thermal stability of membrane materials, defect-free production, minimal fouling during operation, and good compatibility with the operating environment. Membranes responsible for such selective behaviour under mild operating conditions consist of porous/non-porous polymers, ceramic and metal films with anisotropic or symmetric structures with homogenous, heterogenous or composite materials, ionic membranes as well as liquid films with selective carrier components [2, 3, 7].

1.3.1 Membrane-separation basics

The membrane process

A membrane is defined as a permselective barrier between two homogeneous phases. Schematic diagrams of membrane-separation processes are shown in Figure 1.4. Membrane processes are continuous steady-state operations consisting of three streams: feed, product (permeate) and reject (retentate). The dashed line in the process boundary is the semipermeable barrier that selectively allows the passage of some components but not others, and allows some components to pass through more rapidly than others. For example, in the case of RO, the membrane allows the passage of water but rejects almost all the ions and salts resulting in a concentrated salt on the feed side of the membrane, and virtually ion-free product on the other side of the membrane. Thus, the most

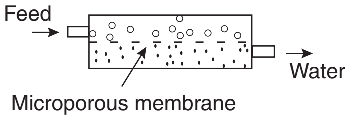
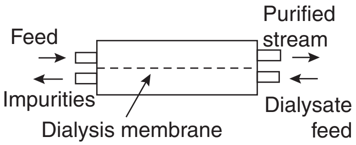
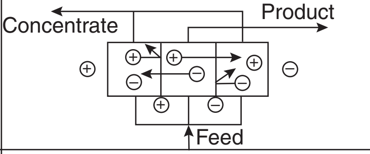
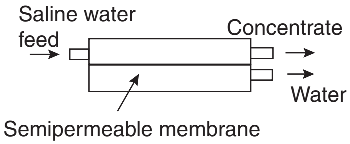
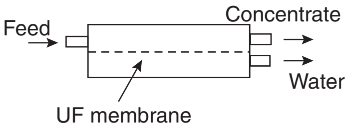
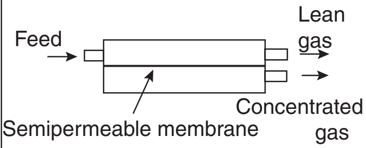
Process	Separation concept	Materials passed	Driving force
Micro-filtration		Water and dissolved species	Pressure difference, typically 10 psi
Dialysis		Ions and low–molecular–weight organics (urea, etc,)	Concentration difference
Electro-dialysis		Ions	Voltage, typically 1–2 V/cell pair
Reverse osmosis		Water	Pressure difference, typically 100–800 psi
Ultra-filtration		Water and salts	Pressure difference, typically 10–100 psi
Gas separation		Gases and vapours	Pressure difference, 1–100 atm

Figure 1.4 Membrane-separation processes. *Source:* [3].

permeable component (water) gets enriched in the permeate stream while the least permeable component gets enriched in the retentate (salt) stream.

No one membrane process is suitable for every fluid stream owing to the nature of feed and product requirements as well as the nature of the membrane process and the membrane designed for that process (see Table 1.3 and Figure 1.4). Even for the same membrane process, the performance varies depending on the type of feed. For example, when a UF membrane is used to sterilise a water supply or to concentrate a viscous liquid such as a fruit puree under the same operating conditions of feed flow rate and pressure, the permeate flow is 70–80% lower in the case of the latter due to the concentration of

Table 1.3 Classification of commercialised membrane processes

Process	Pore size	Driving force	Transport mechanism
Microfiltration	0.05–10 μm	Pressure, 1–2 bar	Sieving
Ultrafiltration	0.001–0.05 μm	Pressure, 2–5 bar	Sieving
Nanofiltration	<2.0 nm	Pressure, 5–15 bar	Donnan exclusion/ sorption-capillary flow
Reverse osmosis	~0.6 nm	Pressure, 15–100 bar	Preferential sorption-capillary flow
Gas separation	Non-porous	Pressure, 15–100 bar	Solution-diffusion
Pervaporation	Non-porous	Partial pressure difference	Solution-diffusion
Dialysis	10–30 Å	Concentration difference	Sieving-diffusivity difference
Electrodialysis	$MW < 200$ Da	Electrical potential	Ion migration
Electrodeionisation	$MW < 200$ Da	Electrical potential	Ion migration
Membrane contactor (membrane distillation)	Porous, hydrophobic	Vacuum	Sieving

rejected solutes on the membrane surface. Thus, there is a clear distinction between the intrinsic membrane characteristics and its performance in a particular application. The main membrane processes are discussed in detail later in the chapter.

Membrane transport

Membrane processes are rate processes and the relative rates of transport of solvent and solute flow through the membrane determine the quality of the product. Substances move through membranes by several mechanisms: viscous and/or diffusion. The transport properties of solutes through a membrane are determined by the permeability of the membrane and by a driving force. The semipermeable membranes allow preferential passage of certain substances under the influence of a driving force. The driving force usually is pressure difference, concentration difference or electrical potential between the feed side and the product side. Sources of various driving forces are detailed in Figure 1.4 and Table 1.3. Flow factors such as axial diffusion of solute, longitudinal convection of solvent and flow-induced drag on the particle at the membrane surface can also affect transport across a membrane.

The extent of the driving force is determined by the potential gradient across the membrane. The membrane controls the transfer of mass between the feed solution and product. If no external forces are applied, the system will reach equilibrium when the potential difference becomes zero. Since the membrane processes are kinetic processes and not equilibrium processes (e.g., distillation, evaporation and crystallisation), when the driving force is constant, the flow through the membrane is constant once steady state has been established. The relationship between permeate flow or flux (J) and the driving force (X) is given by $J = k \times X$ where k is the proportionality factor and X the potential gradient per unit membrane thickness.

Mass transport through a membrane has been described by several semiempirical mathematical models including Fick's, Hagen-Poisseuille's and Ohm's laws. For pressure-driven membrane-separation processes (RO, NF, UF, MF, GS), the transport relationship is given by:

$$J = K \cdot \frac{\Delta P}{t} \tag{1.1}$$

where J is the trans-membrane flux, K the membrane permeability constant, ΔP the pressure difference across the membrane and t the membrane thickness. The driving force is $\Delta P - \Delta \Pi$ when there is an osmotic pressure difference, $\Delta \Pi$, across the membrane.

The importance of the thickness of the membrane is evident from Equation (1.1) since flux is inversely proportional to thickness. The Loeb–Sourirajan RO membranes produced by the phase-inversion technique have an effective skin thickness of 0.1–0.2 μm that makes it possible to achieve acceptable fluxes (2–20 $\mathrm{l/m^2/h}$) at reasonable feed pressures (30–60 bar g) for water desalination. UF membranes with a similar but less tight skin structure (pore size 1–50 nm vs. ~0.6 nm for RO membranes) have fluxes on the order of 15–150 $\mathrm{l/m^2/h}$ (lmh) at feed pressures of 1–5 bar g. The ability to minimise thickness without introducing defects relies upon controlling the membrane morphology during fabrication.

The flux also depends on the physical make-up of the membrane and the pore size. The pure water flux vs. hydraulic pressure difference curve is linear. Liquid flux for membrane processes is shown in Figure 1.5. The data show how the permeation rate varies with the size of the species and pore size (implicit in type of membrane). The ordinate represents the flux of water per unit pressure gradient. Since the pore radius of an RO membrane is ~0.6 nm, water molecules whose radius is about 0.1 nm can pass through the membrane freely while dissolved ions and organic solutes (e.g., sucrose) cannot. These solutes are either rejected at the membrane surface, or are more strongly attracted to the solvent water phase than to the membrane surface. The "preferential sorption" of water molecules at the solvent–membrane interface, which is caused by the interaction force working between the membrane, solvent, and solute responsible for the separation [8]. As the pore size decreases and tends toward a non-porous skin structure, the transport mechanism changes from convective flow through pores to SD in the membrane polymer. The latter is the transport mechanism in GS and PV.

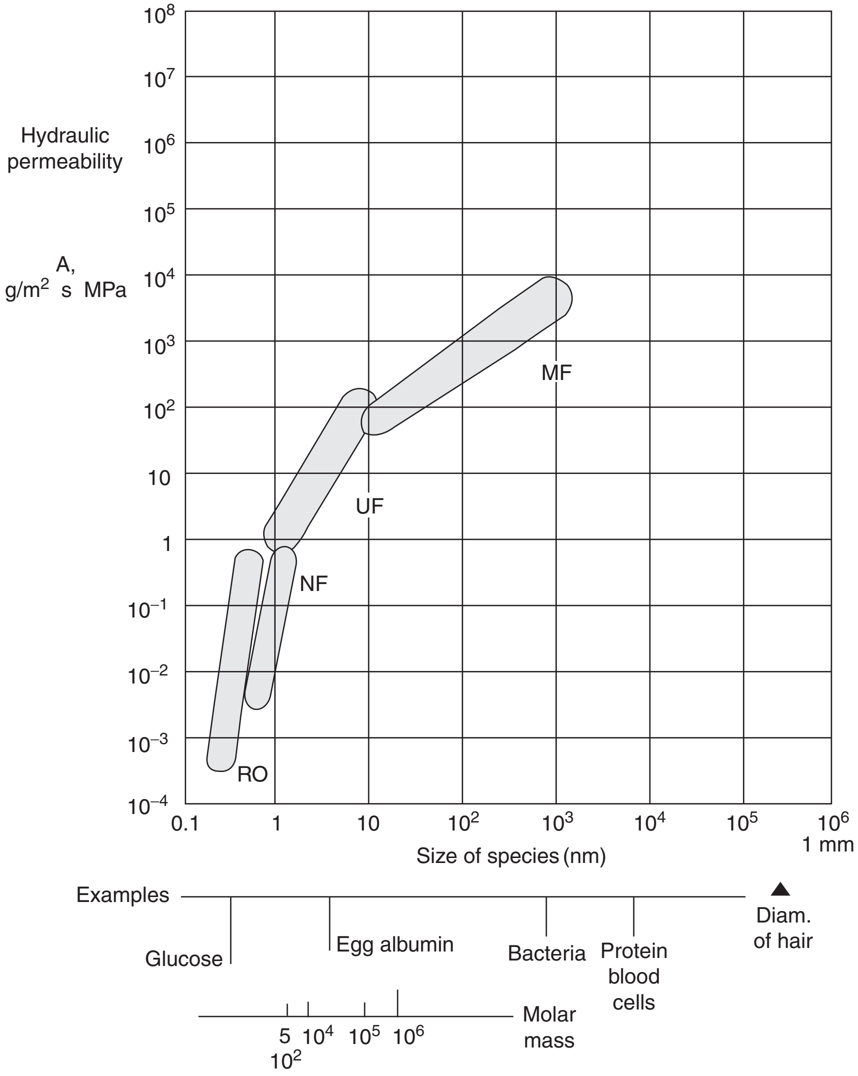


Figure 1.5 Solvent flux vs. solute size and solute type for various membrane processes.

A membrane process property related to flux is product recovery defined below. In liquid separations, especially RO and NF, it is one of the key performance indicators:

$$\%\text{Recovery} = \frac{\text{product flow}}{\text{feed flow}} \times 100$$

Membrane selectivity

Membrane separation is governed by the chemical and physical nature of the membrane material. Separation occurs because of differences in size and shape, chemical properties, or electrical charge of the substances to be separated; for example, microporous membranes control separation by size and discrimination. In the case of porous membranes, species small enough to enter the pores are transported by convective flow while non-porous membranes rely on sorption and diffusion through the membrane as discussed earlier. Furthermore, membranes do not have a sharp separation between species. In the case of UF membranes; for example, a rule of thumb is that the nominal molecular cut-off rating of the membrane selected should be an order of magnitude lower than the average size of the solute to be rejected or retained. Synthesis of UF membranes with a sharp cut-off has been an elusive goal since the 1960s [10]. Rejection coefficient, R, is a reliable indicator of the separating ability of a membrane process:

$$\%\text{Rejection},\ R = \frac{\begin{array}{c}\text{feed/bulk solute concentration} - \text{product solute}\\ \text{concentration}\end{array}}{\text{feed/bulk solute concentration}} \times 100$$

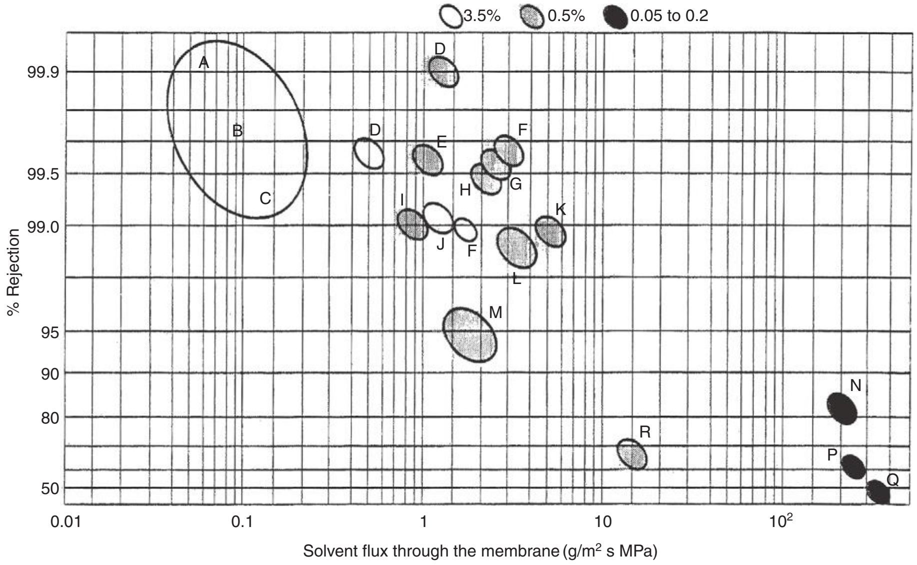
For a perfectly selective (ideal) membrane, $R = 100\%$. For UF and MF processes the retention coefficient defined below is a better measure of selectivity because the build-up of solute particles on the membrane surface due to concentration polarisation (CP) or gel layer affects solute transport through the membrane:

$$\%\text{Retention} = \frac{\begin{array}{c}\text{membrane surface solute concentration} - \text{permeate}\\ \text{solute concentration}\end{array}}{\text{membrane surface solute concentration}} \times 100$$

Membrane performance is a trade-off between membrane selectivity and membrane productivity. Membrane selectivity, α ($=A/B$), is defined by the ratio of permeability of components through the membrane where A is the water permeability coefficient and B is the solute permeability coefficient. In the case of RO and NF membranes, water/NaCl selectivity for seawater RO membranes is about 10,000. The higher the selectivity, the lower the permeate flux or productivity. This relationship for various RO membranes used with dilute NaCl solution is shown in Figure 1.6. The shaded regions refer to different feed concentrations and to different types of membranes. The data is fairly independent of the feed concentration but is a function of the physical and chemical properties of the membrane.

Concentration polarisation

In pressure-driven liquid-phase processes such as RO, NF, UF and MF, solutes and particles transfer to the membrane surface with the solvent by convection. The accumulation of solutes on the membrane surface is called CP, which is represented by the



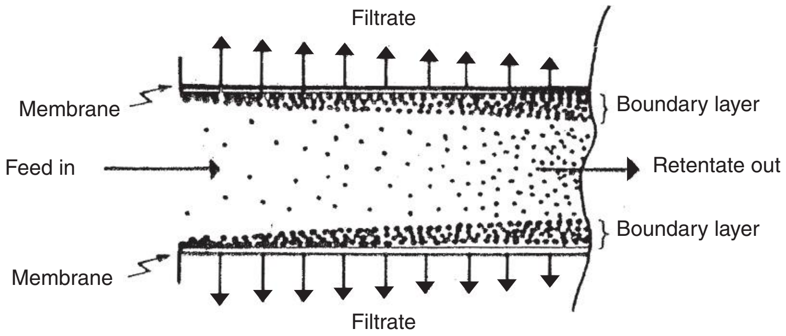
Membranes from various manufacturers: A, Hollosep–cellulose triacetate hollow fibre membrane (Toyobo); B, sulphonated polysulphone composite hollow fibre membrane (Albane International); C, B10–aromatic polyamide hollow fibre membrane (Du Pont); D, PEC-1000–composite flat-sheet membrane (Toray); E, NS-200–composite polyfurfuryl alcohol membrane; F, FT-30–composite polyamide flat-sheet membrane (Film Tec/Dow); G, NTR-7199–composite polyamide/polyurea flat-sheet membrane (Nitto Denko); H, TFC-803 (PA-300)–composite polyetheramide flat-sheet membrane (Fluid Systems/Signal; I, NS-100–composite polyurea flat-sheet membrane; J, TFC-801 (RC-100)–composite polyetherurea flat-sheet membrane. (fluid systems/Signal); K, NTR-7197–composite polyamide/polyurea flat-sheet membrane (Nitto Denko); L, B-15—asymmetric polyamide flat-sheet membrane (Du Pont); M, asymmetric cellulose acetate flat-sheet membrane (FilmTec/Dow); P, Romembra SU-composite polyamide flat-sheet membrane (Toray); Q, NF-50–composite flat-sheet membrane (FilmTec/Dow); and R, NTR-7250–composite polyvinyl alcohol flat-sheet membrane (Nitto Denko). Species: Sodium chloride Temp. 25 °C

Figure 1.6 RO membrane performance data for various polymers. *Source: E.K. Lee, Encyclopedia of Physical Science and Technology, Academic Press, 1987.*

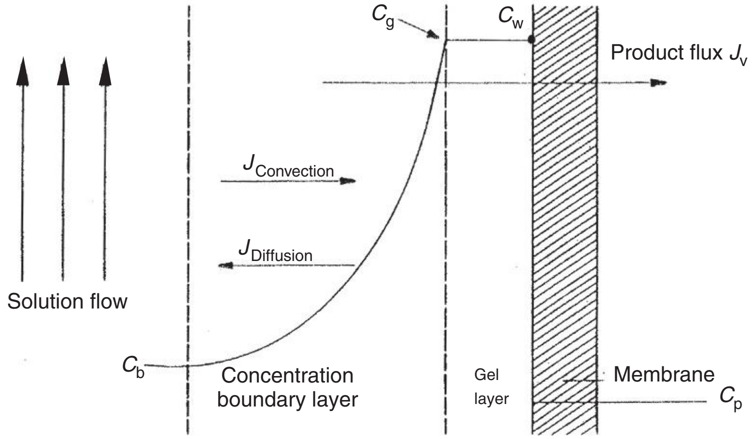
concentration gradient shown in Figure 1.7. The retained solutes that flow into the boundary layer by convection are removed by slower back-diffusion. The magnitude of CP is determined by the balance between convection toward the membrane and back-transport from the membrane due to concentration gradient. Mechanisms that induce back-transport of solutes include [11]:

- molecular (Brownian) diffusion,
- shear-induced diffusion, and
- interaction-induced migration (due to electro-kinetic and surface forces).

Diffusive back-transport is the most common back-transport mechanism [12], and is represented by the mass transfer coefficient, $k = D/\delta$ where D is the solute diffusivity and δ is the boundary-layer thickness. The possible effect of slip flow velocity on diffusive back-transport [13, 14] is discussed in Chapter 6. Steady-state conditions are reached when the convective transport of the solutes to the membrane is equal to the sum of the permeate flow and the diffusive back-transport of the solutes. This steady-state is



Schematic of concentration boundary-layer development



Concentration profile for a gel-polarised UF membrane

Figure 1.7 Concentration/gel polarisation model schematic. In the absence of a gel layer, $C_g = C_w$.

normally reached in less than a minute. The steady-state solute balance is expressed by the Film Theory Model [11, 12]:

$$JC = D \cdot \frac{dc}{dx} + J \cdot C_p \tag{1.2}$$

i.e.

$$\begin{matrix}\text{Rate of convection} \\ \text{towards the membrane}\end{matrix} = \begin{matrix}\text{rate of diffusion} \\ \text{back into solution}\end{matrix} + \text{rate of permeation}$$

where J is the solvent flux, C the feed solute concentration, C_p the permeate solute concentration, D the solute diffusivity and x a length coordinate. Integration over the boundary layer ($x = 0$ to δ, $C = C_w$ to C_b) gives for 100% rejection, ($C_p = 0$):

$$J = k \ln\left(\frac{C_w}{C_b}\right) \tag{1.3}$$

where k is the mass transfer coefficient, and C_w and C_b are the concentrations of the solute at the membrane surface and in the bulk solution, respectively, as shown in Figure 1.7. In the case of $R < 100\%$ (which is typical of membranes), Equation (1.3) is modified to:

$$J = k\ \ln\left(\frac{C_w - C_p}{C_b - C_p}\right) \tag{1.4}$$

Equation (1.3) shows that the flux is directly related to k, and for a given flux, C_w is exponentially related to the ratio of flux to mass transfer coefficient, i.e., J/k:

$$\frac{C_w}{C_b} = \exp\left(\frac{J}{k}\right) = C_M \tag{1.5}$$

The ratio C_w/C_b is known as the "polarisation modulus," C_M. Equation (1.5) is the basic equation of CP; C_M increases with increasing J (higher flow of solutes to the membrane surface means increasing C_w) and decreasing k $(=D/\delta)$. The magnitude of C_M depends on the solute diffusivity, D. Thus, for typical fluxes and low molecular compounds such as inorganic ions (salts) C_M is <2.0, for large organic macromolecules such as humic acids C_M is >5.0, and in the case of proteins C_M can be >10. Hence, any technique that decreases C_w such as turbulence or surface shear that would minimise δ, promote diffusive back flow (shear-induced diffusion), and would result in higher solvent flux through the membrane as also demonstrated by the slip-flow model in Chapter 6.

The pure water flux in pressure-driven processes is directly proportional to the applied hydraulic pressure as per Equation (1.1) and is shown in Figure 1.8. The curves also show that for feed solutions containing solutes, as ΔP increases the flux reaches a plateau (Region III) and becomes independent of pressure. This steady-state flux is called the "limiting flux," J_{lm} or gel layer limited flux:

$$J_{lm} = k\ \ln\left(\frac{C_g}{C_b}\right) \tag{1.6}$$

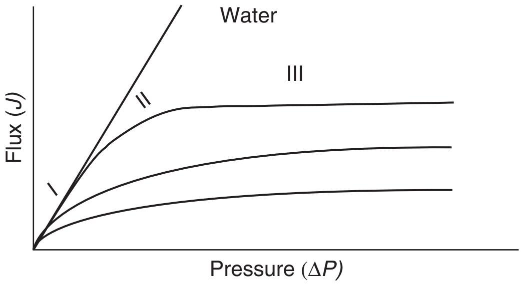


Figure 1.8 Flux (J) vs. pressure (ΔP) relationship. Flux increases with higher k and lower C_b.

where C_g is the gel concentration beyond which the concentration in the boundary layer cannot increase. In order to reduce the formation of a gel layer, membrane systems should be operated in the so-called "critical flux" region, Region II in Figure 1.8. Critical flux is defined as the limiting flux below which a flux decline over time does not occur [15]. The critical flux increases with higher cross-flow velocity (higher Reynolds number) and lower solute concentration, C_b. The limiting flux behavior for various feed waters in RO membrane modules is illustrated in Figure 2.27 in Chapter 2.

CP results in the precipitation of components on the membrane surface in the case of sparingly soluble salts, and to the formation of gel or cake layer. The flux is reduced drastically especially in UF/MF systems; flux decline with time in UF/MF is illustrated in Figure 2.34. It follows a simple empirical equation (see also Equation 1.14):

$$J = J_o t^n \tag{1.7}$$

where J is the actual flux, J_o the initial flux and n is a variable exponential factor ($n < 0$) that can be a function of cross-flow velocity.

The secondary membrane not only impairs flux, it also affects the separation properties of the membrane and results in fouling. In RO and NF systems, CP also contributes to higher osmotic pressure – higher than that represented by the bulk feed concentration. Higher hydraulic pressures are, therefore, required to achieve the desirable permeate flow rate. In RO and NF systems the solute concentration in the boundary layer is controlled to less than 20% to prevent scaling and fouling. CP, however, is reversible as long as it does not result in fouling; for example, when the permeate line is closed the flux drops to zero, and C_w reverts to C_b (see Figure 1.7) [11].

The solute concentration at the membrane surface is typically 20–50% higher than in the bulk solution due to CP. High molecular weight compounds and colloids form a highly viscous or truly gelatinous mixture at high Schmidt numbers ($\mathrm{Sc} = \upsilon/D$, ratio of kinematic viscosity to diffusivity) when their concentration exceeds 5–15% by weight. The thickness of the dynamic or secondary membrane shown in Figure 1.7 is typically less than 20 μm [12]. The gel layer does not adhere strongly to the membrane, and the effect can be minimised by turbulence promoters and surface shear by cross-flow. However, once the membranes get fouled, the original flux is not fully restored even after cleaning. In some cases such as biofouling, it is often irreversible. Fouling is discussed in detail later in this chapter and in Chapter 2.

According to Equations (1.3) and (1.6), flux is related to the boundary-layer mass transfer coefficient, k. Both k and C_w are calculated from the data plot shown in Figure 1.9 based on the gel polarisation model (Region III in Figure 1.8). Wall concentration, C_w (or C_g), is determined by extrapolating the semilog plot of J vs. C_b to x-intercept (zero flux), and k is the negative slope of the curve. The procedure for calculating k using the

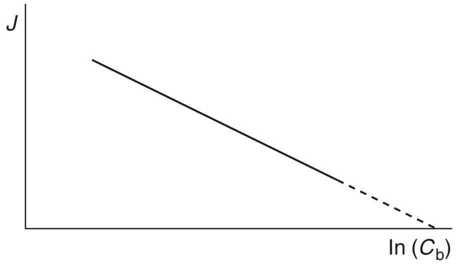


Figure 1.9 Flux (*J*) vs. feed/retentate concentration (ln C_b).

well-known relationship between dimensionless numbers Sherwood, Schmidt and Reynolds numbers is given in Chapter 6. A recent comprehensive review is provided by [11].

1.3.2 Membrane materials and properties

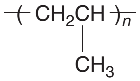
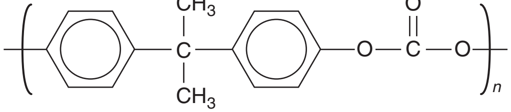
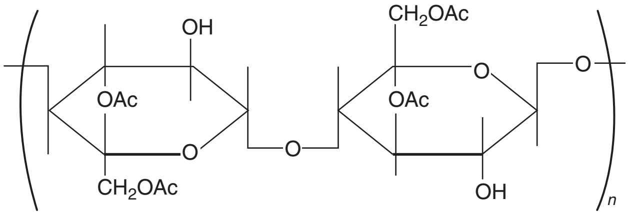
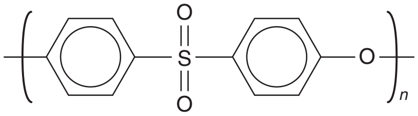
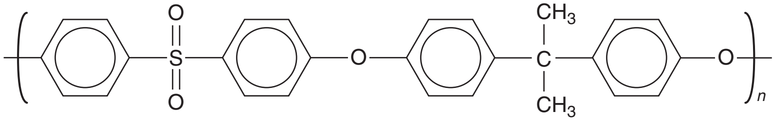
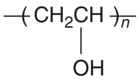
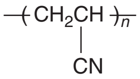
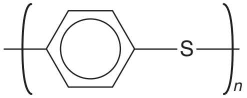
Synthetic membranes can be made from a large number of materials. Not all materials are, however, suitable for pressure-driven membrane processes with the exception of CA and its derivatives. Membranes should combine high permeability and high selectivity with sufficient mechanical stability recognising that materials more permeable to a fluid tend to have less ability to separate; for example, water from mixtures of salts and vice versa. Preferably for liquid separations the membrane should have both hydrophilic and hydrophobic characteristics. Polymer (or other material) is selected based on the processing requirements, fouling tendency as well as thermal and chemical stability of the membrane. A list of common polymers used for membranes are given in Table 1.4 and Figure 1.6.

There are four main types of polymeric membranes: (a) Loeb–Sourirajan phase separation RO, UF and MF membranes, (b) interfacial composite RO and NF membranes, (c) solution-coated composite GS membranes, and (d) other anisotropic membranes such as plasma polymerisation coated. Several methods of manufacturing synthetic membranes are given in Table 1.5. Each method produces different membrane morphology: porosity, pore size distribution, and ultrastructure. Membrane formulation techniques are discussed in detail in several texts [8, 16–18].

Polymeric membranes

Polymers provide a range of properties important for separations, and modifying them can improve membrane selectivity. Since it is desirable to use a polymer, which is chemically and thermally stable, materials with high glass transition temperatures, T_g, high melting points and high crystallinity are preferred. T_g is a property that defines the state of a polymer; a glassy state below T_g, and a rubbery state above T_g. Glassy polymers have stiffer polymer backbones and, therefore, let smaller molecules, such as hydrogen

Table 1.4 Characteristics of common polymeric membrane materials

Polymer	**Structure**	**T_g (°C)**	**Melting temp. (°C)**
Polyethylene	$-(\mathrm{CH_2})_n-$	−60 to −90	137–143.5
Poly (vinylidine fluoride)	$-(\mathrm{CH_2CF_2})_n-$	−40	160–185
Polypropylene	 $-(\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{CH}}})_n-$	−10	167–170
Polycarbonate		150–155	240
Teflon	$-(\mathrm{CF_2})_n-$	−113	327
Cellulose acetate		69	230
Poly (ether sulphone)		225	NA
Polysulphone		190	NA
Poly (vinyl alcohol)	 $-(\mathrm{CH_2}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{CH}}})_n-$	65–85	228–256
Polyacrylonitrile	 $-(\mathrm{CH_2}\underset{\mathrm{CN}}{\underset{\vert}{\mathrm{CH}}})_n-$	80–104	319
Poly (phenylene sulphide)		85	285

NA, not available. See also Figure 6.15.
Source: [19].

Table 1.5 Synthetic membrane manufacturing methods

Process	Materials
Phase inversion: solvent evaporation, temperature change, precipitant addition	Polymers: CA, PA, PP, PS, nitrocellulose
Stretching sheets of partially crystalline polymers	Polymers: PTFE
Irradiation and etching	Polymers: polycarbonate, polyester
Moulding and sintering of fin-grain powders	Ceramics, metaloxides, PTFE, PE

and helium, pass faster while large-sized hydrocarbons permeate the membrane more slowly. In the case of rubbery polymers, the permeabilities of hydrocarbons are higher than the much smaller gas molecules. A rubbery polymer is an amorphous polymeric material that is above its softening or glass transition temperature, T_g, under the conditions of use. The degree of crystallinity has a large influence on the mechanical and transport properties of a polymer. Crystalline polymers show a high chemical and thermal stability and are usually used for MF membranes. However, as a polymer becomes more stable, it becomes more difficult to process into a membrane as it is no longer soluble in suitable solvents. The molecular structure and thermal characteristics of several polymeric membrane materials are given in Table 1.4 [19]. Amorphous glassy polymers such as PS are used for UF membranes as they are convenient for control of the small pore size required and display a high T_g. Polymers such as polypropylene (PP) and polyamides (PA) are semicrystalline, consisting of an amorphous and a crystalline fraction.

Membrane surface morphologies and properties such as roughness, charge and hydrophilicity have remarkable affects on performance and fouling. Interfacial properties such as interfacial tension and adsorption are considered to be the most important physical properties of the membrane material because the solid membrane phase is in contact with a liquid or gas phase. Physical properties refer to the degree of change in the physical structure of the material in a given environment such as the degree of swelling of a polymeric membrane in an organic solvent and the change in crystallinity at high or low temperatures. Interfacial properties play a critical role in the performance of UF and MF membranes due to van der Waal's interactions, hydrogen bonding, electrostatic effect, charge transfer effects and dipole moments. For example, the precipitous drop in permeation flux with hydrophobic membranes is the result of irreversible adsorption (fouling) of solutes such as protein on the membrane surface (see Figure 2.34) whereas cellulosic hydrophilic membranes, which swell in water, present a more "water-like" surface to the proteins.

Despite the excellent chemical and thermal stability of hydrophobic polymers (e.g., polytetrafluoroethylene (PTFE) and polyvinylfluoridine (PVDF) membranes are used in UF and MF of organic solutions), stable hydrophilic polymers are more effective as membrane materials because of their reduced adsorption tendencies. In general, hydrophilic membranes, such as CA, polyethylene (PE), polyvinylpyrrolidone (PVP) and inorganic alumina are less susceptible to fouling than hydrophobic membranes, e.g., PVDF, polysulphone (PS), polyether sulphone (PES) and polypropylene (PP).

In the case of RO membranes, the Hilderbrand's solubility parameter (SP) of a polymeric material can be used to select suitable polymeric materials. It has also been used for the study of PV membranes. The solubility parameter expresses the nature and magnitude of the interaction force working between molecules: between the permeant molecule and the molecules of the membrane material [8]. The SP of polymers, from which RO membranes with excellent performance have been prepared, are between 24 and 35. In this range the membrane material hydrophobic/hydrophilic ratio is well balanced; a low SP reflects hydrophobicity of the polymer, whereas hydrophilicity is associated with a high SP value.

RO membranes

The first-generation RO membranes were CA even though they are limited in terms of chemical, thermal and mechanical stability. The most common cellulose esters in use today are a blend of CA (40.1% acetyl) and CTA (43.2% acetyl). The membranes undergo hydrolysis when operated beyond a pH range of 4–6, and are biodegradable; CA gets slowly hydrolysed in water, which reduces the acetyl content in the membrane, and affects its performance adversely [3, 8, 17]. Although the cellulose polymer is hydrophilic, it is not water soluble because the polymer is quite crystalline, and because of intermolecular hydrogen bonding between the hydroxyl groups. CA membranes swell in polar organic solvents, plasticising them. However, CA membranes have some tolerance to chlorine, unlike PA membranes, and are also less prone to fouling. CA membranes are used in various systems: dialysis (regenerated CA), MF (cellulose nitrate (CN) and CTA), ultrafiltration (CTA), reverse osmosis (CTA) and gas separation (CA). Toyobo hollow fibre CTA membranes are used in many large seawater RO plants.

Aromatic polyamides are superior to aliphatic polyamides because of their superior mechanical, thermal, chemical and hydrolytic stability and superior selectivity properties. Aliphatic PA membranes have low rejection and moderate flux. Aromatic PA is widely used for RO and NF and GS membranes, whereas aliphatic PA such as nylon-6, nylon 6-6 and nylon 4-6 are generally used for MF membranes. The linear aliphatic nylons 4/6, 6/6 and 6 are structurally regular chains consisting of a series of methylene groups joined together by the strongly hydrogen-bonding amide linkage. Cross-linked aromatic PAs form the skin layer of TFC membranes; for example interfacially polymerised PA formed from 1-3 diaminobenzene and 1,3,5 benzenetri carboxylic acid chloride. The residual negative charge resulting from incomplete reaction and subsequent hydrolysis and ionisation of the third acid-chloride group helps in reducing colloidal fouling [3, 8, 17].

Table 1.6 Characteristics of CA and PA membranes

Property	Regenerated CA	Polyamide[a]
Membrane type	Homogenous asymmetric	Homogenous asymmetric; thin-film composite
Salt rejection	~95%	>99%
pH operating range	4–6	2–11
Feed pressure (max)[b]	15–30 bar g	40 bar g
Hot water sanitisable (80°C)	No	Yes[c]
Surface charge	Neutral	Negative
Chlorine (oxidants) tolerance	1–2 ppm[d]	<0.1 ppm
Pre-treatment	High	Very strict
Organics removal	Good	Effective
Biological growth	Problematic	Not a problem
Surface	Hydrophilic	Hydrophobic–hydrophilic; contact angle 50–60°
Fouling tolerance	Good	Fair
Surface roughness	Smooth	Rough
Membrane module types	[e]SW, FP, HF, T	SW, FP, HF[f], T[f]

[a] RO and NF membranes only.
[b] Brackish water desalination.
[c] Special TFC membranes.
[d] CTA membranes = 5 ppm.
[e] Spiral wound, flat-plate, hollow-fibre, tubular.
[f] Not applicable to TFC membranes.

General features of CA and PA membranes are given in Table 1.6. For a comprehensive review of RO membrane materials see [20]. Properties of notable asymmetric and TFC RO membranes are summarised in Table 1.7.

Membranes made by interfacial polymerisation have a dense, highly cross-linked polymer layer formed on the surface of the support membrane [6, 16, 20, 21] (see Figure 6.15). The dense cross-linked polymer layer, which can only form at the interface, is extremely thin (≤0.2 μm) resulting in high flux, and since the polymer is highly cross-linked, the selectivity is high. The first TFC membrane produced by this method, called NS 100 polyureas (Dow/Film-Tec), was based on the reaction of a poly(ethyleneimine) in water and toluene-2,4-diisocyanate or isophthaloyl in hexane [3, 6, 20]. The membrane had a high permeation rate. The next generation of interfacial composite membrane was PA 300. Early TFC membranes such as NS 100 and PA 300 were very sensitive to degradation by chlorine (only few hundred ppm h). Subsequently, a highly efficient interfacial composite membrane, FT-30, was developed by Dow/Film-Tec produced by the reaction of phenylenediamine with trimesoyal chloride. FT-30 is a fully aromatic but less highly cross-linked than polyurea PA 300, has very high water flux, exceptional high salt rejection (>99.5%) and some tolerance to chlorine (1000 ppm h). The FT-30 membrane spiral-wound element successfully competed with the DuPont

Table 1.7 Known RO membranes and their properties

Membrane polymer	Commercial name	Membrane performance
Asymmetric		
Cellulose acetate	(Loeb–Sourirajan)[a]	15 lmh flux, 99%R at 100 bar g, 4% NaCl
Aromatic polyamide–polyamide-hydrazide	–	28 lmh flux, 99.5%R at 100 bar g, 3.5% NaCl, 30°C
Polyiperzine-amide	–	28 lmh, 97.2%R at 80 bar g, 0.36% NaCl
Polybenzimidazoline	–	5 lmh, 95%R at 6 bar g, 0.1% NaCl
Polyoxadiazole	–	3 lmh, 92%R at 45 bar g, 0.5% NaCl
Thin-film composite		
Polyfurane	NS-200	33 lmh, 99.8%R at 100 bar g, 3.5% NaCl
Polyether-polyfurane	PEC-1000	21 lmh, 99.9%R at 69 bar g, 3.5% NaCl
Sulphonated polysulphone	Hi-Flux CP	2.5 lmh, 98%R at 69 bar g, 3.5% NaCl
Polyamide–polyethylenimine	NS-100	29 lmh, 99%R at 100 bar g, 3.5% NaCl
Polyamide–polyepiamine	PA-300, RC-100	42 lmh, 99.4%R at 69 bar g, 3.5% NaCl
Polyvinylamine	WFX-X006	83 lmh, 98.7%R at 40 bar g, 0.25% NaCl
Polypyrrolidine	-	33 lmh, 99.7%R at 40 bar g, 0.5% NaCl
Polypiperazine-amide	NS-300	138 lmh, 68%R at 100 bar g, 3.5% NaCl
Polyamide – cross-linked fully aromatic	FT-30	42 lmh, 99%R at 15 bar g, 0.2% NaCl
Polyamide – 2 cross-linked fully aromatic	UTC series	33 lmh, 98.5%R at 15 bar g, 0.5% NaCl
Aralkyl polyamide – cross-linked	A-15	11 lmh, 98%R at 55 bar g, 3.2% NaCl
Polyamide – 3 cross-linked fully aromatic	X-20	42 lmh, 99.3%R at 15 bar g, 0.2% NaCl

[a] Generic name.

Source: Based on [20].

asymmetric hollow fibre aromatic polyamide B-9 Permasep® membranes released in 1972. The FT-30 chemistry is now used in modified form by all the major RO desalination membrane producers [20]. The success of FT-30 led to the release of a number of similar TFC membranes including CPA2 and ESPA (Nitto Denko/Hydranautics), UTC-70 (Toray) and X-20 (Tri-sep). Cross-linked fully aromatic polyamide X-20 has shown superior resistance to fouling and chlorine due to its relatively neutral charge and stronger polyamide-urea bond linkage [20].

In summary, a variety of organic polymers have been used for the top skin layer of TFC membranes [22], as shown in Figure 1.6:

- Polyamides – *heterocyclic/aromatic* (e.g., NTR-729HF, NTR-739HF, UTC-60, UTC-20HF, NF-40, NF-40HF); *aromatic* (e.g., NTR-759HF, CPA2, UTC-70, BW-30, NF-50, NF-70); *aromatic/alcyclic* (e.g., A-15).
- Polyureas – *aliphatic/aromatic* (e.g., NTR-719HF, IFCI, TFS series, PA 300, UTC-40HR).
- Polyether – *sulphonated aromatic* (e.g., NTR-7400).

Note, membrane manufacturer designations are as follows: NTR (Nitto Denko), UTC (Toray), NF & BW (Dow/Film-Tec), CPA & IFCI (Hydranautics/Nitto Denko), PA & TFCs (UOP), A (DuPont).

These membranes are either positively charged or negatively charged [22]. The very high salt rejection of polyamide TFC membranes without sacrificing high flux is due to its ionic character, which results in co-ion repulsion. The negatively charged TFC membranes have an iso-electric point between 4 and 5. Below a pH of 4.0, the membranes have a net positive charge, and above 5.0, a net negative charge. Hence, during RO plant operation, the feed water pH should be between 7.0 and 8.5 to enhance rejection.

Unlike PA membranes, polyether urea (PEU) membranes are neutral to slightly positive. PEU (and CA) membranes, unlike aromatic PA membranes, have a smooth surface and are, therefore, less prone to fouling [23]. For RO feed water such as surface and municipal water, which are treated with cationic polymeric coagulants, PEU membranes, not negatively charged PA membranes, are used to minimise fouling.

One of the few drawbacks of the PA membranes is that they are highly susceptible to degradation by chlorine with extended exposure due to chain deformation and alteration of the average inter-chain displacement within the PA membrane skin structure as discussed in Chapter 6. The net result is increased permeability and decreased selectivity, and eventual degradation. Membranes based on polypiperazine amides improved resistance to chlorine apparently due to reduced amidic hydrogen [24]. Intolerance to chlorine also means that RO/NF feed water must be dechlorinated when using PA membranes. Unfortunately, in the absence of chlorine, membranes are susceptible to biofouling, which is often irreversible. By comparison, CTA hollow-fibre membranes can tolerate up to 5 ppm chlorine as compared to 2 ppm for CA membranes and <0.1 ppm for PA membranes [25]. The possibility of using sulphonated block copolymers or self-assembled lyotropic liquid crystals to fabricate chlorine-resistant membranes has been explored [21]. Most work on these new materials has involved thick films on the order of 50 μm, but the reported intrinsic water and salt permeabilities are close to those of TFC membranes when normalised for thickness. The challenge is to make these films thinner, i.e., about 100–250 nm thick, in order to be competitive with TFC membranes.

Inorganic membranes

There are four general categories of inorganic membranes: ceramics, sintered metals, glass and zeolite [17, 19, 20, 26]. These membranes are now viable alternatives to polymeric membranes for some UF and MF applications because of their outstanding thermal and chemical stability. Several inorganic RO membranes (ceramic, carbon), mixed-matrix RO membranes (a combination of organic and inorganic material) and carbon nanotube/polymeric RO membranes have been fabricated and tested for possible applications [20]. The intent is to develop membranes that are less prone to fouling by making them smoother, hydrophilic and more negatively charged.

Ceramic UF and MF membranes are microporous sieves in which separation takes place on the basis of the size and speed of a particle through a tortuous path of the pore. Capillary action, adsorption phenomena and surface charge all play roles in retention and separation. Although ceramic membranes can be manufactured with a sharp pore size distribution, they are limited in their size-exclusion capability.

Ceramic UF and MF membranes are made generally by sintering and sol–gel processes. Sintering is limited to pore sizes of about 0.1 μm. UF membranes are generally prepared by the sol–gel technique. γ-Alumina (γ-Al_2O_3) and α-alumina are the most common ceramic membrane materials. Others include zirconia (ZrO_2), titania (TiO_2), silicon carbide (SiC) and glass (SiO_2). Alumina-based MF membranes and porous carbon substrates are made into UF membranes by depositing a layer of ZrO_2 on the surface. Characteristics of typical ceramic membranes are detailed in Table 6.13. A profile of a ceramic membrane is shown in Figure 6.14.

Because of their greater rigidity, ceramic microfilters accommodate fluxes 5–10 times greater than those of asymmetric polymeric membranes, and can be backwashed frequently without damaging the membrane skin layer. Ceramic membranes offer applications in high temperature applications, whereas polymeric membranes are restricted to temperatures less than 90°C. Ceramic membrane elements also have a greater resistance to cleaning chemicals, and can be steam sterilised and autoclaved repeatedly, which makes them well suited for biopharmaceutical processing. Another advantage of ceramic membranes is a significantly longer life, up to 10 years. For most polymer membranes, typical life varies from one to two years for hydrophilic membranes and three to five years for hydrophobic membranes. Ceramic membranes are, however, much more expensive than polymeric membranes and are brittle.

Other inorganic membranes include:

1. zeolite membranes, which have very narrow pore sizes, and are very good prospects for GS and PV membranes;
2. sintered metal membranes; and
3. organo-mineral membranes that are intermediate between polymeric and ceramic membranes.

Mineral membranes are obtained by sintering metal powders or stainless steel filaments with diameters between 1.5 and 80 μm [17–19]. They can be more expensive than ceramic membranes, and are limited in selection by their pore size range. Organo-mineral membranes are hybrid membranes, e.g., UF organo-mineral membranes are composed of a polymeric matrix (mostly PS) in which zirconia grains are dispersed finely as a filler material. The organo-mineral membranes have a considerably higher flux than traditional polymeric membranes.

Charged membranes

Charged membranes are highly swollen gels containing polymers with a fixed ionic charge. Ion-exchange (IX) membranes are usually homogeneous (symmetric) produced by polymerisation of functional monomers and cross-linking agents, or made by chemical modification of polymers [16, 17]. The membrane polymer is usually hydrophobic; for example, polystyrene, and to a lesser degree, polyethylene and polysulphone. In the case of polymer electrolyte membrane fuel cells, high temperature fluoropolymer charged membranes are used. The IX membranes must not only be highly permselective but must also have low electrical resistance.

IX membranes are either cation-exchange membranes (CEM) or anion-exchange membranes (AEM). CEM are usually made from polystyrene copolymerised with divinylbenezene and suphonated to attach SO_3^{2-} ion-exchange groups [16, 17, 26]. AEM are polystyrene-divinylbenzene polymer-based membranes with quarternary amines as the positive ion-exchange carrier groups. Ion-exchange membranes are used in several membrane processes including ED, electrodeionisation (EDI), fuel cells, electrodialytic water dissociation (water splitting), diffusion dialysis, Donnan dialysis and electrolysis. Donnan exclusion is an important rejection mechanism for charged membranes; for example, charged NF membranes.

Molecular weight cut-off

Molecular weight cut-off (MWCO) has emerged as one of the most useful tools for characterising UF membranes. The early UF membranes were used for purification of biological solutions for retaining macromolecules such as proteins. Since macromolecules are characterised by their molecular weights, the ability of UF membranes to retain these macromolecules is based on their molecular weight. Thus, the term MWCO came into being for characterising UF membranes. It is arbitrarily defined as the molecular weight at which 90% of the macromolecular solute is rejected by the membrane.

The main limitations for defining MWCO precisely are as follows [10, 26]:

1. UF membranes, pore size distribution is not “sharp” as alluded to earlier in the chapter.
2. Most UF membranes, being hydrophobic, adsorb proteins on the surface and inside the pores due to membrane–protein interaction resulting in higher retention

(a) due to reduced pore size, and (b) due to the secondary film formed on the membrane surface. Adsorption is controlled by many factors such as concentration, pH, ionic strength and temperature as discussed later in this chapter.

3. It is difficult to pick the 90% point on the S-shaped retention vs. molecular weight curve.
4. It is difficult to select the marker protein since polymers of the same molar mass have different molecular size, e.g., linear polyacrylic acid passes through a membrane that retains a globular protein of the same molecular mass. In addition, the shape of the protein changes in the vicinity of the membrane surface. Hence, the feed concentration must be kept to a minimum to prevent CP.

The definition is not absolute because the macromolecule to be retained may or may not be spherical. However, it is a useful tool for pre-screening and selecting UF membranes for a particular application. The rules of thumb for good separation are (a) the molecular mass must differ by a factor to ten to separate two solutes of different molecular weights, and (b) the MWCO rating of the membrane must be at least one-half of the solute to be retained. Another factor that affects separation of a macromolecule is its molecular shape. For example, high rejections are achieved for globular proteins as compared to flexible polymers with extended chains, such as polystyrene, polyethylene glycol and dextran. In the case of very dilute solutions of flexible polymers, however, the rejection decreases to zero with pressure due to shear-induced deformation [10, 17].

Bubble point

Bubble point is used to characterise the pore size of MF membranes (the pores of UF membranes are too small to be tested by bubble point) [17, 26]. It is also used to test the integrity of membrane assembly including membrane seals. According to the Capillary Theory, the smaller the diameter of the pore filled with water, the harder it is to blow water out of the pore. The bubble point pressure is a direct measurement of the largest pore in the membrane. Based on the surface tension of the fluid in the membrane pores and the wetting angle of the membrane polymer, the diameter of the pore can be calculated using the Young–Laplace equation:

$$\Delta P = \frac{4\gamma\cos\theta}{d} \tag{1.8}$$

where ΔP is the trans-membrane pressure, γ the surface tension, θ the liquid–solid contact angle and d the pore diameter. For a fluid that wets the membrane completely, $\cos\theta = 1$. The test method is also used to ensure the sterility of injectable drugs in pharmaceutical manufacturing.

1.4 MEMBRANE PROCESSES

Membrane processes have been widely adopted over the last 30 years in spite of inherent limitations such as fouling, thermal and chemical resistance and maximum achievable purity. One reason for their wide success is the emergence of integrated/hybrid membrane processes for several applications, some of which are discussed in Chapter 3. The principal characteristics of membrane processes are listed in Table 1.3. All processes except dialysis, ED and EDI are pressure driven, and all except PV and MD do not involve a phase change.

1.4.1 Reverse osmosis

RO is a process for removing solutes such as dissolved ions from a solution using a semipermeable membrane under hydraulic pressure (see Figure 1.4 and Table 1.3). When a semipermeable membrane is used as a barrier to separate water from a concentrated solution of ions, the water moves through the membrane to the concentrated solution due to osmosis to even out the water concentration or equilibrate. Water continues to flow until sufficient osmotic pressure builds up on the concentrated solution side to prevent further flow of water up the concentration gradient. When pressure greater than the osmotic pressure is applied as illustrated in Figure 1.10, the flow is reversed. The process is called "reverse osmosis" and results in a concentrated salt solution on the feed side of the membrane and a near pure solution on the other side of the membrane; in effect water gets squeezed out and flows out through the membrane under pressure. The effective water flow through the membrane at constant temperature is defined by the following equation:

$$J_w = A(\Delta P - \Delta\pi) \tag{1.9}$$

where J_w is the membrane water flux, A the membrane permeability coefficient for water, ΔP the hydraulic pressure differential across the membrane and $\Delta\pi$ the osmotic

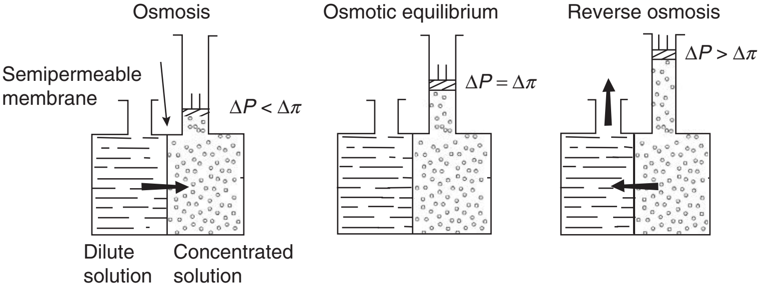


Figure 1.10 Osmotic phenomena. At osmotic equilibrium, the osmotic pressure ($\Delta\pi$) across the membrane is exactly counterbalanced by the hydrostatic pressure (ΔP) applied to the concentrated solution. *Source: [3].*

pressure differential across the membrane. In practice, the membrane is permeable to some low molecular weight solutes (rejection is always less than 100%). Hence, the real osmotic pressure is $\sigma\Delta\pi$ where σ is the reflection coefficient. The value of A is approximately in the range of $3(10^{-3})$–$6(10^{-5})\ \mathrm{m^3/m^2\ h\ bar}$ for RO membranes, and $2(10^{-2})$–$3(10^{-3})\ \mathrm{m^3/m^2\ h\ bar}$ for NF membranes [17]. Osmotic pressure depends on solute concentration, solution temperature and the type of ions present. For dilute solutions (applicable to membrane cases), the osmotic pressure is approximated using the van't Hoff relationship:

$$\pi = \nu_i c_i RT \tag{1.10}$$

where π is the osmotic pressure, ν_i the number of ions formed when the solute dissociates (e.g., ν_i is 2 for NaCl and ν_i is 3 for $BaCl_2$), c_i the molar concentration of the solute, R the gas constant and T the absolute temperature. Thus, $\nu_i c_i$ is the total concentration of ions in $\mathrm{kmol/m^3}$.

The solute (salt) flux through the membrane is given by the following equation:

$$J_s = B(\Delta C_s) \tag{1.11}$$

where J_s is the solute flux, B the solute permeability coefficient and ΔS the solute concentration difference across the membrane. The value of B is in the range of $5(10^{-3})$–$1(10^{-4})\ \mathrm{m^3/m^2\ h}$ for RO membranes with NaCl as the solute. While the water flux increases linearly with pressure difference (Equation 1.9), the solute flux is independent of pressure and is a function of the concentration difference (Equation 1.11). Hence, when the membrane is operating near the osmotic pressure of the feed, the salt passage is not diluted by the product water. During normal operation, when the permeate water flux drops, it follows that the permeate salt concentration will increase.

The effect of operating variables on RO membrane performance is depicted in Figure 1.11. The qualitative graphs "i" through "vi" are summarised as follows [27]: In graph "i" water flux increases with increase in feed pressure at constant π based on Equation (1.9); in graph "ii" product quality increases with feed pressure since water flux increases but solute flux stays constant based on Equation (1.11); in graph "iii" water flux increases with temperature as viscosity drops faster than the rise in π at 25°C (a rule of thumb is that flux increases 3% per °C rise in temperature); in graph "iv" product water quality decreases (higher solute concentration in permeate or lower solute rejection) with rise in temperature due to higher π, and because solute flow has a higher activation energy than water flow; in graph "v" water flux declines as water recovery increases because an increase in solute concentration in the feed/reject stream results in higher π, and also higher CP; and in graph "vi" product water quality decreases with an increase in water recovery due to higher CP, and possibly precipitation of sparingly soluble salts when they exceed their solubility limits. RO process energy requirements and costs are discussed in Chapter 5.

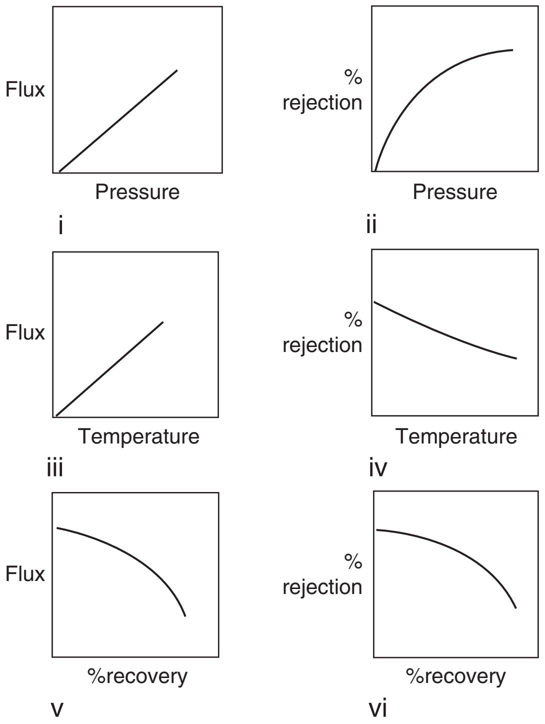


Figure 1.11 The effect of operating variables on RO membrane performance. *Source: [27].*

Homogeneous asymmetric CAs and polyamides made by the phase inversion process and cross-linked TFC polyamides have been the workhorse of RO plants for more than 30 years [21]. Both CA and PA membranes possess an economically viable combination of high rejection and water flux [8]. However, TFC membranes now dominate the RO/NF market with CA membranes a distant second. For example, with the exception of Toyobo CTA polymer, all new seawater RO desalination plants deploy interfacial composite membranes of the fully aromatic type manufactured by Dow, Hydranautics (Nitto Denko), Tri-Sep and Toray. Along with the ability to remain stable over a greater pH range than cellulose-based membranes, TFC membranes exhibit much higher intrinsic water permeabilities because of their extremely thin (~100 nm) polyamide-selective layers [21]. A typical spectrum of TFC membranes for various applications is given in Table 1.8.

The choice of membrane and membrane element is usually determined by the composition of feed water (e.g., fouling potential) and product water quality. Membranes are synthesised with rejection tailored to the type of application; for example, in the case of SWRO membrane rejection is typically >99.6%, whereas in the case of BWRO,

Table 1.8 Typical TFC membranes for various applications

Membrane type	Remarks
Seawater RO membrane[1]	Seawater conversion to industrial water and drinking water Purify high TDS brackish water (>10,000 ppm)
Brackish water RO membrane[2]	Production of high-purity water, concentration of food and heavy metal recovery from well water, river water, lake water, or industrial waste water
Low pressure RO membrane[3]	Lower pressure brackish water membrane Ideal for small drinking water systems due to low energy consumption
Fouling-resistant RO membrane[4]	Improved fouling-resistant characteristics possibly (not revealed) due to a hydrophilic character and a net negative charge. Applicable where fouling tendency is high
Household RO membrane[5]	For removing solutes larger than 10^{-4} μm, carcinogens such as THM, heavy metal ions, bacteria and germs in household water
NF membrane[6]	Water softening; >98% rejection of divalent ions Removal or concentration of dyes, paints and food liquids

Test Conditions:

1. 55 bar g; 32,000 ppm NaCl; 25°C; 6.5–7.0 pH; 10% recovery.
2. 15.5 bar g; 2000 ppm NaCl; 25°C; 6.5–7.0 pH; 15% recovery.
3. 10 bar g; 2000 ppm NaCl; 25°C; 6.5–7.0 pH; 15% recovery.
4. 15.5 bar g; 2000 ppm NaCl; 25°C; 6.5–7.0 pH; 15% recovery.
5. 4 bar g; 250 ppm NaCl; 25°C; 6.5–7.0 pH; 15% recovery.
6. 15.5 bar g; 2000 ppm $MgSO_4$; 25°C; 6.5–7.0 pH; 15% recovery.

Source: CSM membrane catalogue.

membrane rejection is typically <99%. RO membrane rejection efficiency varies depending on the solute [27, 28]:

- Multivalent ions (Ca^{2+}, Mg^{2+}) have a higher rejection than monovalent ions (Na^{+})
- Undissociated, or poorly dissociated substances have lower rejections (e.g., silica).
- Acids and bases are rejected to a lower extent than their salts.
- Rejection of weak acids and bases is highly pH dependent; when ionised, the rejection is high, and low when non-ionised (e.g., boric acid).
- Co-ions affect the rejection of a particular ion (Na^{+} has a higher rejection as Na_2SO_4 than as NaCl).
- Undissociated low-molecular weight organic acids are poorly rejected while their salts are well rejected.
- Trace quantities of univalent ions are generally poorly rejected.
- The average rejection of nitrate is significantly less than that of other monovalent ions.
- Negative rejection is sometimes observed for phenol and benzene with CA membranes.

- Rejection of neutral organic solutes generally increases with the molecular weight or diameter of the solute (e.g., caprolactam rejection is higher than ethanol). Organic components with MW >100 Da are rejected almost completely.

A list of RO applications is given in Table 1.9. Several case studies are discussed in Chapter 3. RO plays a major role in providing potable water, defined as <1000 mg/l total dissolved solids (TDS) by the W.H.O. or <500 mg/l TDS based on U.S. EPA criterion. Desalination of seawater (50–100 bar g; 35,000 mg/l TDS) and brackish water (15–25 bar g; 1000–10,000 ppm TDS) are the largest applications of RO. The highest rejection RO membranes are those that can make potable water from seawater using multi-staged, single-pass RO units.

Boiler feed water is another major application. RO membranes reduce the conductivity to 5–20 μS/cm depending on the TDS of feed water and RO system design, and make it economical to polish RO product water with IX or EDI. Similarly, high-purity

Table 1.9 List of RO applications

Industry	Applications
Desalination	Potable water production Seawater Brackish water
Water reclamation	Municipal wastewater
Ultrapure water	Semiconductor industry
High-purity water	Pharmaceuticals Medical usage Beverages
Utilities; power generation	Boiler feed water
Chemical process industries	Process water reuse Effluent water reuse Water/organic separation Organic liquid mixtures separation
Metals and metal finishing	Mining effluent treatment Plating rinse water Reuse and recovery of metals
Food processing	Dairy processing Sweeteners concentration Juice and beverage processing Light beer and wine production Waste stream processing
Textiles	Dyeing and finishing chemicals recovery Water reuse
Pulp and paper	Effluent disposal and water reuse
Biotechnology/medicine	Fermentation products recovery and purification
Hazardous waster	Removal of environmental pollutants from water

water for nuclear power plants is produced by RO membranes. Increasingly integrated UF-RO or MBR-RO systems are being used to reclaim wastewater at power plants and industrial sites for recycling, and for water pollution control by concentrating waste streams.

High-purity water production for pharmaceuticals, beverage and microelectronics by RO-based membranes are discussed in Chapter 3. In the microelectronics plants, it takes about 4.5 m^3 of high-purity water to wash and rinse a 15 cm wafer during for the fabrication of microchips. A large semiconductor plant can use 5500–7500 m^3/day of ultrapure water, which is produced by a combination of several unit operations; MF, RO, EDI, IX, UV sterilisation, membrane degasification and UF. Similarly, RO process is the key unit operation in the production of USP (United States Pharmacopeia) grade water. Hot water sanitisable TFC membranes are now routinely used in the pharmaceutical, food and beverage industries ensuring RO systems can be sterilised up to 85°C instead of using chemicals.

RO is used extensively in the dairy industry for pre-concentrating milk from 10 to 25 (wt.%) solids prior to evaporation thereby lowering the cost of evaporation, without denaturing the proteins and with minimal wastewater. Other dairy applications include concentration of cheese whey and milk, desalting of salt whey and treatment of waste streams. Whey concentration by RO is limited to 20% total solids (concentration factor = 4 ×) by the solubility limits of lactose as discussed in Chapter 3. RO is used for concentrating sugar solutions, fruit and vegetable juices and beverages for retaining salts and low-molecular weight flavour compounds. However, high osmotic pressure and flavor leakage through the membrane can be a problem.

1.4.2 Nanofiltration

NF is closely related to RO, and is sometimes called “loose RO” (Table 1.3). The basic principles of the RO process discussed above are applicable to NF except that the rejection of solutes depends both on molecular size and Donnan exclusion effects, which are due to the acid groups, e.g., carboxylic or sulphonic acid groups, on the polymer backbone. The equilibrium between the charged membrane and the bulk solution is characterised by an electric potential called the Donnan potential. Ions smaller than the pore size are rejected because of Donnan exclusion [6, 7, 17].

NF membranes are mostly PA TFCs; the rejection is $>95\%$ of divalent ions (Table 2.10). As in the case of RO TFC membranes, the PA rejecting barrier is a fragile film (<0.2 μm thick) on a UF support membrane. The average pore size of NF membranes is 2 nm, which is between the size for RO and UF membranes. The range of operating pressures are also between those for RO and UF; for example, NF operates at lower pressure and at higher flux than brackish water RO: 40–45 lmh at 5 bar g for NF vs. 20–25 lmh at 15 bar g for RO.

The solute rejection characteristics vis-à-vis RO are as follows [17]:

- Monovalent ions (Na, K, Cl, NO_3): >98% for RO, >50% for NF
- Divalent ions (Ca, Mg, SO_4, CO_3): >99% for RO, >95% for NF
- Microsolutes ($MW > 100$ Da): >90% for RO, >50% for NF
- Microsolutes ($MW < 100$ Da): 0–90% for RO, 0–50% for NF
- Bacteria, viruses: >99% for RO, <99% for NF

Depending on the charge of the NF membrane, the rejection of various salts has been characterised as [29]:

- Neutral NF membrane – rejection of salts depends on the molecular size, $Na_2SO_4 > CaCl_2 > NaCl$.
- Anionic NF membrane – positive charges repel cations especially divalent cations such as Mg^{2+} while attracting anions especially SO_4^{2-}. Salt rejection is $CaCl_2 > NaCl > Na_2SO_4$.
- Cationic NF membrane – negative charges repel anions such as SO_4^{2-} while attracting cations especially Ca_{2+}. Salt rejection is $Na_2SO_4 > NaCl > CaCl_2$.

Several advantages of NF over RO and UF are highlighted below [7, 30]:

- Because of its ability to selectively reject low molecular weight organic compounds and divalent compounds, NF is a better alternative to RO and UF for treating wastewater streams, e.g., desalting cheese whey, removing heavy metals and separating dyes and colour compounds in the textile industry.
- Separation of salts with monovalent ions from organics in the MW range of 200–1000 Da. NF is superior because it can simultaneously concentrate high MW compounds and remove monovalent salts.
- In the treatment of bleaching effluents from pulp and paper plants, it is cheaper than RO, which has lower permeate flux and higher energy cost. It is more efficient than UF in rejecting low molecular weight toxic chlorinated compounds.

NF applications include [7]: (a) water softening, (b) selective removal of multivalent ions from brine solutions such as seawater, (c) cleaning up of contaminated groundwater, (d) treatment of effluents containing heavy metals and oils, (e) selective salt rejection and organics removal at offshore oil platforms, (f) pulp and paper waste water treatment to remove colour, (g) electroless copper plating, (h) cheese whey production, (i) yeast production, (j) pharmaceuticals, (k) food processing and (l) removing trace amounts of small organic and carcinogenic molecules from sources of drinking water.

The largest application of NF is in water softening. Besides removing hardness, NF is also used for removing organic colour compounds and trihalomethane (THM) precursors such as humic acids. In Florida, where shallow aquifers have a colour intensity similar to surface waters, and also have a high THM formation potential, NF is the preferred technology; the U.S. EPA has recommended NF for its Disinfectant and Disinfection By-Products Rule (the so-called DBRs) requirements. The membranes are designed for removing TOC and THM precursors with a medium to high salt passage for surface and groundwater applications where good organic removal is required with partial softening in order to maintain a minimum level of hardness for organoleptic properties and preservation of water distribution lines.

1.4.3 Ultrafiltration

UF membrane process can be defined as between NF and MF with pore size range of 0.001–0.05 μm (see Table 1.3). Both UF and MF membranes are porous in nature, but UF membranes always have an asymmetric structure as shown in Figures 1.2 and 1.3 with a much denser skin layer, i.e., smaller pore size and lower surface porosity that produces higher hydrodynamic resistance. The thickness of the top layer is generally less than 1.0 μm. Flux of pure water through a UF/MF membrane is defined by Darcy's law of flow through porous materials as (see also Equation 1.1):

$$J = A(\Delta P) \tag{1.12}$$

where A is the membrane permeability constant and ΔP the trans-membrane pressure. The value of A is a function of membrane porosity, pore size and membrane thickness, and varies from 0.5 m^3/m^2 day bar for dense membranes to 5 m^3/m^2 day bar for more open membranes [17]. In actual process applications, the UF flux varies between 150 $l/m^2/h$ (lmh) for potable water and 5.8 lmh for polyvinyl alcohol [26]. Some estimates of typical cross-flow UF plant capacities are given below:

- Water: 400 m^3/h
- Dextrose: 125 m^3/h
- Whey: 60 m^3/h
- Polyvinyl alcohol: 20 m^3/h

The model most frequently used for describing flow through pores is based on the well-known Hagen–Poiseuille equation for laminar convective flow through straight capillaries with $A \approx \varepsilon r^2$:

$$J = \frac{\varepsilon r^2 \cdot \Delta P}{8\mu\tau \cdot \Delta x} \tag{1.13}$$

where J is the flux in cm/s, ε the porosity, r the pore radius, ΔP the applied pressure, μ the dynamic viscosity, τ the tortuosity factor (=1 for cylindrical pores) and Δx the membrane thickness. There is a fairly good correlation between pore size and water flux based on the reported literature [31]. The direct proportionality between flux and the applied pressure is, however, only true for water. The flux declines drastically with time due to the formation of a gel layer and fouling as shown in Figure 2.34 (see also Equation 1.7):

$$J = \frac{\Delta P}{\eta(R_m + R_c)} \tag{1.14}$$

where J is the flux, ΔP the pressure drop across the membrane and cake, η the fluid viscosity, R_m the membrane resistance and R_c the cake resistance.

The solute flux, J_s, through a pore is equal to the sum of convective and diffusive effects:

$$J_s = K_c V C_s - K_d D \frac{dC_s}{dZ} \tag{1.15}$$

where K_c is the hindrance factor for convective transport, V the filtration velocity, C_s the average solute concentration, K_d the pore hindrance factor for diffusive transport, D the solute diffusivity and Z the pore axial dimension. The rate of solute transport and rejection are adversely affected by non-hydrodynamic interactions between the solute and the pore wall, namely, electrical interactions and solute-solute interactions [16].

Typical performance curves for UF are shown in Figures 1.8 and 1.9. Figure 1.9 shows a plot of flux as a function of log of feed/retentate concentration (see also Figure 2.32).

Figure 1.8 shows flux as a function of pressure; at low trans-membrane pressure (Region I), flux is directly proportional to pressure (Equation 1.12). The magnitude of flux is the same as water when the viscosity is the same. As the pressure is increased beyond a certain threshold value, the flux becomes constant and independent of pressure (Region III). Region II curve reflects the start of CP, which stabilises in Region III due to steady-state conditions, and controls both flux and selectivity. Region II, called the "critical flux" region, is the ideal operating range [15]. However, it is difficult to design equipment to operate in this region [26].

Since microsolutes osmotic pressure is low or negligible, UF operates at very low pressures, typically between 2 and 5 bar g. Further, due to the larger pores in the membrane skin, the UF membranes have an order of magnitude higher flux than RO membranes. UF performance parameters are calculated using the equations given in Section 1.3 and illustrated in Chapter 2.

UF membrane separation depends upon membrane pore size, solute–membrane interactions, shape and size of the macromolecule and CP. For maximum separation efficiency there should be a 10-fold difference in the sizes of the species to be separated. In addition, since all liquid separation membranes have a certain, pore size distribution (e.g., there is a bi-modal distribution in the case of RO membranes predominantly small pores, ≤ 10 Å, and occasional large pores, ≥ 100 Å, that are attributable to the inevitable existence of defects in the skin layer) MWCO of UF membranes should be at least one-half that of the smallest solute to be removed. Characteristics of UF membranes based on pore size are listed in Table 6.12.

UF membranes are manufactured by the phase-inversion process. The most widely used polymer is polysulphone (PS), but other polymers are also used: CA, PES, polyacrylonitrile (PAN) and PVDF (Table 1.4). Typically, CA-based membranes have a higher flux at equivalent rejections than PS membranes. Although CA membranes are less prone to fouling, PS membranes are necessary for many applications because of their higher stability. In the food industry, where steam sterilisation is required, PES is used instead of PS. Among the newer membranes in use are polyimide (PI) polymeric membranes. Polyimide UF membranes are promising because of their resistance to many organic solvents [32] such as hexane, benzene, methanol, acetic acid, acetone, ethyl ether, ethoxy ethanol and chlorinated hydrocarbons.

A list of UF applications is given in Table 1.10. Industrial UF was developed primarily for the treatment of wastewater to remove particulate and macromolecular matter.

Table 1.10 UF and MF applications

Concentration

- Proteins – enzymes, milk proteins, egg white
- Polymer latices – styrene butadiene, polyvinyl acetate, polyvinyl chloride
- Starch and pectin
- Yeast production, mammalian cell harvesting

Recovery

- Electrodeposition paint from wash and rinse baths
- Textile sizing agents – polyvinyl alcohol, carboxymethyl cellulose
- Lignin from Kraft black liquor in pulp and paper processes
- Indigo dyes, printing inks

Clarification/stabilisation

- Fruit juices and wine – removal of haze components
- Beer – removal of cellular debris and bacteria
- Sugar refining – removal of polysaccharides, proteins, colloidal impurities
- Sterile filtration of biologicals – removal of bacteria and viruses

Effluent treatment

- Oily wastewater – from washing operations
- Bleach effluents – pulp and paper industry
- Leather and tanning efflunts

Purification

- Blood fractionation – plasmapheresis, hemofiltration
- Separation – Antibiotics or vaccines from fermentation broths
- Buffer exchange – purification of pharmaceuticals by solvent diafiltration

Water treatment

- High-purity water – final filtration in semiconductor, pharmaceutical and beverage applications
- Potable water – removal of bacteria and viruses
- RO pre-treatment

Source: Zeman and Zydney, Copyright® 1996 from Microfiltration and Ultrafiltration by LJ. Zeman and A.L Zydney. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

Its applications now include water treatment, food processing, biotechnology and chemicals processing. UF is used for removing macromolecules, colloids, colloidal silica, emulsified oil, endotoxins, pyrogens, viruses and bacteria.

UF has been traditionally used for removing high molecular weight organic compounds such as proteins and colloids and oils [18, 31]. Semicontinuous dead-end UF membrane systems were introduced in the mid-1990s for municipal water treatment applications, including treatment of surface water for production of safe drinking water and advanced tertiary treatment of municipal wastewater for recovery and re-use [33–35]. UF membranes remove very small size contaminants, including essentially all of the suspended solids, colloidal particles, and large size microorganisms such as Cryptosporidium and Giardia. High-quality and consistent UF product water feeding RO/NF plants improves the latter membrane performance; higher sustained membrane flux, lower operating pressure, increased product recovery and less frequent membrane cleaning.

Major UF food applications are in the dairy industry [18, 26, 31]. Dairy applications have the largest share of membrane capacity in the world with applications in whey processing – treatment of cheese whey for recovering milk proteins – and cheese-making. Membrane systems are also used for the production of whole and skim milk concentrates and in the manufacture of lactose-reduced milk products.

In the beverage industry it is used to improve product yield and quality. UF systems remove proteins, suspended colloids, polyphenolic compounds, starch, pectin, and microorganisms from natural juice providing a brilliantly clear juice (permeate) that is stable even after extended storage. UF is commonly used for product concentration (i.e., solvent removal) in bioprocessing; concentration of cell-free fermentation broths containing complex biological compounds such as monoclonal antibodies as well as biomolecule/product recovery from very dilute solutions. UF systems are also used for virus removal in the production of therapeutic proteins and vaccines and for antibiotics recovery.

Other major industrial applications include electroplating rinse water processing for paint recovery, treatment of oil/water emulsions, treatment of industrial wastewater containing heavy metals, oil and grease, as well as textile and pulp and paper industries [18, 26, 31]. Electrodeposition is one of the most successful large-scale commercial applications of UF, which is an ideal process for recovering the electropaint and eliminating significant loss of paint with the aid of hollow-fibre membranes.

UF is used to treat wastewater to meet the municipal effluent discharge standards and to recover valuable component for recycle as in the case of oily wastewater. The sources of oily wastewater include metal works, textile industries, automotive, aeronautical and animal/vegetable fats industries and industrial laundromats. Hydrophilic UF membranes (e.g., polyacrylonitrile and PES) are used for recovering oil from oily waste waters instead of hydrophobic membranes (e.g., PVDF) that get fouled with oil resulting in loss of flux. The oil droplets are completely retained by the UF membrane, although the membrane is permeable to free (soluble) oil. UF permeate of highly stable emulsified feed stream can be discharged to a municipal wastewater system. The concentrated recovered oil is less than 5% of the original waste volume. Similarly, tubular UF membranes are used for treating industrial laundry wastewater to recover heavy metals such as lead and chromium to remove oil prior to effluent discharge [18, 26, 31].

UF is also used in high-purity water production for microelectronics and pharmaceuticals as the final polishing step. Double-skinned PES hollow fibre UF membranes provide high particle retention; the membranes have a skin or barrier layer both on the inside and the outside of the fibre. This morphology provides greater structural support reducing possible particle shedding. Further, the two skin layers also ensure sterile conditions by preventing migration of any bacteria (colonised in the porous support layer) downstream. The UF polishing modules operate in a dead-end mode and in or near Region I (see Figure 1.8) because there is virtually no CP.

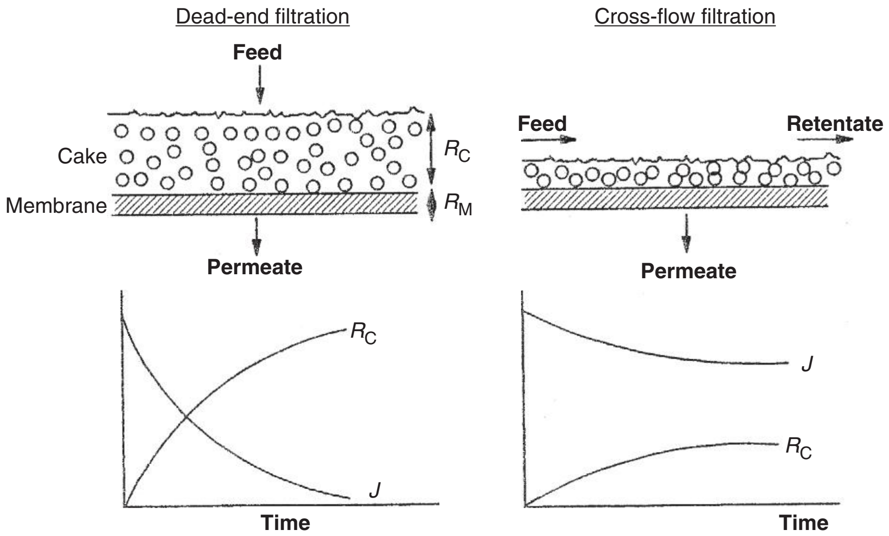
1.4.4 Microfiltration

MF is the oldest membrane process (Table 1.1) and historically operated in dead-end mode in small volume applications, which remains a very important application (Figure 1.4). In dead-end filtration the feed solution flows perpendicular to the membrane surface. Unlike cross-flow (tangential flow) filtration, there is no reject stream, only a feed stream and a permeate stream, as shown in Figure 1.12. The permeate drags all the solids in the feed solution to the membrane surface resulting in adsorption and deposition of solutes on the membrane surface. The pore size of MF membrane is in the range of 0.05–10 μm (Table 1.3). In cross-flow membrane processes (e.g., RO, NF, conventional UF), the feed solution flows tangentially across the membrane surface. The cross-flow or tangential velocity continuously removes particles from the membrane surface by shear forces especially when operating in a turbulent regime. The net effect is reduced cake build-up and less fouling [18, 31].

The basic flux relations and separation principles for UF process discussed above are applicable to cross-flow MF. The polarisation model discussed in Section 1.3 is also applicable to MF except that the diffusivities of larger particle and colloids are an order of magnitude smaller than those for macromolecules separation in UF. However, in the case of symmetric[1] MF membranes, the separation mechanism is not always a simple sieve mechanism where, the particles, whose sizes are smaller than the pore size, flow freely through the pore while the larger particles are rejected. In many cases the particles to be separated are adsorbed onto the surface of the pore, resulting in a significant reduction in the size of the pore. Since particles also deposit on top of the membrane forming a cake-like

---

[1] MF symmetric membrane barrier layer thickness = 10–150 μm; MF asymmetric membrane barrier layer thickness = 1 μm; UF (asymmetric) membrane barrier layer thickness = 0.1–1.0 μm; RO/NF (asymmetric) membrane barrier layer thickness = 0.1–1.0 μm [17].



Difference between dead-end (conventional) filtration and cross-flow filtration. R_C is the resisitance of the cake formed on the membrane by the impermeable solutes, R_M is the resistance of the membrane and J is the flux.

Figure 1.12 Dead-end vs. cross-flow filtration. *Source: Cheryan, Copyright® 1998 from Ultrafiltration and Microfiltration Handbook by M. Cheryan. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.*

secondary filter layer, the particles that are separated by the membrane are often much smaller than the pore size. The flux drops drastically with time due to the formation of a gel layer as shown in Figure 2.34 (see also Equations 1.7 and 1.14).

The choice of the membrane depends on several factors: chemical and thermal resistance to the process conditions, sharp separation, wettability of the membrane, tendency to adsorb hydrophobic materials and resistance to cleaning. The most common polymeric materials are PTFE, PVDF, PP, PS, CA/CN, CTA, PE, polycarbonate, polyester, polyether imide and nylon 6. Of these, only PTFE, PVDF and PP have excellent to good chemical stability. Even though hydrophilic CA/CN and CTA membranes have limited chemical stability, they are best suited for treating high fouling feeds using tubular membranes.

MF membranes are prepared by sintering, track-etching, stretching or by phase inversion. They are usually symmetric unlike UF membranes. MF membranes with well-defined pores are now manufactured in inorganic materials such as alumina and zirconia. α-Alumina-based ceramic membranes are available in multi-tube sheet and monolith honeycomb modules [17, 18, 26]. Ceramic MF membrane modules cost three to four times the polymer membrane modules. Some of this high initial cost is off-set by the lower operating costs because of much longer life of ceramic membranes. Characteristics of some commercial ceramic membranes are given in Table 6.13.

A list of MF applications is given in Table 1.10. MF is primarily used for clarifying liquids, whereas UF is used for fractionating solutions. In bioengineering MF is used for removing microorganisms from fermentation products (e.g., antibiotics) during downstream processing and for recovering penicillin [26, 31, 36]. Examples of downstream processing include clarification of fermentation broths, sterile filtration, cell recycle in continuous fermentation, harvesting mammalian cells, cell washing, mycelia and lysate recovery, enzyme purification and vaccines. In the beverage industry, MF is used to remove yeast from alcoholic beverages and to remove turbidity from fermentation products. In the food industry, it is used to recover bacteria for disinfecting milk and for separating fat from milk [31]. MF can also be used to remove long-chain traces of saturated fat from food oils such as sunflower oil. Membrane filtration reduces algal loading from 400,000 algae cells/ml to less than 50 algae cells/ml.

Commercial municipal water treatment applications are described in detail in Chapter 3. Typical applications include [33–35]:

- Potable water: Large-scale applications for producing potable water by removing *cryptosporidium* and *giardia* cysts with the aid of backwashable MF/UF membranes.
- RO pre-treatment: MF/UF provides excellent pretreatment for RO systems eliminating conventional filtration and clarifiers, especially for seawater RO desalination.
- Tertiary water treatment: MF/UF treatment of secondary treated wastewater followed by RO and ultraviolet radiation or ozonation to produce drinking water.
- Water reclamation: Backwashing enables the MF/UF systems to run on feed water with turbidity up to 500 NTU.
- Oil–water treatment: MF and UF reduce the oil content of water to <5 ppm.

Submerged membrane filtration systems

Submerged MF (sMF) membrane filtration was introduced in the late 1980s for water and wastewater treatment [33]. sMF is a low cost (no membrane pressure vessel), low maintenance process well suited for low pressure UF and MF systems. In the sMF process HF or flat sheet membranes are immersed vertically in a water tank open to atmosphere pressure. Water enters each membrane cell and is drawn through the outside of the membrane to the inside either through gravity, by a filtrate pump or by suction producing filtered permeate [33]. CP is controlled by bubbling air from the bottom of the tank. The membranes are backwashed intermittently using filtrate and air. Periodic chemical cleaning is performed when the maximum TMP is reached. Unlike standard membrane systems, the sMF operates under a slight vacuum. Low operating pressures provide increased membrane life, reduced replacement costs and energy requirements and fouling (particles are not forced into the membrane pores under high pressure). Classification of various UF/MF modules is given in Table 6.14.

Membrane bioreactors

There are two types of MBR technologies: (a) external MBR (eMBR) in which the membrane modules are placed outside the bioreactor (MT only), and (b) submerged MBR (sMBR) where the membrane module is placed inside the bioreactor (FS and HF). The types of membranes used in MBRs are: (i) flat sheet (FS), (ii) hollow fibre (HF) and multitube (MT). Submerged membrane bioreactor (sMBR) technology employing MF/UF membranes is being used increasingly for biological wastewater treatment since its commercialisation around 1990 by Kuboto [37, 38]. Biological wastewater treatment is used to remove all organic and nitrogen containing substances by anaerobic or aerobic conversion. Conventional wastewater treatment is composed of two reactors: an aerated and a non-aerated reactor. In the sMBR process, the biological reactor is integrated with the immersed membrane unit, which is placed in the nitrification area. The air sparged along the membrane surface creates turbulence at the membrane surface, cleaning or scrubbing it. Membrane bioreactors are able to remove more than 95% of the chemical oxygen demand (COD) while the reduction of biological oxygen demand (BOD) is even higher. Polymeric MF membranes with a pore size of 0.1–0.4 μm are the main membranes used in sMBR systems while tubular inorganic membranes are generally used in eMBR units. The eMBR units are preferred to sMBR units when treating concentrated effluents or concentrated biomass to avoid membrane fouling; higher shear rate is achieved with higher recycle flow rate. A key area of process deficiency is fouling by microorganisms as a result of microbial products, concentration and size of particles. In addition, there is concern about whether oxygen can become the limiting factor during aerobic biological activity. The MBR process is discussed in detail in Chapters 2 and 3.

Dead-end cartridge filters

Dead-end filtration has been used most commonly for laboratory and medical filtration. The advantage of dead-end filtration is high product recovery and simple operation. The filter cartridges (depth filters), however, cannot be backwashed or cleaned because of internal pore blockage; instead, they are discarded. In the case of charged cartridges, the separation is based on two mechanisms: pore blockage/surface retention due to size, and surface/pore adsorption due to electrostatic interaction. In the absence of a charge, the pore size rating is nominal (80–90% retention), whereas in the presence of a charge, the pore size rating is absolute. The flux declines with time as discussed earlier. The cartridges are replaced when the pressure drop across the cartridge filter exceeds the pressure drop limit, typically 0.7–1.0 bar.

A newer pleated cartridge filter design with 100% higher surface area is shown in Figure 1.13. The new cartridges have flow rates exceeding 20 l/m per 25 cm length, which is more than double that of traditional pleated cartridges. Given the pore size

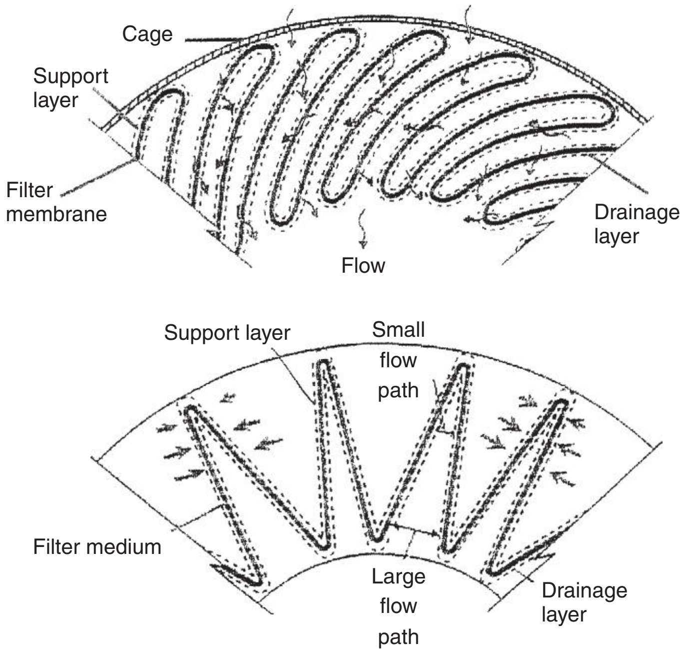


Figure 1.13 Schematic of cartridge membrane filters: Top – deep-pleated filter with increased surface area (Pall Corp.); Bottom – traditional pleated filter with less surface area and non-uniform flow.

range of dead-end MF membranes (0.1–10 μm), low cost and simple operation, it is not uncommon to see microfilter cartridges cover the entire pore size range deployed at different process stages in a high-purity water plant.

1.4.5 Dialysis

Dialysis pertains to the transport of a solute across a membrane by diffusion resulting from a concentration difference (see Figure 1.4 and Table 1.3). Since concentration difference, ΔC is the sole driving force, the difference should be large and the membrane should be thin to reduce the diffusion path [3, 17]. The process is slow compared with pressure-driven membrane processes. Unlike UF or RO where solvent passes through the membrane, it is the solute that passes through the membrane. Separation in dialysis is governed by the small pores and diffusion, and therefore small molecules diffuse faster than large ones. The membrane pores must be very small to prevent convective transport of the solution resulting from a small pressure difference across the membrane. The solute flux across the membrane is given by the relation, $J = U\Delta C$, where U is the sum of resistances: membrane and the two film resistances. In continuous flow systems, ΔC may be taken as the log mean concentration difference across the membrane.

In certain pharmaceutical and animal cell culture applications that require addition and removal of small molecular weight products simultaneously while retaining high molecular weight solutes, sterile dialysis membrane modules have possible applications.

Hemodialysis

Dialysis has the largest market segment of all the membrane processes [2]. The biggest market application of dialysis is in artificial kidneys for hemodialysis to treat patients suffering renal failure, to remove biotoxic metabolites from the blood stream. Hemodialysis is governed by the molecular mass (size) of the uremic toxins to be eliminated relative to the mass of serum proteins. The process is described as follows: "Blood is drawn from the patient and passed through the lumen of the hollow fibres, while water is passed through the shell side of the unit. Since water is loaded with salts, it has the same osmotic pressure as blood cells as there would be in a pressure-driven process. Urea diffuses from the blood into the water, and is removed quite selectively but is mixed again with salts. The urea-loaded salt solution is disposed of as "waste" [3]. Since the process is very gentle, there is less damage to blood cells than there would be in a pressure-driven process. The human kidney processes about 1000 l of aqueous solution every week. A typical patient suffering from chronic kidney failure requires 150 treatments per year.

Hemodialysis units are usually hollow-fibre devices with a membrane area of 0.5–1.5 m^2. The classical membrane material is regenerated cellulose, closest to the natural material. Other membranes include polyether sulphone (PES) and polysulphone (PS), which are made somewhat hydrophilic by blending with PVP, a necessary requirement to address the problems of biocompatibility and fouling by proteins [39]. The membranes are asymmetric (10–100 μm thick) with a narrow pore size distribution and the pore diameter less than 10 nm [17].

Diffusion dialysis

Diffusion dialysis (DD) is an ion-exchange membrane-separation process driven by a concentration gradient across the membrane, i.e., ion transport is driven by the concentration gradient with Donnan criteria of co-ion rejection and preservation of electrical neutrality [17, 40]. Since it is a spontaneous process, DD results in an increase in entropy and a decrease in Gibbs free energy; hence it is thermodynamically favorable.

A DD unit consists of a multi-cell stack containing anion-exchange (AEX) membranes or cation-exchange (CEX) membranes. The membrane thickness is 100–500 μm. Typically, the membranes are polystyrene cross-linked with divinyl benzene containing anion or cation-exchange groups. For example, in the case of acid recovery, protons and anions penetrate the AEX membranes while the salt cations are rejected. The net result is the more than 90% removal of acids from a mixture of salts.

The energy consumption in DD is very low as compared to other membrane processes. It is a simple, economical, and energy efficient process wherein the feed and permeate are pumped counter-currently as in most dialysis types of processes. No external driving force such as pressure difference or electrical potential difference is required. The only power required is by the metering pumps on the stack outlet side. Since DD relies on concentration difference and there is no external force driving the separation, the process is very slow, systems have low capacities and require large membrane areas for separation. However, this is not a drawback for specific applications; a 6-stack DD system with a capacity of 6 m^3/day is sufficient for regenerating a 24 m^3/day deionised water ion-exchange system.

The process is used extensively in the metals industry for recovering acids and metals. Hydrofluoric acid and nitric acid are used as etching agents for stainless steel. In order to recover the acid, DD is used since the protons pass through the membrane but Fe^{3+} ions cannot [17]. Other applications include recovery of acids from ion-exchange regeneration processes and in metal refining. It is also applied for the separation and recovery of acid/alkali waste solutions and purifying/separating alkalis. It is used to remove electrolytes from colloidal suspensions to render the latter more stable, e.g., it is used to recover NaOH from certain industrial wastes that are contaminated with organic substances. The Na^+ and OH^- ions pass through the permeable membrane cell walls into the surrounding water, which is next evaporated to recover sodium hydroxide while the organic waste in the cells is disposed of.

1.4.6 Electrodialysis

The dialysis principle is used for desalting liquids using ED (see Figure 1.4 and Table 1.3). Essentially, ED employs charged membranes and uses electrical energy to flow the ions against concentration gradient causing separation and purification. Under the driving force of a direct-current (DC) electric potential that is applied perpendicular to the flow, cations (positive ions) travel toward the cathode and the anions (negative ions) travel toward the anode as shown in Figure 1.14. The net result is the water within the cell is demineralised. The flow of ions occurs on the basis of electrochemistry – electrochemistry deals with the relationships between electrical and chemical phenomena.

ED is a low-pressure process that uses ion-selective membranes to desalinate water. ED employs flat-sheet synthetic ion-exchange membranes and uses electrical energy to flow the ions against concentration gradient causing separation and purification. The cation permeable membrane has a fixed negative charge (its fixed exchange sites are anionic). The cations in solution enter the membrane when a voltage is applied to the system. They do not exchange with cations in the membrane because the electrical forces for ion motion are greater than the attractive forces between the cation and the membrane. Since the membrane structure is negatively charged, it repels anions. The opposite is true for the anion-permeable membrane. The cations can pass thorough the cation permeable membrane but they cannot permeate the anion-permeable membrane. Conversely, the

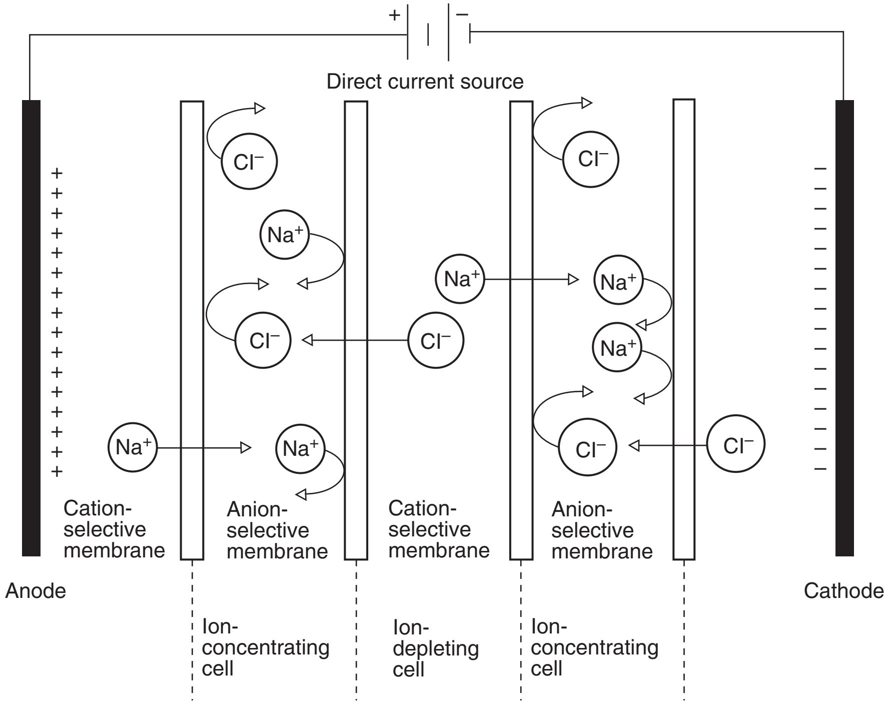


Figure 1.14 An electrodialysis cell.

anions cannot permeate the cation-permeable membranes. In addition to high permselectivity, the membrane must have low resistance. This means it is conductive to counter ions and does not unduly restrict passage [41, 42].

Ion-exchange membranes are highly swollen gels containing polymers with a fixed ionic charge [16]. In the interstices of the polymer are mobile counter ions. Membranes must be mechanically strong and robust. They must not swell or shrink appreciably as ionic strength changes, and they must not wrinkle or deform under thermal stress. The polymers are usually hydrophobic and insoluble. Polystyrene is the major polymer used, with polyethylene and polysulphone finding limited application. Cation-exchange membranes are polystyrene copolymerised with divinylbenzene, and then sulphonated. Anion-exchange membranes have quaternary ammonium groups fixed in a polystyrene-divinylbenzene polymer carrier.

ED modules consist of a large number of thin, continuous flow cells to make the process efficient for large-scale usage; the membrane stack is composed of hundreds of parallel cells where the ions are depleted and concentrated in alternate cells. Depending on water temperature, solids content, flow rate and applied voltage, one ED membrane stack produces about 30–60% desalination. To achieve a practical level of 75–95% or higher salt removal, the membrane stacks are staged, e.g., two stages for 75% salt removal, four stages for 94% salt removal and six stages for 98% removal. The water recovery can be up to 95%. A flow schematic of an ED stack is shown in Figure 2.35.

ED is susceptible to fouling and scaling like other membrane processes. Fouling and scaling increase stack resistance and power requirements. The fouling/scaling problem is overcome by using an ED reversal (EDR) process in which the applied DC polarity is reversed every 15–20 min. This prevents insoluble compounds from depositing on the membrane surface. Polarity reversal also reduces or eliminates the need for adding acid and anti-scalants to the feed water. Further, periodically or continuously rinsing the electrodes removes gases formed at the electrodes. ED does not remove non-ionised compounds such as silica, and most colloids. Hence, unlike in the case of RO, silica does not foul ED membranes.

Stack current can be predicted by the theoretical relationships of Faradays's and Ohm's laws:

A Farad, F, is the amount of electric energy required to transfer 1 g equivalent of salt from one electrode to another: $F = 96{,}500\ \mathrm{A\ s} = 26.8\ \mathrm{A\ h}$.

For ED, Faraday's law can be written as:

$$I = \frac{F Q_{\mathrm{p}} N}{e N_{\mathrm{cp}}} \tag{1.16}$$

where I is direct current, A; N is the change in normality of dilute stream between inlet and outlet; F is Faraday's constant; Q_{p} is flow of dilute stream; e is current efficiency; and N_{cp} is number of cell pairs. The power, W, required for an ED stack is found from Ohm's law:

$$W = V \cdot I = I^2 R\,(V = I \cdot R) \tag{1.17}$$

where V is stack voltage and I is direct current; R is stack resistance. R is the combined resistance of the membranes and the water filling the spacer flow paths. The current required is proportional to the reduction in salt content for a given flow rate. The required current includes losses for current leakage through the stack manifold and water transfer through the membrane.

The power consumption is directly proportional to the salt concentration of the feed water varying between 1.1 kW h/m^3 for 1000 mg/l feed water to 2.6–4.0 kW h/m^3 for 5000 mg/l feed water. About 25–33% of power is used to drive the feed circulation pumps [26].

Other process variables that affect ED performance include polarisation, current density and stack voltage.

Polarisation occurs when the ion transport through the membrane exceeds the arrival of replacement ions at the membrane surface. This can be due to:

- Changes in pH in the solution
- Loss of current efficiency
- Increase in resistance
- Ionisation of the water with H^+ and OH^- causing severe stack malfunction

Current density (mA/cm^2): In theory, the higher the current density, the smaller the membrane required and the lower the capital cost.

Stack voltage (V): The required voltage depends on the resistance of the stack and on current density. Voltage is varied manually based on the required current density.

Since the first ED plants were produced in the early 1950s, several thousand brackish water plants have been installed around the world. ED is used mainly for desalting brackish waters constituting about 10% of world's capacity. The remaining 90% is RO. It is not used for desalting high salinity waters such as seawater because of high energy consumption, which increases with salt content as discussed above; ED energy consumption is 10–25 kW h/m^3 vs. 3–5 kW h/m^3 for RO. Several examples of ED applications and ED systems are discussed in Chapters 3 and 5.

A special application of ED is the concentration of NaCl from seawater for the production of table salt [41, 42]. This application is confined to Japan, South Korea and Taiwan. These ED plants concentrate the salt content from 35,000 mg/l in seawater to 150,000–200,000 mg/l prior to evaporation and crystallisation. ED as a pre-concentration step leads to substantial savings in energy costs. Large plants with a capacity of 20,000 to more than 200,000 tons of salt per year are in operation in Japan. A TSX-200 ED unit contains 3500 cell pairs in a stack. The cell pair area is 2 m^2 and the cell thickness is 0.4 mm. The production capacity is ~30,000 tons NaCl per year. The power consumption of the electrodialyser is 155 kW h/ton NaCl.

Seawater contains relatively high concentrations of sulphate, calcium, magnesium and other multivalent ions that can precipitate in the concentrated salt compartments of the plant causing severe scaling. This problem has been solved by applying a thin electrolyte layer of opposite charge to IX membrane on the surface facing the seawater solution [42]. Since the Donnan exclusion effect is much stronger for multivalent ions than univalent ions, the polyelectrolyte layer rejects multivalent ions but allows the univalent ions to pass relatively unhindered.

Besides brackish water desalination, ED is used extensively for deashing whey, and the desalted product is a useful baby food additive. It is used in separating electrolytes from non-electrolytes. ED is also used to remove specific pollutants such as heavy metals, nitrates and radium from contaminated waters.

1.4.7 Gas separation

Membrane GS has evolved rapidly in the last 25 years. Gas diffusion through non-porous membranes occurs due to a concentration gradient or for gases it is directly proportional to pressure. Hence, membrane GS is often described as a pressure-driven diffusion process. Separation is achieved because of differences in the relative transport rates of the feed components (Table 1.3). A membrane will separate gases only if one or more components pass through the membrane more rapidly than others. GS membranes are unique in that they are able to separate two or more gases (fluids) unlike liquid separation membranes which separate dissolved and suspended solids from the fluid [43, 44]. The basic mechanisms of porous and non-porous membranes are delineated as follows:

Porous membranes

- Convective flow through large pores (>1000 Å) and there is no separation.
- Knudsen diffusion through pores (100–1000 Å) – pores with diameter less than the mean-free path of the gas molecules allow lighter molecules to preferentially diffuse through pores.
- Molecular sieving or surface diffusion (5–100 Å) – large molecules are excluded from the pores because of their size.

Non-porous membranes

- Solution diffusion – gas dissolves in the membrane material and diffuses across it.

The membranes used in most commercial applications are non-porous in structure where separation is based on the SD mechanism. This mechanism involves molecular-scale interactions of the permeating gas with the membrane polymer. The model assumes that each component is sorbed by the membrane at one interface, transported by diffusion across the membrane through the voids between the polymeric chains (the so-called "free volume") and desorbed at the other interface. According to the SD model, the flux of gas through a membrane is given by

$$J = \frac{P \cdot \left(p_{\mathrm{f}} - p_{\mathrm{p}}\right)}{t} \tag{1.18}$$

where P is gas permeability, p_{f} and p_{p} are the partial pressures of the gas on the feed side and the permeate side, respectively, and t is the thickness of the membrane. For commercial membranes, t is ≤ 0.2 μm. P is a property of the membrane material and is independent of membrane thickness. Permeability (P) = gas solubility (S) in the polymer × diffusivity of the gas (D) in the polymer. Solubility is thermodynamic in nature and is affected by polymer–penetrant interactions as well as excess inter-chain gaps in glassy polymers. The diffusion coefficient is kinetic in nature, and is determined by the polymer–penetrant dynamics.

Gases can have high permeation rates due to high solubilities, high diffusivities or both. Generally speaking, the diffusion coefficient becomes smaller whereas the solubility increases with an increase in the molecular size of the gas. On the basis of their relative permeabilites through the membranes, gases have been classified as "fast" or "slow" [43]:

$$\underset{\text{Fast}}{H_2O,\ H_2,\ He,\ H_2S,\ CO_2}\quad O_2\quad \underset{\text{Slow}}{Ar,\ CO,\ N_2,\ CH_4}$$

Thus, gases with higher permeabilites enrich on the permeate side of the membrane, while gases with lower permeabilities enrich on the feed/reject side of the membrane.

Virtually every polymeric GS membrane is either entirely glassy or primarily glassy with a minor crystalline component since they are more size and shape selective than rubbery polymers [43]. A rubbery polymer is an amorphous polymeric material that is above its softening or glass transition temperature, T_g, under the conditions of use as discussed earlier in the chapter. Gas molecules permeate through a rubbery polymer quickly because the binding force between molecular segments of the polymer is not strong, and segments can move relatively easily to open a channel through which even large molecules can pass. Further, solubility often dominates diffusion characteristics for transport in rubbery polymers. Thus, volatile organic compounds (VOCs), which have a strong affinity (high solubility) for polymeric materials, permeate through a rubbery polymeric membrane much faster than the much smaller oxygen and nitrogen. Membranes prepared from rubbery polymers such as polydimethylsiloxane (PDMS) and composite PEI/silicone rubber membranes are, therefore, effective in removing VOCs from air [45]. The permeability of rubbery membranes is 1000 times higher than the permeability of glassy membranes.

A glassy polymer is an amorphous polymeric material that is below its softening or glass transition temperature, T_g, under the conditions of use. Because the chain segmental motions in glassy polymers are restricted as compared to rubbery polymers, glassy polymers are able to discriminate between extremely small differences in molecular dimensions of common gases (0.2–0.5 Å). Unlike rubbery polymers, transport in glassy polymers is not governed by solubility but by the size of the molecule and diffusion coefficient. Thus, since hydrogen molecules have the smallest size (high diffusion coefficient), membranes prepared from glassy polymers are used effectively for hydrogen separation. Similarly, in CO_2/CH_4 separation, carbon dioxide permeates through glassy membranes much faster than methane, partly because a CO_2 molecule is slightly smaller than a CH_4 molecule, and partly due to the stronger affinity of the polymeric materials to CO_2.

Typical examples of glassy polymeric membranes in commercial use are CA, PS and PES. Aromatic PS is among the most successful GS membrane polymers. However, rigid polymers, such as polyetherimide (PEI) and polyimide (PI), with higher T_g and greater resistance to organic solvents are required. Polyimide membrane is highly chemically durable and is also thermal resistant [32]. Therefore, it is possible to eliminate special pre-treatment steps such as scrubbing, adsorption, absorption and cooling. Polyimides can withstand temperatures up to 300°C. Because of the limitations of materials used in modules, however, 150°C is the upper limit of operating temperature. Higher temperature translates into fewer modules since the permeation rate of gases increases with the operating temperature. PI membranes are also highly resistant to widely used solvents such as methanol, ether, benzene, toluene, xylene and gasoline. Perhaps the most important property is that PI membranes have a higher selectivity at a comparable permeability than other membranes for gas separations involving He/CH_4, CO_2/CH_4, H_2/CH_4 and O_2/N_2 [32, 43]. This is a major improvement given that, in general, membranes with higher permeability coefficients possess lower selectivity.

PI membranes are used to separate hydrogen, helium and carbon dioxide from various gases. Of these, H_2 separation/recovery is the largest market for PI membranes. One important application is in the separation of CH_4 from N_2. In most polymers used for GS membranes, the permeability of CH_4 is greater than that of N_2. However, in the case of aromatic PI, the reverse is true. Although the solubility of CH_4 in PI is higher than in other polymers, N_2 has a substantially higher diffusivity in PI than in other polymers.

Advanced organic and inorganic membranes and materials include polymers of intrinsic microporosity (PIMs), microporous PVDF, perovskite and palladium alloy membranes [45]. PIM membranes have displayed both high permeability with high selectivity for various gas mixtures. Major commercial and promising applications of membrane GS are delineated below [43–45]:

- *Nitrogen production (90–99.5% purity).* This is likely to be one of the largest applications of GS membranes. The main applications include nitrogen blanketing of tanks and vessels, purging of process vessels and pipelines before shut downs for safety uses in the chemical process industry and controlled atmosphere storage of fresh produce. The latter requires dry nitrogen for the preservation of perishable food. Membranes preferentially permeate oxygen, carbon dioxide and water leaving a non-permeate (reject) stream enriched in dry nitrogen, which is used to maintain an inert atmosphere during storage and transportation of fresh produce.
- *Hydrogen recovery.* Hydrogen is an expensive chemical feedstock. Hence, recovery of hydrogen from mixtures of hydrocarbon gases increases process efficiency and reduces operating costs. Hydrogen is recovered from naphtha during the synthesis of substitute natural gas (SNG), and from the purge gas from an ammonia synthesis reactor. The purge gas in ammonia synthesis contains nitrogen, argon and helium. Unless recovered, it is purged with inert gases or used only for its fuel value. Installation of GS polysulphone hollow fibre membranes in a high-pressure purge gas loop in ammonia plants to recover H_2 was the first major commercial breakthrough for gas membrane technology. Other commercial applications include recovery from tail gases from catalytic reforming, hydrocracking and hydrodesulphurisation. Membrane GS has an edge over other technologies used in hydrogen recovery; cryogenic distillation is energy and cost intensive, and pressure swing adsorption is complex.
- *Synthesis gas ratio adjustment.* Synthesis gas is a mixture of hydrogen and carbon monoxide. It is generally produced from natural gas by steam reforming or by partial oxidation/steam reforming. It is the feedstock for manufacturing various chemicals including acetic acid, methanol, ethylene glycol, acetic anhydride, acetaldehyde, ethanol and oxoalcohols. As produced, the H_2/CO ratio is >2.0, whereas a ratio of between 1 and 2 is required for the production of the above chemicals. Membranes

such as PI and PS are used to adjust the H_2/CO ratio by virtue of the higher diffusion rate of hydrogen.

- *Carbon dioxide removal.* Separation of carbon dioxide from nitrogen and low-molecular weight hydrocarbons is a multi-stage process because of the low selectivities. Several applications have achieved commercial success including the removal of CO_2 from natural gas and from biogas, and in enhanced oil recovery. In the treatment of natural gas, membranes are used to remove impurities such as CO_2, H_2S and moisture to produce pipeline grade gas. Similarly, in the treatment of biogas (produced from anaerobic digestion of sewage, municipal waste, agricultural waste and landfills), these "fast" gases permeate rapidly across the membrane yielding methane-rich retentate.
- *Dehydration.* The applications include the production of dry nitrogen and moisture-free natural gas and methane from biogas.
- *Helium recovery*. Helium is abundant in natural gas resources. Because of its low boiling point and inert character it is used in many manufacturing facilities. Spiral wound and hollow fibre membranes have been commercialised for helium recovery from natural gas and for purification of crude helium contaminated with air.
- *Removal of VOCs.* Removal of various organic and other relatively high boiling species from vent gas streams is considered to be one of the largest growth areas of GS membranes. Membrane GS have found a definite niche in this application where they are able to remove much larger organic molecules compared to gases such as nitrogen, which usually make the bulk of vent streams. Even though the diffusion coefficients of organic molecules are smaller than those of permanent gases, they have a high permeability rate due to their much higher solubilities in siloxane-based rubbery polymers such as PDMS and composite PEI/silicone rubber membranes.

1.4.8 Pervaporation

PV combines the evaporation of volatile components with their permeation through a membrane. It involves the use of a liquid feed to produce a vapour permeate and a liquid reject. The feed is usually supplied at above 100°C and at a pressure slightly above 1 bar. The permeate pressure is maintained at vacuum well below atmospheric. Vapourisation occurs as the permeating species pass through the membranes. Mostly asymmetric composite hydrophilic membranes such as composite poly vinyl alcohol (PVA)/PS (or polyacrylonitrile) are used [43, 44]. Membranes made from a thin layer of PDMS cast on PAN have been found to be useful in separating polar compounds from non-polar ones in dealcoholisation of liquors. Flat sheet and spiral wound modules are commonly used.

The major applications of PV include the removal of small amounts of water from organic solutions (e.g., drying of iso-propanol/water, butanol/water and ethanol/water azeotropes to produce a relatively pure organic chemical), drying of organic liquids by removing low concentrations of water (a few %) from nearly pure organics and the removal of small amounts of organics from water (e.g., in wastewater cleanup). Ethanol purity levels of 99.85% are attained in separating ethanol/water mixtures using a distillation/PV hybrid process (see Chapter 3). It has been used to remove alcohols from fermentation broths where continuous removal of ethanol is required so as to not inhibit the production activity of microorganisms. Similarly, PV units are used for recovering isopropanol from water with a purity of 99% alcohol starting with a feed containing 94% alcohol and 6% water. Water formed during the esterification reaction must be removed for reusing the alcohol.

The sales of PV systems are very small because of unfavorable economics: (a) reheating of permeate between stages is required to sustain a meaningful flux, and (b) large membrane surface area is required due to a low driving force with pressure drops limited to 1 bar.

1.4.9 Membrane contactors

Membrane contactor (MC) is a phase-contacting device for use in gas absorption and stripping (degassing) processes as well as in biomedical gas transfer processes [44, 46]. The function of the membrane is to facilitate diffusive mass transfer between contacting phases such as liquid–liquid, gas–liquid and gas–gas. The membrane phase contactor uses polyolefins, e.g., polypropylene (PP) microporous hollow fibres membranes, which are packed densely in a high surface area module. Since membranes are hydrophobic and have small pores (0.05–0.1 μm), water does not pass through the membrane pores easily. The pressure required to force water to enter the pore is called the “breakthrough pressure,” which for a PP membrane with a pore size of 0.05 μm is greater than 10 bar g.

A MC module contains thousands of microporous hollow fibres, which are knitted into a fabric that is wound around a distribution tube with a central baffle as shown in Figure 1.15. The baffle ensures the water is distributed across the fibres, and also results in reduced pressure drop across the contactor. The hollow fibres are packed densely in a membrane module with a surface area of up to 4000 m^2/m^3. The liquid flows outside (shell side) the membrane, while vacuum is applied on the inside of the fibre (tube side) forming a film across the pores of the membrane. Mass transfer takes place through this film and the pores due to the difference in the gas partial pressure between the shell side and tube side. Since the membranes are hydrophobic, they are not wetted by water, thereby, effectively blocking the flow of water through the membrane pores. The membrane provides no selectivity. Rather its purpose is to keep the gas phase and the liquid phase separated. In effect, the membrane acts as an inert support that allows intimate contact between gas and liquid phases without dispersion. Vacuum on the tube side of the membrane increases the mass transfer rate as in a vacuum tower. The efficiency of the process is enhanced with the aid of nitrogen sweep gas flowing on the permeate side of the membrane.

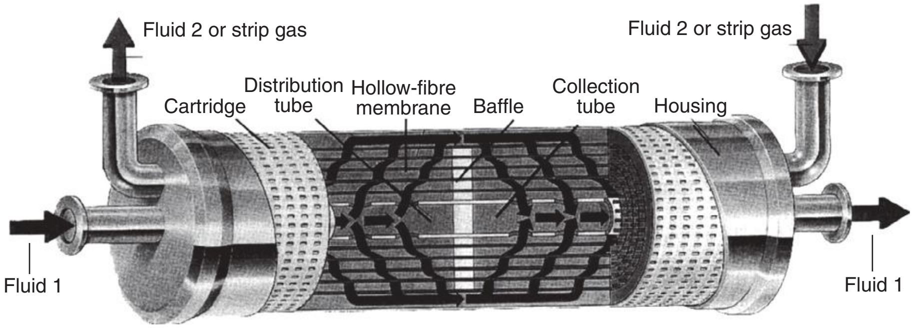


Figure 1.15 A Liqui-cel$^{®}$ membrane contactor module.

MCs are used commercially for stripping dissolved oxygen from ultrahigh purity water for semiconductors manufacture (see Figure 2.12). MCs have also been commercialised in the beverage industry for carbonation (adding CO_2). More than 1000 MC units are in operation worldwide with most being used for gas stripping. Blood oxygenation is the earliest application of MC. A large number of microporous hollow fibre oxygenators are in use in hospitals. One interesting potential application is in aerobic fermentation processes, which require O_2 for the cells in the fermentation broth, and simultaneously require the removal of CO_2 formed during fermentation [46].

1.4.10 Other membrane technologies

Membrane distillation

MD is an extension of MC for applications requiring concentration of aqueous solutions with non-volatile solutes such as salts and sugars, e.g., water desalination. It is a non-isothermal process that involves features of membrane technology including polarisation and fouling. Two liquids at different temperatures are separated by a hydrophobic (non-wetting) PVDF membrane (pore size ~0.2–0.4 μm). The feed is heated typically to about 100°C and the downstream side is cooled with distilled water. The temperature gradient across the membrane generates a vapour pressure difference that results in vapour molecules permeating through the microporous membrane from the high vapour pressure side to the low vapour pressure side. Separation occurs by the vapourisation at the openings of the pores and followed by vapour transport through the membrane pore network [17, 47]. The water vapour flux is proportional to the vapour pressure difference between the warm feed and the cold permeate. Because of the exponential rise in vapour pressure with temperature, the flux increases dramatically as the temperature difference across the membrane is increased. Dissolved salts in the feed solution decrease the vapour pressure driving force, but this effect is small unless the salt concentration is very high.

MD is an attractive process for treating high salinity waters such as seawater and RO reject brine concentrates because it is not constrained by high osmotic pressure.

However, the performance is adversely affected by fouling, pore wetting, mass transfer inefficiency due to entrapment of air within the membrane pores, poor heat transfer, heat losses and high energy consumption [47]. Under the best case scenario the energy consumption is 15 kW h/m^3, which is very high vis-à-vis seawater RO desalination [48].

Membrane reactors

Molecular separation along with simultaneous chemical transformation has been made possible with membrane reactors [17]. The selective removal of reaction products increases conversion of product-inhibited or thermodynamically unfavourable reactions; for example, in the production of ethanol from corn [31]. Enzyme-based membrane reactors were first conceived 25 years ago by UF pioneer Alan Michaels [49]. Membrane biocatalytic reactors are used for hydrolytic conversion of natural polymeric materials such as starch, cellulose, proteins and for the resolution of optically active components in the pharmaceutical, agrochemical, food and chemical industries. Membrane bioreactors for water treatment were introduced earlier in this chapter and are discussed in detail in Chapters 2 and 3.

Catalytic membrane reactors have been realised with the development of high-temperature operation membranes. Reactions in catalytic membrane reactors include dehydrogenation, hydrogenation and oxidation [17]. However, a number of practical limitations have hindered commercial applications: low separation factor, leakage at higher temperatures, poisoning of catalyst and mass transfer limitations. Membrane reactors can produce hydrogen for fuel cell power plants from methanol or natural gas by steam reforming more efficiently, and with a higher quality as compared to conventional technologies [30]; the membrane reactor produces hydrogen while effectively removing hydrogen during conversion using solid oxide membranes.

Dynamically formed membranes

Dynamically formed membranes (DFM) were developed at Oak Ridge National Laboratory in the 1960s for water desalination, but have been more effectively used to remove dyes from textile manufacturing process effluent. These membranes are formed by flowing materials such as zirconia colloid and zirconia polyacrylic complex in low concentrations (1000 mg/l) over porous carbon or sintered stainless steel tubes. The performance of the membrane depends mainly on the characteristics of the membrane-forming material; permeate flux and membrane retention are strongly dependent on the particle shape and size distribution. Membrane supports with pore sizes varying from 1 to 10 μm are typically used. If the membrane becomes damaged or clogged, it is removed or regenerated; hence, the term "dynamic membrane" [50]. Other applications of DFM include lime softening treatment, toxic heavy metals removal, clarification of turbid waters and for treating rinse water from semiconductor manufacturing plants.

A variation of the DFM is the supported-liquid membrane used in rejuvenating or regenerating RO membranes. Because the ultra-thin skin layer of RO membranes is fragile, it degrades with time by the use of strong chemical cleaning agents, abrasion, enzyme activity, aging or manufacturing defects. This degrades membrane performance with a noticeable loss of salt rejection. Surface regeneration involves *in situ* application of water dispersible synthetic polymers, natural gums and resins, surface active agents and bentonite clays. Typically, additives are added in very low concentrations (<100 ppm), and the mixture is recirculated until the salt rejection is restored. The process has been described by Kesting [16] as follows: "Certain surface active feed additives are capable of forming membranes not by intrusion into a porous support but by concentrating themselves at the interface between a liquid solution and a dense membrane in the solid state which they cannot permeate."

The performance of polyamide RO membranes damaged by chlorine was virtually restored by adding polymers and/or surfactants in very low concentrations (25–75 ppm) to the feed; the rejection increased from <50% to >95% in 83% of the cases, and to >97% in 38% of the cases [51, 52]. Test results are shown in Figure 1.16. Besides restoring salt rejection, tannic acid and a water dispersible polyester maintained stable performance in a continuous week-long pilot run. One possible reason why tannic acid, a proven regenerating agent, was the most effective is that it is a very good dispersant on low-energy surfaces such as graphite and synthetic polymers.

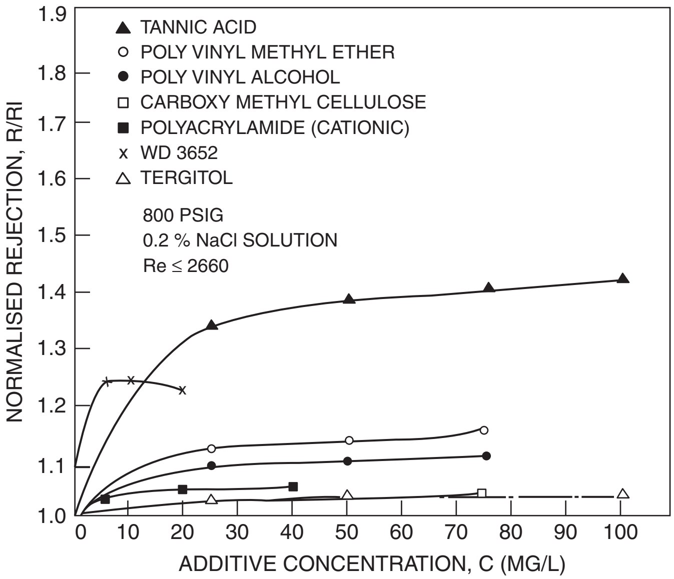


Figure 1.16 The effect of additives on normalised salt rejection of chlorine-damaged PA-300 polyamide membranes.

Regeneration requires that a relatively stable liquid membrane be created, i.e., show near-term permanency of more than 200 h. This is possible if the additives have the following properties:

- are good dispersants on low-energy surfaces such as synthetic polymers (tannic acid and lecithin (a lipid) are such materials);
- have polar and non-polar groups well-spaced or, preferably, on opposite sides of the backbone; then hydrophobic groups can strongly adsorb to the membrane without being masked by the hydrophilic groups. Water dispersible polyesters were found to be very stable;
- have the capability to strongly adsorb either through physical adsorption or through electrostatic interaction. For example, positively charged quaternary ammonium chloride is highly effective in regenerating CA membranes;
- can hydrogen bond inter-molecularly to the membrane material. Strong solute-membrane interactions are exhibited in systems with distinct hydrogen bonding;
- capabilities of the additive with functional sites of membrane matrix.

Electrofiltration

Electrochemical effects can play a major role in increasing the performance of conventional MF and UF processes. According to the conventional Film Theory Model, the polarised layer is described as arising due to the convective transport of particles to the membrane surface and their diffusive back-transport into the bulk solution as shown in Figure 1.7. Charged particles experience an extra force, electrostatic repulsion, as they are brought closer together in the polarised layer. In the case of charged particles, therefore, flux augmentation due to electrostatic effects can be very significant for particles <100 nm in size. The main types of electrofiltration processes are summarised in Table 1.11 [53]. Results of tests conducted with several MF membranes and colloidal solutions are summarised below [54]:

- Flux levels are an order of magnitude higher than in the absence of imposed force fields.
- Both electric and ultrasonic fields reduce membrane fouling caused by the deposition of colloidal material over a range of operating conditions.
- The rate of fouling is affected by electric field strength and frequency, concentration of colloids, particle size, particle shape and the surface properties of the dispersed phase.
- Electric fields improve filtration by electrophoresis and other secondary electrokinetic effects like electro-osmosis. Flux is enhanced with ultrasonic fields largely as a result of cavitation.
- Synergistic effects were observed when electric and acoustic fields were applied simultaneously. The coupling mechanism is believed to be due to a combination of effects induced by cavitation and electro-kinetic phenomena.

Table 1.11 Electrically enhanced membrane filtration

Process	Electric field	Membrane	Remarks
Electrofiltration	Continuous	Polymeric, inorganic	Reduced concentration polarisation and fouling, improved selectivity[a]
Pulsed electrophoretic cleaning	Pulsed	Polymeric, inorganic	Reduced fouling, low power consumption, minimal changes in feed attributable to electrolysis
Electrolytic membrane cleaning	Pulsed	Electrically conducting	Reduced fouling, low power consumption; works in all conductivity ranges
Electrolytic membrane restoration	Pulsed	Polymeric, inorganic, or electrically conducting	Cleaning membranes under mild chemical conditions
Electroosmotic backwashing	Pulsed or continuous	Polymeric, inorganic	Reduce fouling, low power consumption, minimal changes in feed attributable to electrolysis

[a] Synergistic effects are observed when electric and acoustic fields are applied simultaneously.

Source: Adapted from [53, 54].

- The cross-flow velocity is an order of magnitude lower than in conventional cross-flow filtration.
- Assisted filtration in conjunction with low cross-flow velocities results in reduced power consumption and lower pumping costs, less degradation of shear sensitive streams and reduced heat transfer requirements in recirculation systems for biological applications.

Polyelectrolyte-enhanced ultrafiltration

Large MW polyelectrolytes such as sodium polystyrene suphonate (PSS) have been used for removing multivalent cations. For example, PSS (MW = 85,000 Da) was used for softening water with 10,000 MWCO membranes [55]. The negatively charged colloidal PSS binds calcium and magnesium; rejections of up to 99.7% of hardness ions were obtained. The permeate flux was 70 lmh at 4 bar transmembrane pressure and 20°C, substantially higher than what is possible with RO and NF membranes. Similarly, cationic polyelectrolytes have been used to remove anions such as chromate and for water softening [56].

Micellar-enhanced ultrafiltration

Because of their unique aggregation and solubilisation properties, surfactant micelles have been used for removing low molecular weight organic compounds by UF [55, 57].

Micellar-enhanced ultrafiltration (MEUF) combines the high selectivity of RO with the higher flux of UF. The basis of MEUF is that at concentrations above the critical micellar concentrations (CMC), surfactant molecules attach to each other forming organised aggregates or micelles. These large aggregates are then easily rejected by UF membranes. The micelles form in such a way that the hydrophobic portions of the molecules align toward the centre away from the surrounding hydrophilic aqueous solution. These aggregates solubilise organics such as VOCs and hydrocarbons.

The MEUF process is based on the formation of micelles and on the increased solubility, in a micellar solution, of an organic, which is sparingly soluble in water. The overall result is a two-phase system: (a) the dispersed or discontinuous phase consisting of micelles, and (b) the continuous or aqueous phase consisting of surfactant monomers. Both these phases exist in a dynamic equilibrium. This concept of phase separation suggests that the permeate concentration should be constant. Experimental data show that this is indeed the case [57, 58].

MEUF is also used to remove multivalent heavy metal ions with ionic surfactants. The ionic micellar surface has a high charge density and a high absolute electrical potential. Therefore, the heavy metal cations electrostatically adsorb onto or near the micellar surface formed by anionic surfactants such as SDS and sodium alkylbenzene suphonate [55, 57]. Similarly, cationic surfactants, e.g., cetylpyridinium chloride has been shown to be effective in removing multivalent hazardous anions [55]. Non-ionic surfactant micelles are larger and hence more effective [58], as detailed in Chapter 6.

Fractionation of macromolecules

Fractionation of proteins by UF has been an important area of membrane development because of factors such as:

(a) the deformation of polymer chains induced by shear forces,
(b) concentration polarisation,
(c) molecular weight distribution, and
(d) membrane pore-size distribution.

Fractionation is only possible when the MW of two proteins to be separated differ by an order of magnitude. With the use of charge modified membranes, however, it has become possible to fractionate mixtures of proteins with MW close to each other [31, 53], e.g., myoglobin (MW = 17,500 Da) and cytochrome *C* (MW = 12,400 Da). Proteins have a net zero charge at their isoelectric points (pI). At a pH value > pI, proteins are negatively charged, and when the pH < pI, protein are positively charged. To illustrate the point, during the separation of myoglobin from cytochrome *C* (CyC), negatively charged UF membranes were used at a pH 9.2, which is also the isoelectric point of CyC (pI 9.2). Since myoglobin (pI 7.09) has a net negative charge at this pH, it was rejected by the negatively charged membrane, whilst CyC permeated completely through the membrane. Conversely, at a pH of 5.5, CyC was rejected by a positively charged membrane and myoglobin passed through the pores.

Similarly, amino acids with widely different pI values can be separated by varying the pH of the solution. It follows that below the pI of the protein, when the protein is positively charged, a positively charged membrane is less prone to fouling, resulting in a higher flux. Note also that when the $\text{pH} < \text{pI}$, proteins foul hydrophilic membranes which are mostly negatively charged.

Activated carbon-enhanced filtration

UF has been used to remove organic matter and THM precursors from surface water with the aid of powdered activated carbon (PAC). Similarly, tubular ceramic MF membranes with a pore size of 0.2 μm were used to treat landfill leachates [59]. Leachate is a difficult water to treat because it contains high quantities of organic matter, colour, heavy metals and suspended solids. The permeate flux was 180 lmh at 1 bar g, 70% higher than with no PAC treatment. The flux increased with increasing dosages of PAC, even though the suspended solids concentration also increased. There were two reasons for enhanced performance: (a) more colloids are adsorbed at higher PAC loadings, and (b) PAC acts as an abrasive and helps to remove the gel layer deposited on the membrane.

Pressure-retarded osmosis

The process derived from RO enables energy generation from a concentration difference. During osmosis water flows from the dilute solution (pure water) to the concentrated solution as shown in Figure 1.10. The osmotic water flow can be used to generate electricity by means of a turbine [17, 60]. The water flow at a $\Delta P < \Delta\pi$ is

$$J = A(\Delta\pi - \Delta P) \tag{1.19}$$

The power, E (W), per unit area is given by the flux (J) multiplied by the hydrostatic pressure (ΔP):

$$E = J\cdot\Delta P = A(\Delta\pi - \Delta P)\cdot\Delta P \tag{1.20}$$

The power generated is maximum when $\Delta P = 0.5\Delta\pi$, which indicates that

$$E_{\max} = \frac{A(\Delta\pi)^2}{4} \tag{1.21}$$

For a saline solution of seawater salinity, power generated using Equation (1.21) is 1.5 W/m^2. Thus, higher power can be generated with a higher salinity solution. Equation (1.21) shows that the maximum power generated is directly proportional to the water permeability coefficient, A, and, hence, high flux membranes are required. The maximum power is also proportional to the square of the osmotic pressure difference. However, the actual power generated is lower due to a reduction in osmotic pressure by the dilution of the brine solution. Further, internal CP – salt trapped in the porous support layer of the membrane – reduces the effective osmotic pressure across the membrane and flux drastically [61]. For the system to be of practical value, two other limitations have to be met: (i) the system requires a fresh water source near the seawater location, and (ii) seawater salinity is not high enough for the process to be economical – a much more concentrated solution, almost eight to nine times salinity than seawater is required [62].

Forward osmosis

Forward osmosis (FO) is a membrane-separation process that uses osmotic pressure difference between a concentrated draw solution and a feed stream to drive water across a semipermeable membrane [63]. The basis of FO is osmosis, a natural and spontaneously occurring process. It is strictly direct osmosis across an RO membrane. A draw solute of high osmotic pressure, e.g., ammonium carbonate passes across one side of the FO membrane, and a high salinity solution, e.g., seawater flows across the other side of the membrane, as shown in Figure 1.17. Water transfers from the seawater to the draw solute side due to osmotic flow. It is then necessary to regenerate the draw solute and recover the water transferred by the FO process, e.g., in a distillation unit. The primary challenge is

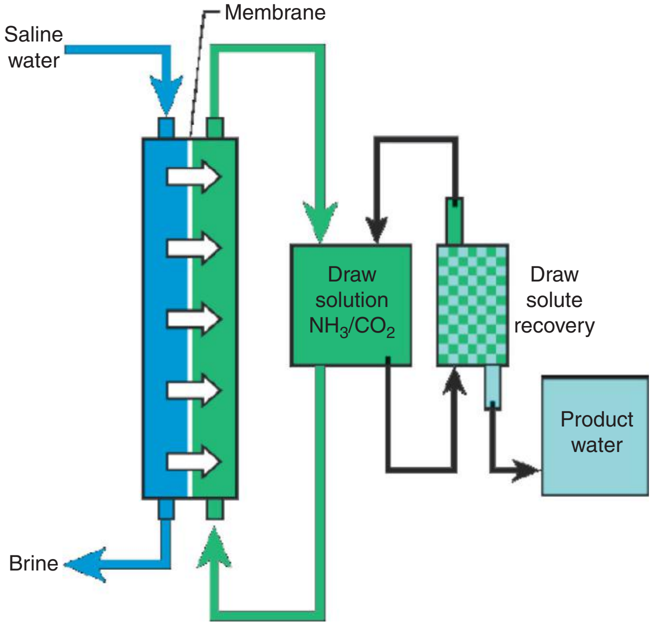


Figure 1.17 Schematic flow diagram of a forward osmosis system with ammonia carbon dioxide draw solution (https://www.google.com/search?q=cellulose+acetate+membrane). *Source: [63].*

the selection of a draw solute so that its presence in the product water meets the drinking water standard, and the draw solute can be removed easily and economically.

The main attraction of FO is that it is not limited by osmotic pressure like RO and, hence, can treat high salinity waters. It is also believed to be less prone to feed-side fouling. However, the dual-separation process is intertwined and complex as shown in Figure 1.17, and needs to overcome several limitations [48, 62]:

- Conventional RO membranes are not suitable because FO differs from RO in having salty solutions on both sides of the membrane. The porous support exposed to the draw solution is subject to fouling and internal polarisation from the draw solution. This means that the concentration of salt ions inside the membrane is very different from the bulk solution, resulting in a loss of osmotic pressure driving force such that conventional RO membranes only achieve <50% of their capability in FO.
- Heat energy is required for the separation of the ammonia and CO_2 from the diluted draw solution and for the evaporation of large amounts of water. A suitable draw solution is required for treating feeds with high osmotic pressure.
- The process is more energy intensive than RO.
- Product water contains about 9 ppm ammonia. Hence, an additional water purification step such as ion exchange is required to ensure that the final product contains <1 ppm ammonia to meet the drinking water standards.
- Even with draw solution optimisation and the benefit of reduced fouling in the regeneration step, the FO process is unlikely to approach the energy efficiency of SWRO.

One potential application is pre-treatment of seawater for RO desalination. Process modeling results showed that a FO–RO integrated system could be effective in meeting boron and chloride water quality requirements for agricultural irrigation without a two-pass RO system [64]. Since it is apparently less prone to feed side fouling, FO pretreatment would be an additional useful asset.

Another useful application of FO is the so-called "osmotic backwash" for cleaning RO membranes [62]. TFC membranes cannot be backwashed because the top thin layer can get detached. However, since forward osmosis transfers pure or fresh water through an RO/NF membrane under osmotic pressure, it can be used to backwash and clean the membrane with the permeate without the risk of damaging the membrane. One process operation is described below:

- Shut down the feed water occasionally for a short time to allow immediate osmotic backwash of the membrane. Water will penetrate the membrane at flux, which is a function of the local salt concentration along the membrane. More water will penetrate the high concentration locations, which are more prone to scale deposition and small precipitates may get dissolved.

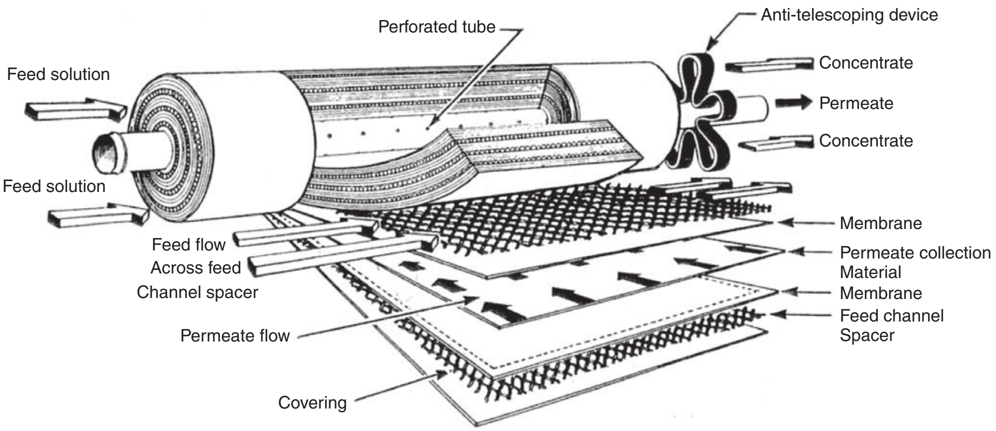


Figure 1.18 A spiral wound membrane module.

1.5 MEMBRANE MODULES

1.5.1 Conventional modules

Characteristics of membrane modules are summarised in Table 1.12. The spiral wound (SW) module shown in Figure 1.18 is used in all RO and NF applications. The RO hollow-fibre (HF) module, similar to the one shown in Figure 1.19, is now manufactured by only by Toyobo, and is used for seawater desalination. UF HF membrane (see Figure 1.3) was used extensively in the dairy industry, but it has largely been replaced by SW modules. However, cross-flow HF modules are commonly used in food processing and industrial wastewater treatment [18, 31].

The tubular membrane (TM) modules shown in Figure 1.20 are 1.5–3 cm in diameter and have the lowest surface area. Tubular membranes are usually preferred to HF and SW membranes for high solids (>0.5%) industrial wastewater applications; TM modules are less prone to severe polarisation and fouling since they are operated under turbulent flow conditions ($Re > 3000$). The TM module is best suited for feeds with high suspended solids because it can handle particulates and can be physically cleaned with foam balls. Although TM plants consume 50% more power than HF or SW plants, TM are relatively inexpensive and have a longer life.

Shear-sensitive biological materials require gentle operating conditions; hence, turbulent flow conditions are not desirable. In contrast to TM modules, SW modules offer gentler flow fields above the membrane surface. Plastic mesh spacers are used in SW modules to promote localised turbulence above the surface of the membrane. The SW modules come in standard sizes of 6, 10 and 20 cm diameter × 100 cm long. The elements fit in a pressure vessel connected in series by O-rings up to eight elements per vessel (see Figure 2.18).

Table 1.12 Characteristics of various modules

Characteristics	Plate and frame	Spiral-wound	Tubular	Hollow-fibre	Submerged	High shear
Packing density (m^2/m^3)	Moderate (200–500)	High (500–1000)	Low–moderate (70–00)	High (500–5000)	Moderate	Low–moderate
Energy usage	Low–moderate (laminar)	Moderate (Spacer losses)	High (turbulent)	Low (laminar)	Low	Moderate
Fluid management and fouling control	Moderate	Good (no solids) Poor (solids)	Good	Moderate–good	Moderate–poor	Very good
Standardisation	No	Yes	No	No	No	No
Replacement	Sheet (or cartridge)	Element	Tubes (or element)	Element	Element (or bundle)	Sheet (or cartridge)
Cleaning	Moderate	Can be difficult (solids)	Good – physical cleaning possible	Backflush possible	Backflush possible	Good
Ease of manufacture	Simple	Complex (automated)	Simple	Moderate	Moderate	Complex

Source: [11].

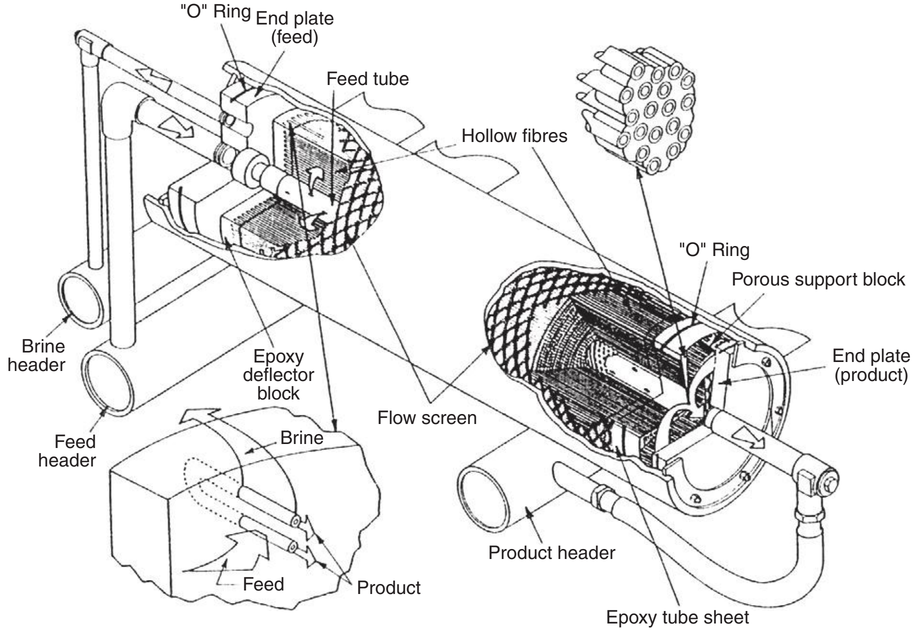


Figure 1.19 A DuPont hollow fibre RO membrane module assembly.

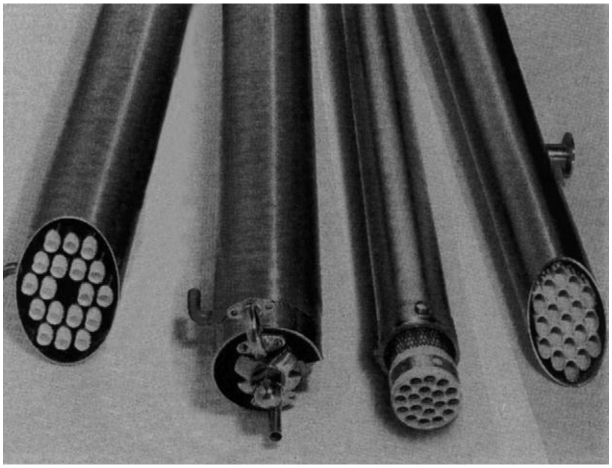


Figure 1.20 Typical tubular membrane modules.

1.5.2 Newer modules

High-performance SW modules

In the production of high-purity water for pharmaceutical and beverage applications, full-fit modules are now used. Full fit means there is no brine seal that provide dead spaces, and potential areas of bacterial growth (see Figure 2.17). In addition, the chemicals can be rinsed out faster. In addition, hot water sanitisable (up to 80°C) RO membrane elements are now available. Other designs include energy-saving polyamide membrane (ESPA®) module commercialised by Hydranautics, ultra-low pressure RO membrane (TFC-ULP®) introduced by Dow/Film-Tec and large diameter, high surface area RO modules. The industry standard for large diameter modules is 40 cm diameter × 100 cm long (nominal) with a surface area of 158 m^2, which is about four times that of 20 cm diameter modules (see Table 2.10). One manufacturer supplies 45 cm diameter SW modules (Koch, MegaMagnum®).

Hollow fibre modules

Dead-end hollow fibre modules are used in UF and MF water treatment applications. They come in two designs, pressurised and submerged, as shown in Figure 1.21. Specifications of various commercial modules are provided in Table 6.14.

Ceramic modules

Ceramic membrane modules are tubular (mini-tubes, 3 mm in diameter), as shown in Figure 1.22. They are the most expensive due to the low surface areas of the module. Ceramic membranes, however, are good candidates for immobilised whole cell reactors, cell harvesting and protein purification because of their excellent chemical, thermal and mechanical properties as discussed earlier. A novel approach to increasing the surface area and, thereby, reduce the capital cost is to use honeycomb monolith ceramic filters containing up to 10 channels/cm^2, modified to produce UF and MF modules [26, 31]. The filters are made of alumina with ZrO_2 layers with pore sizes between 40 and 500 Å. Typically, a 100 cm long × 15 cm diameter module has a membrane surface area of 10 m^2.

Short flow-path modules

Back in 1989, during a visit to an industrial laundromat in Connecticut that was using tubular PVDF UF membranes to remove emulsified oil, grease and priority pollutants, we observed there was no permeate flow in the end section of membrane modules, the so-called “far downstream” section. This came as no surprise to us; the solute concentration profile continues to grow with the length of the membrane as shown in Figure 1.23. The severity of CP with membrane length in UF modules was proven with the help of mathematical models in the 70s [13, 14]; short-length UF membrane modules reduce CP [65].

Short flow path disc-tube (DT) RO membrane modules developed by Rochem for treating highly turbid waters and fouling feeds are now used extensively to minimise concentration polarisation, scaling and fouling. Typically, for RO systems the Silt Density Index (SDI) of feed water must be less than 5 to prevent premature fouling.

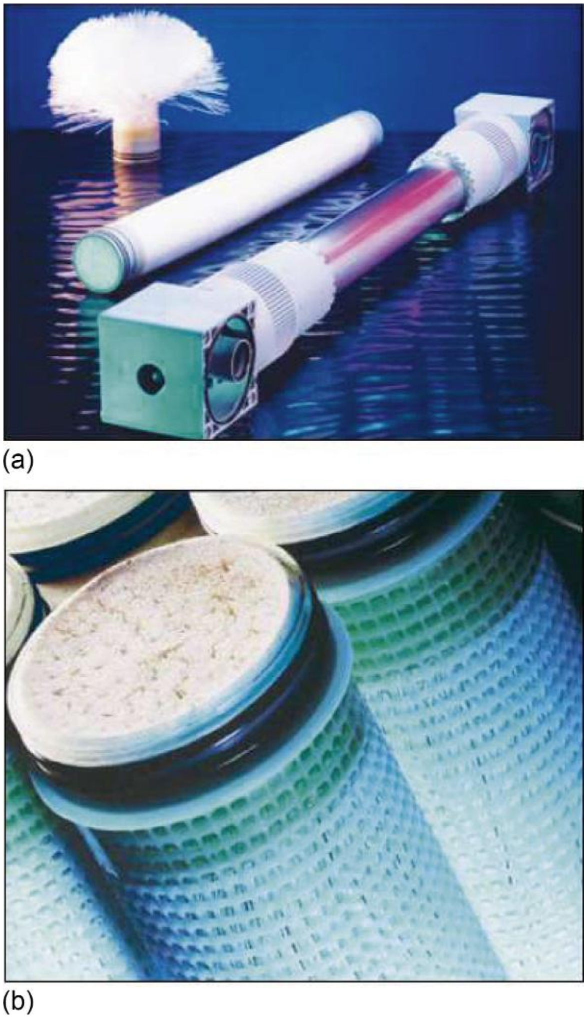


Figure 1.21 UF/MF membranes: (a) hollow fibres, membrane element and pressure vessel; (b) hollow fibre membrane element. *Source: USFilter/Memcor*®.

An empirical measurement, SDI is the method of choice for measuring the colloidal fouling potential of RO feed water (ASTM standard D-4189-82, 1987). Because of their unique design, DT modules can tolerate feed water with an SDI value as high as 16 [66]. The salient features of the DT module shown in Figure 1.24 are:

- The extremely short flow path (7.5 cm vs. 100 cm for the shortest TM, SW or HF module) limits CP.
- High permeate flux: 70 lmh at 70 bar g.

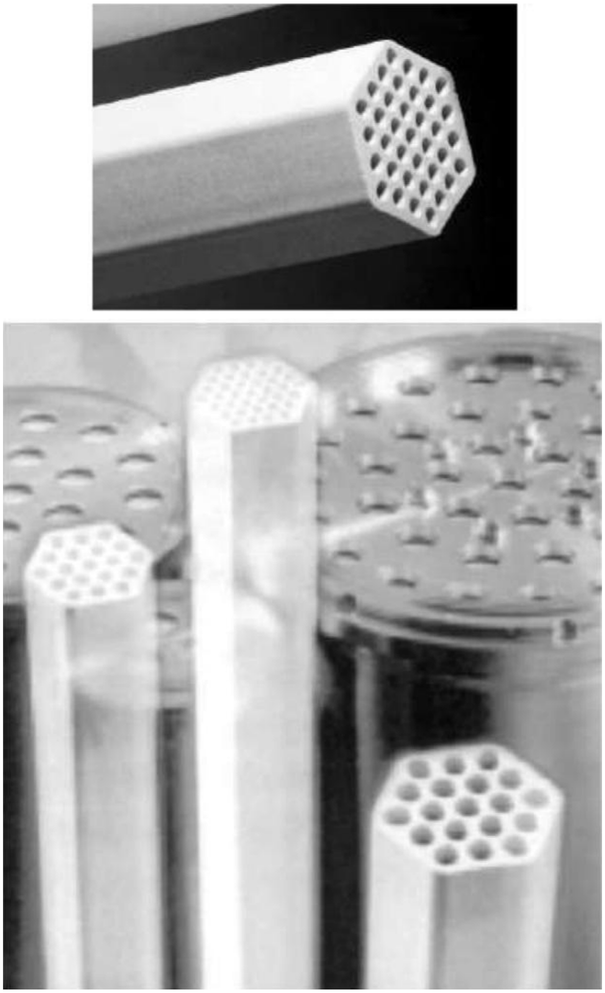


Figure 1.22 Ceramic membrane elements with 3 mm i.d. circular mini tubes. *Source: USFilter/ Membralox®.*

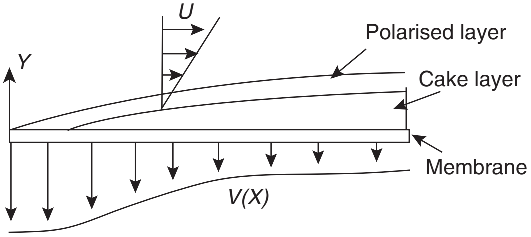


Figure 1.23 A schematic of concentration polarisation and permeate flux, $V(x)$ profiles. U is axial velocity. *Source: [68].*

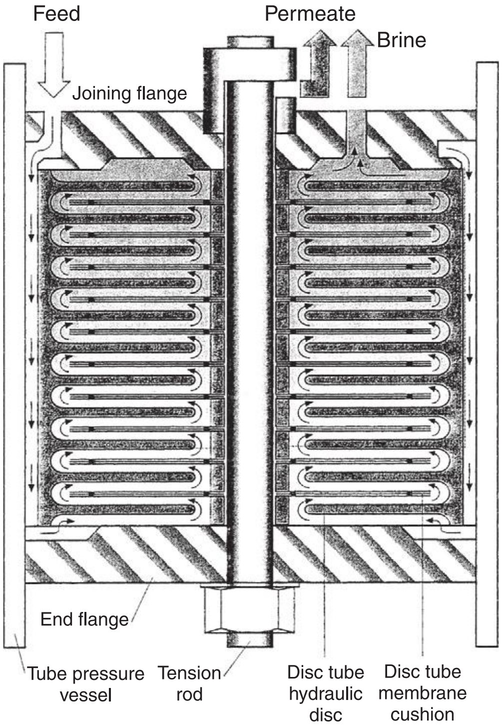
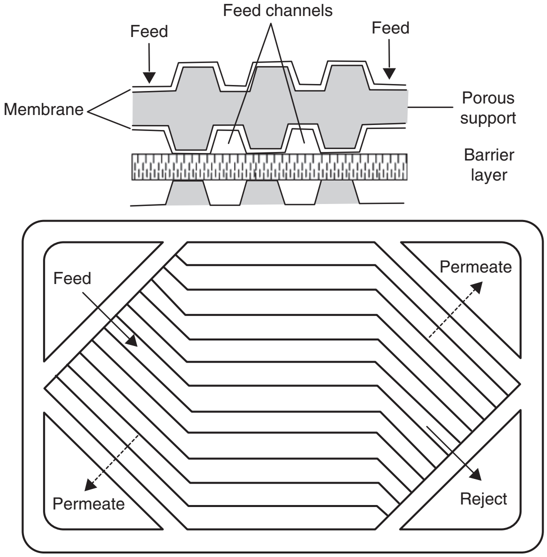


Figure 1.24 A ROCHEM short flow-path membrane module. Each disc is ~8 cm long.

- The delayed formation of the gel layer allows longer cleaning intervals and, thereby, extends membrane life. The flow is turbulent.
- The open channels allow efficient cleaning of the membranes.
- The packing density is high; 150 m^2 of membrane area/m^3 of module.

Advanced PAF membrane module

A novel plate-and-frame (PAF) membrane and module design consists of a composite membrane, wherein a proprietary polymer is coated on a porous grooved support, as shown in Figure 1.25. The uniqueness of the design lies in the enhanced surface area achieved by forming a membrane on the channel walls, thereby, increasing the surface area two to three times, which is not the case with the existing PAF modules commonly used in PV applications. By providing high surface area modules, the relative cost of PV could be reduced. Further, to increase surface shear and control fouling, short, narrow, non-uniform, multi-path channels are formed. These turbulence promoting pathways, without any fouling prone constrictions such mesh spacers as used in SW modules, could go a long way in mitigating fouling in UF and MF membrane systems.



A novel membrane module design. Top: Cross-sectional view of a membrane-coated channel. Bottom: Channel flow pattern. High surface-area modules could reduce the relative cost of pervaporation. The short, narrow, non-uniform, multi-path channels that create higher shear are formed. The turbulence promoting pathways could go a long way to mitigate fouling in ultrafiltration and microfiltration membrane systems.

Figure 1.25 Schematic of an advanced module design.

Flux-enhancing techniques

Several flux-enhancing techniques are summarised in Table 1.13 [11]. Among the commercialised modules are high shear modules such as the vibratory VSEP module shown in Figure 1.26, the rotating disc module and the vortex flow filtration rotating cylinder module. These modules are designed to minimise CP and fouling, and therefore are used with high solids (up to 50%) feeds. The application of cross-corrugated membranes to enhance mass transfer has also been shown to be effective [67]. The mass transfer correlation turbulent flow in corrugated membranes that fitted to the data was $\mathrm{Sh}=0.023\ \mathrm{Re}^{0.58}\ \mathrm{Sc}^{0.333}$ vs. $\mathrm{Sh}=0.023\ \mathrm{Re}^{0.8}\ \mathrm{Sc}^{0.33}$ for turbulent flow in standard membranes.

1.6 MEMBRANE FOULING

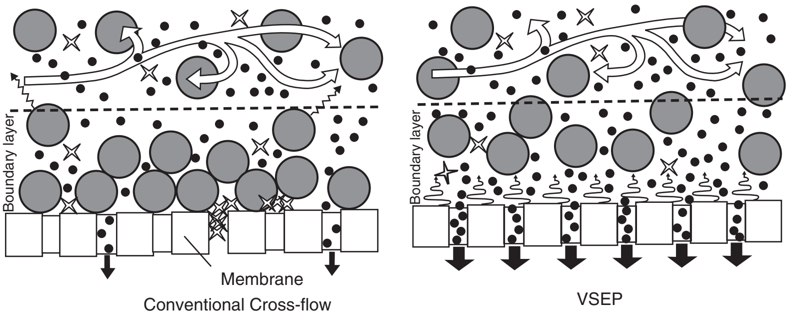
Membrane fouling is a membrane system phenomena. The type of feed water determines the severity of fouling. For example, seawater RO membranes are mainly fouled by organic and particulate matter, whereas brackish water RO membranes are primarily fouled by dissolved but sparingly soluble salts. Substances that foul membranes are listed

Table 1.13 Flux-enhancing strategies

Process/technique	Effect/comments
Feed-channel spacers – spiral-wound modules and some flat-sheet modules	Eddies and increased shear
High shear – vibrating membrane	Generates high shear at membrane surface
High shear – rotating the membrane	Generates high shear and Taylor vortices
High shear – rotor above the membrane	Generates high shear at membrane surface
Dean vortices	Induced flow in curved channels
Pulsing the feed	Unsteady-state flow generates eddies
Baffles	Eddies. Enhances pulsations
Air bubbling	Bubbles generate eddies and shear transients
Backpulsing	Permeate reversal removes deposits. Best for hollow-fibre MF and UF membranes
Cross-corrugated membranes[a]	Enhanced mass transfer

[a] [67].

Source: [11].



Vibrational energy in a VSEP system focuses shear waves at the membrane surface, repelling solids and foulants. Culkin, B.; Armando. A.D. (September/October 1992) Courtesy: Filtration & Separation

Figure 1.26 Conventional cross-flow vs. VSEP membrane module. *Source: Filtration & Separation, Sep/Oct 1992.*

in Table 2.4. Fouling is mitigated by pre-treatment of raw water and by operating membrane systems under well-designed controlled conditions (see Tables 2.6 and 2.7).

Fouling causes a loss in water flux and quality, reduced operating efficiency, lost service time, premature membrane replacement and higher operating costs. In addition, anticipated lower throughput warrants more membrane surface area resulting in higher capital costs. Prevention and/or reduction in the rate of fouling and CP are, therefore, important factors in the design and operation of membrane systems. For example, fouling can get exacerbated at higher water fluxes in RO systems.

The flux of a solvent through a membrane is roughly proportional to the applied pressure but for liquids other than pure water this proportionality does not exist due to CP and/or fouling (see Figure 2.27), and the permeate flow may be as low as 20% of that of pure water (see Figure 2.34). The permeate flux stabilises after an initial rapid decline. The steady-state flux value is a function of the nature of the feed (e.g., viscosity, solute concentration and diffusivity, pH, ionic strength) and operating conditions such as fluid shear rate at the membrane surface and trans-membrane pressure drop. Typically, fouling factors for RO, UF and MF membranes are 30%, 80% and 90%, respectively. Usually, a rapid flux decline indicates the presence of foulants rather than mineral scales.

1.6.1 The fouling phenomena

The causes of fouling vary depending on the nature of the solute and solute–membrane interactions. Fouling is often the result of a strong interaction between the membrane and the components in the feed stream; for example, fouling by colloids, iron and biomaterials can be especially severe. As a general rule, a reversible flux reduction is due to CP, whereas an irreversible flux reduction is due to fouling.

Most fouling substances are hydrophobic and carry a surface charge [18, 31, 68]. Proteins such as bovine serum albumin (BSA) are more readily adsorbed on the surface of hydrophobic membranes due to hydrophobic interactions than hydrophilic solutes such as dextran. Adsorption from only 10 mg/l BSA solutions can result in a 25% loss of flux with an accumulation of less than 10 mg/m^2 of protein (corresponding to a full monolayer of protein on the surfaces). The adsorbed layer is also more difficult to remove from a hydrophobic membrane than from a hydrophilic membrane. Similarly, during the removal of natural organic matter using NF membranes, the flux decline for the hydrophobic organic matter fraction was 60% compared to 20% for the hydrophilic fraction. Biofouling of membranes is a severe problem; the slightly negative charge of bacteria and cell hydrophobicity result in the formation of a biofilm gel layer [69].

Hence, fabricating (or modifying) membranes that are more hydrophilic and, therefore, less prone to fouling with the added benefit of enhanced flux, has been a key priority for more than 30 years.

1.6.2 Fouling-resistant membranes

Surface chemistry

Many of the membrane polymers do not contain the desired properties; they are susceptible to fouling or are not durable. Hydrophilic surfaces contain (i) hydrogen-bond acceptors, (ii) are electro-neutral and (iii) do not contain hydrogen bond donors. Hence, they tend to be best at resisting protein adhesion. It is believed that films with these chemical properties can bind a thin layer of water to the surface, providing a steric or energetic barrier to adhesion [20, 21]. Surface roughness also increases the adhesion of substances to the membrane surface. For example, CA membranes are less prone to fouling as compared to PA membranes because the former have a smooth surface. Surface properties of the state-of-the-art TFC polyamide membranes are prone to fouling because they do not possess the above-mentioned key characteristics required for resisting fouling. Several chemistries that meet the criteria for fouling resistance have been reported [21]:

- Smooth surface
- Chemistry of polymers that resist adhesion of protein or organic macromolecules, e.g., polyethylene oxide
- Zwitterions such as poly(sulphobetaine)
- Sugar-derived molecules
- Polyglycerol

Polymer modification

The development of modified charged hollow fibre UF membranes 30 years ago proved to be a major success for electrocoat paint recovery, one of the early UF applications [26, 31]. There are two types of electrocoating processes: anodic deposition where the item to be painted is positively charged and the paint is negatively charged, and cathodic deposition where the item to be painted is negatively charged and the paint is positively charged. In order to avoid fouling by charge interactions, positively charged membranes are used for cathodic paint recovery, and negatively charged membranes are used for streams for recovering anodic paints. The difference in flux is remarkable, as shown in Figure 2.16.

Hydrophilic–hydrophobic blend membranes

Hydrophilic membranes such as regenerated CA are less susceptible to fouling than hydrophobic membranes such as PVDF, PS, PES and PP. The influence of the membrane material on the fouling of membranes shows that the flux of hydrophilic membranes is only marginally reduced, whereas the flux reduction of hydrophobic membranes is significant [70]. In general, hydrophilic polymers such as cellulosics and aliphatic polyamides (nylon-4,6, nylon-6, nylon-6,6, nylon-11, nylon-12) have restricted chemical and thermal stability. Blending of two polymers, one to give the membrane sufficient chemical and thermal stability, the other to render the membrane more hydrophilic, therefore, has been used to prepare stable UF hydrophilic membranes [71]; for example, a blend of hydrophilic polymer, PVP and hydrophobic PS and PES polymers.

Surface modification

Among the surface modification techniques investigated is surface fluorination. Fluorination makes the membrane surface hydrophilic (the contact angle reduced from 90° to 56°) by adding fluorine and oxygen to the membrane polymer. Fluorination of PS membranes nearly doubled the flux when treating potato starch waste (0.6% solids, mainly starch and proteins) with a 100,000 Da MWCO membrane [72]. Similarly, when TFC membranes were fluorinated with hydrofluoric and fluorosilicic acids, the surface-modified membrane showed an order of magnitude increase in flux without any reduction in rejection [73].

As in the case of PS membranes, PVDF membranes have high chemical and thermal stability but are sensitive to fouling. Asymmetric PVDF membranes were coated with a hydrophilic layer (<1.0 μm) of polyether/polyamide block co-polymer to produce composite hydrophilic UF membranes [74]. The performance was comparable to cellulosic membranes with lower susceptibility to fouling and reduced flux decline during UF of wastewater oil emulsions containing 6% (wt.) oil. Similarly, PVDF MF membranes, surface treated by grafting 2-methacryloyloxyethyl phosphorycholine (MPC), showed a flux decline of only 10% as compared to a decline of 86% for the uncoated membrane during the filtration of BSA solutions, as shown in Figure 1.27 [75].

Polydopamine and polydopamine-*g*-PEG coatings increase hydrophilicity of the membrane surfaces and have previously been shown to improve fouling resistance toward model oil/water emulsions in laboratory studies. Polyacrylonitrile hollow fibre UF and polyamide spiral wound RO membrane modules were surface-modified with an aqueous solution containing dopamine to deposit polydopamine on the membrane surfaces and other wetted parts inside the modules [76]. UF modules were further

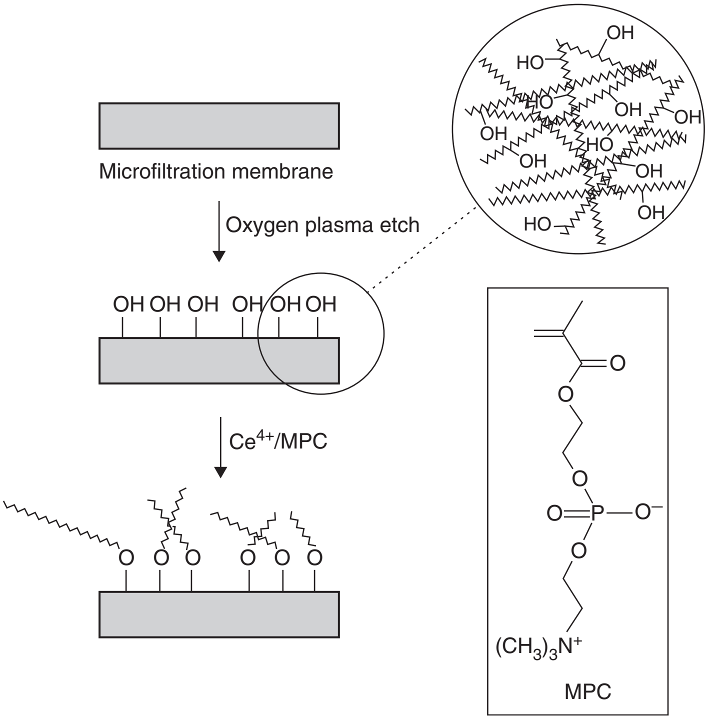


Figure 1.27 An example of surface treatment of a PVDF microfiltration membrane to minimise fouling. *Source:* [75].

modified by grafting poly(ethylene glycol) (PEG) brushes to the polydopamine coating. In a pilot-scale test treating hydraulic fracturing flowback water from the Barnett Shale area in Texas, the fouling performance of modified UF and RO membrane modules was compared to that of unmodified analogues. UF modules were used to remove most of the highly fouling organic matter in the feed before desalination by RO. Polydopamine-modified UF modules maintained higher flux, lower trans-membrane pressure drop and improved cleaning efficiency relative to unmodified modules. The polydopamine coating, however, did not mitigate RO fouling, presumably because most of the organic foulants had been removed by UF pretreatment. However, higher and more stable salt rejection was observed in modified RO modules than in unmodified modules.

Coating membrane surfaces to address fouling issues was reported in a recent review [20]. For example, hydranautics LFC and LFC3-LD RO membranes were introduced in 1996 and 2005, respectively, for applications in wastewater treatment/reclamation. These neutrally charged membranes are designed to minimise the adsorption of organic foulants. The reported stable performance over time has been attributed to a poly(vinyl alcohol) (PVA) coating on the surface of conventional fully aromatic TFC polyamide membranes. Coatings of PVA and poly(*N*,*N*-dimethylaminoethyl methacrylate) have also shown higher resistance to chlorine damage. Hydrophilic dendritic polymers have also been used to modify membrane surface to reduce fouling.

Other surface modification techniques include the use of free radical-, photochemical-, radiation- redox- and plasma-induced grafting. These are used to covalently attach some useful monomers onto the membrane surface [20]. Gas plasma treatment is also used to induce surface modification; water permeability is improved by oxygen plasma treatment due to the introduction of hydrophilic carboxylate groups, whereas argon plasma treatment can enhance chlorine resistance by increasing the extent of cross-linking at the nitrogen sites.

Other works include the use of atmospheric gas plasma surface activation and graft polymerisation on the surface of conventional polyamide TFC membranes resulting in enhanced anti-fouling properties. After surface activation by gas plasma, a polymeric brush layer is formed by free radical graft polymerisation using methacrylic acid or acrylamide monomers. This brush layer can effectively reduce the ability of foulants to adhere to the surface as shown in various fouling tests; the modified membrane was less prone to scaling than commercial low-fouling membrane, LFC1. Further, both atmospheric gas plasma treatment and graft polymerisation can be readily scaled to commercial-scale membrane manufacture.

Various water soluble solvents such as acids and alcohols have been used to treat TFC membrane surfaces [20]. Mixtures of alcohol (ethanol and iso-propanol) and acid (hydrofluoric and hydrochloric add) in water have been used to improve flux and rejection, a result of partial hydrolysis and skin modification initiated by the alcohol and acid. The presence of hydrogen bonding is believed to encourage interaction between the acid and water, which produces more surface charge and eventually enhances the hydrophilicity and water flux. Post-treatment of a membrane surface with ammonia or alkyl compounds, particularly ethylenediamene and ethanolamine, increased both flux and salt rejection. A 70% increase in flux was attained by soaking composite membranes in solutions containing various organic species, e.g., glycerol, sodium lauryl sulphate and the triethylamine salt of camphorsulphonic acid. Post-treatment of membranes using an aqueous solution of PVA and a buffer solution also improves the abrasion resistance as well as the flux stability of the membrane [20].

Ceramic/polymeric hybrid membranes

The advantages of ceramic UF and MF membranes discussed earlier in the chapter are often offset by their low selectivity, which makes their use economically unfeasible for many applications. These membranes separate solutes from solvents primarily by site exclusion, and to a lesser extent, by interactions with the membrane surface. The selectivity of ceramic membranes can be improved by modification of the membrane surface either by polymer grafting or graft polymerisation. The latter has the advantage of providing a covalently bonded brush layer of high surface coverage with minimal diffusional limitations and steric hindrance effects.

A composite ceramic membrane was formed [77] by the graft polymerisation of a hydrophilic polymer, PVP, onto the surface of silica membranes (pore size = 3.0 μm). The flux of an unmodified UF membrane of an oil/water emulsion (4.7%) decreased with time as compared to the flux of the composite membrane. The decline in flux was caused by fouling and/or the immediate formation of an oil gel layer on the surface of the unmodified membrane. The modified membrane, in contrast, was not only more resistant to adsorption of oil, but also had a higher oil rejection. The performance of the modified ceramic membrane depends upon the configuration of the grafted chains in response to solvent–polymer interactions. Thus, the hydrophilic PVP polymer chains tend to expand or extend away from the surface in aqueous solutions, preventing oil adsorption on the membrane surface. Simultaneously, the hydrophilic polymer allows the passage of water molecules preferentially over oil.

Neo-dynamic membranes?

A potential solution to prevent fouling is to develop fouling release membranes that do not resist the adhesion of foulants, but have an active layer with a low surface energy so that adhered foulants can be readily washed away by hydrodynamic mixing in the membrane module [21] provided the water flux and salt rejection of the resulting membrane are not compromised.

1.7 CONCLUDING REMARKS

Membrane technology has progressed remarkably in the last 50 years since the discovery of the asymmetric CA RO membrane by Sourirajan and Loeb [3–5]. In 1965 desalination global capacity was ~160,000 m^3/day, and virtually all of it was by thermal distillation. By 2013 the global desalination capacity was 60 million m^3/day with more than 60% by RO [78]. According to a report published in 2013 by McIlvane Company, the sales of membranes and equipment for water treatment may exceed $10.4 billion in 2014 of which one-third is for desalination [79].

What began as a mission to desalinate water by RO in the 1950s, membrane processing evolved into a dynamic multi-application water purification and separation technology including treatment of industrial process waters and wastewaters in the 1980s followed by the development of semicontinuous dead-end membrane filtration technology in the 1990s. Membrane technologies such as NF, PV and GS materialised from developments in RO. These successes in turn led to the development of non-traditional membrane processes such as MD and forward osmosis. However, membrane fouling remains problematic.

Size discrimination between permeated water and non-permeated species has undergone an impressive three to four order-of-magnitude refinement, while maintaining economically attractive productivities by engineering of materials, membrane morphologies and membrane elements [80]. Continuing advances in development of new membranes with better thermal, chemical and improved transport properties will lead to more efficient membrane systems. Development of newer membrane modules and operating procedures in recent years has provided a key stimulus for the growth of the membrane industry such as submerged membrane filtration for treating municipal water. Membrane filtration has expanded membrane applications in the areas of water reclamation and reuse enormously.

Seawater is an unlimited source of water. Currently, seawater RO is the best available technology for desalinating seawater [48]. There is room for improvement to make the process more affordable and less energy intensive, although the progress will be incremental at best [21].

One challenge that has eluded researchers is the development of chlorine-resistant TFC polyamide-based RO membranes, the workhorse of water treatment.

Several inorganic membranes (ceramic, carbon), mixed-matrix membranes (a combination of organic and inorganic material) and carbon nano-tube/polymeric membranes have been developed and tested to address fouling issues and increase membrane permeability without sacrificing membrane selectivity [20, 21]. If developments pertaining to new membranes are successful, membrane separation science could become the all-encompassing and relatively inexpensive water purification technology with a reduced carbon footprint to meet increasing and critical water demands worldwide in the twenty-first century [81].

REFERENCES

[1] W.J. Koros, Evolving beyond the thermal age of separation processes: membranes can lead the way, AIChE J. 50 (10) (2004) 2326–2334.

[2] H. Strathmann, Membrane separation processes: current relevance and future opportunities, AIChE J. 47 (5) (2001) 1077–1087.

[3] H.K. Lonsdale, The growth of membrane technology, J. Memb. Sci. 10 (1982) 81–181.

[4] S. Loeb, S. Sourirajan, Sea water demineralization by means of an osmotic membrane, Adv. Chem. Ser. 38 (1963) 117–132.

[5] S. Loeb, The Loeb–Sourirajan membrane: how it came about, ACS Symp. Ser. 153 (1981) 1–9.

[6] R.J. Petersen, Composite reverse osmosis and nanofiltration membranes, J. Memb. Sci. 83 (1993) 81–150.

[7] A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004.

[8] T. Matsuura, Synthetic Membranes and Membrane Separation Processes, CRC Press, Boca Raton, FL, USA, 1994.

[9] J.D. Ferry, Ultrafilter membranes and ultrafiltration, Chem. Rev. 18 (1936) 373–455.

[10] A.S. Michaels, Ultrafiltration, in: E.S. Perry (Ed.), Progress in Separation and Purification, vol. I, Interscience, New York, NY, 1968, p. 297.

[11] G. Anthony Fane, Module design and operation, in: A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 67–88.

[12] W.F. Blatt, A. Dravid, A.S. Michaels, L. Nelsen, Solute polarization and cake formation in membrane ultrafiltration: causes, consequences, and control techniques, in: J.E. Flinn (Ed.), Membrane Science and Technology, Plenum Press, New York, NY, 1970, p. 47.

[13] R. Singh, R.L. Laurence, Influence of slip velocity at a membrane surface on ultrafiltration performance – I. Channel flow system, Int. J. Heat Mass Transfer 22 (1979) 721–729.

[14] R. Singh, R.L. Laurence, Influence of slip velocity at a membrane surface on ultrafiltration performance – II. Tube flow system, Int. J. Heat Mass Transfer 22 (1979) 731–737.

[15] R.W. Field, D. Wu, J.A. Howell, B.B. Gupta, Critical flux concept for microfiltration fouling, J. Memb. Sci. 100 (1995) 259.

[16] R.E. Kesting, Synthetic Polymeric Membranes, John Wiley & Sons, New York, NY, 1985.

[17] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Holland, 1997.

[18] L.J. Zeman, A.L. Zydney, Microfiltration and Ultrafiltration, Marcel-Dekker, New York, NY, 1996.

[19] K. Scott, (Section 2), Handbook of Industrial Membranes, Elsevier, Oxford, UK, 1995.

[20] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination – development to date and future potential, J. Memb. Sci. 370 (2011) 1–22.

[21] M. Elimelech, W.A. Philip, The future of seawater desalination: energy, technology, and the environment, Science 333 (2011) 712–717.

[22] T. Matsuura, Future trends in reverse osmosis membrane research and technology, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 37–75.

[23] M. Elimelech, X. Zhu, A.E. Childress, S.J. Hong, Role of surface morphology in collided fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes, J. Memb. Sci. 127 (1997) 101.

[24] J. Glater, S.-K. Hong, M. Elimelech, The search for a chlorine-resistant reverse osmosis membrane, Desalination 95 (1994) 325–345.

[25] A. Kumano, N. Fujiwara, Cellulose triacetate membranes for reverse osmosis, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 21–46.

[26] W. Eykamp, Section 22, Alternative separation processes, in: D.H. Perry, D. Green (Eds.), Perry's Chemical Engineers' Handbook, seventh ed., McGraw-Hill, New York, NY, 1999.

[27] S.V. Cabibbo, D.B. Guy, A.C. Ammerlaan, A. Ko, R. Singh, Reverse Osmosis Technical Manual, NTIS Publication, Springfield, Virginia, USA, 1979.

[28] R. Rautenbach, R. Albrecht, Membrane Processes, John Wiley & Sons, Ltd., Chichester, UK, 1989.

[29] J.M.M. Peters, J.P. Boom, M.H.V. Mulder, H. Strathmann, Retention measurements of nanofiltration membranes with electrolyte solutions, J. Memb. Sci. 145 (2) (1998) 199–209.

[30] E. Drioli, M. Romano, Progress and new perspectives on integrated membrane operations for sustainable industrial growth, Ind. Eng. Chem. Res. 40 (2001) 1277–1300.

[31] M. Cheryan, Ultrafiltration and Microfiltration Handbook, CRC Press, Boca Raton, FL, 1998.

[32] H. Ohya, V.V. Kudryavtsev, S.I. Semenova, Polyimide Membranes, Gordon and Breach, Amsterdam, The Netherlands, 1996 (Chapter 6).

[33] A.G. Fane, Submerged membranes, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 239–270.

[34] M.D. Kennedy, J. Kamanyi, S.G.S. Rodriguez, N.H. Lee, J.C. Schippers, G. Amy, Water treatment by microfiltration and ultrafiltration, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 131–170.

[35] P. Cote, M. Liu, S. Siverns, Water reclamation and desalination, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 171–187.

[36] C.A. Heath, G. Belfort, Synthetic membranes in biotechnology: realities and possibilities, in: A. Fiechter (Ed.), Advances in Biochemical/Biotechnology, Springer-Verlag, New York, 1993, vol. 47.

[37] M.K. Timmer, J.T.F. Keurentjes, Nanofiltration bioreactors, in: A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 416–433.

[38] G.T. Daigger, B.E. Rittman, S. Adham, G. Andreottiola, Are membrane reactors ready for widespread application? Environ. Sci. Technol. 39 (19) (2005) 59–68.

[39] K.W. Boddeker, Liquid Separations with Membranes, An Introduction to Barrier Interference, Springer-Verlag, Berlin, 2008.

[40] J. Luo, C. Wu, T. Xu, Y. Wu, Diffusion dialysis-concept, principle and applications, J. Memb. Sci. 366 (2011) 1–16.

[41] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination 264 (3) (2010) 268–288.

[42] Y. Tanaka, Ion Exchange Membrane Electrodialysis: Fundamentals, Desalination, Separation, Nova, New York, NY, 2010.

[43] R.E. Kesting, A.K. Fritzche, Polymeric Gas Separation Membranes, John Wiley & Sons, New York, 1993 (Chapter 7).

[44] J.L. Humphrey, G.E. Keller II, Separation Process Technology, McGraw-Hill, New York, NY, 1997 (Chapter 5).

[45] Membranes for gas separations, Chem. Eng. News 83 (40) (2005) 49–57.

[46] K.K. Sirkar, Membrane contactors, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 687–702.

[47] M. Khayet, Membrane distillation, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 297–369.

[48] R. Semiat, Energy issues in desalination processes, Environ. Sci. Technol. 42 (22) (2008) 8193–8201.

[49] A.S. Michaels, Membrane technology and biotechnology, Desalination 35 (1980) 329–351.

[50] D.G. Thomas, Chapter 14, Dynamic membranes – their technological and engineering aspects, in: S. Sourirajan (Ed.), Reverse Osmosis and Synthetic Membranes, National Research Council Canada, Ottawa, Canada, 1977.

[51] D.B. Guy, R. Singh, On-site regeneration of reverse osmosis membranes, Water Supply Improvement Assoc. J. 9 (1) (1982) 35–44.

[52] R. Singh, Surface properties in membrane filtration, Chem. Eng. Prog. 85 (6) (1989) 59–64.

[53] W.R. Bowen, Chapter 8, Electrochemical aspects of microfiltration and ultrafiltration, in: J.A. Howell, V. Sanchez, R.W. Field (Eds.), Membranes in Bioprocessing, Chapman & Hall, London, UK, 1993.

[54] E.S. Tarleton, R.J. Wakeman, Electro-acoustic crossflow microfiltration. Filtr. Sep. May (1994) 274.

[55] J.F. Scamehorn, S.D. Christian, R.T. Ellington, Use of micellar-enhanced ultrafiltration to remove multivalent metal ions from aqueous streams, in: J.F. Scamehorn, J.H. Harwell (Eds.), Surfactant-Based Separation Processes, Marcel-Dekker, New York, NY, 1989.

[56] A. Tabatabai, J.F. Scamehorn, S.D. Christian, Water softening using polyelectrolytes – enhanced ultrafiltration, Sep. Sci. Technol. 30 (2) (1995) 211.

[57] R. Singh, Removal of volatile organic compounds by ultrafiltration, Desalination 104 (1996) 203–214.
[58] R. Singh, Investigation of ultrafiltration rejection of surfactant micelles by dynamic light scattering, Sep. Sci. Technol. 31 (9) (1996) 1351–1356.
[59] C. Vishvanathan, S. Muttamara, S. Babel, R. Ben Aim, Treatment of landfill leachate by crossflow microfiltration and ozonation, Sep. Sci. Technol. 29 (3) (1994) 315.
[60] S. Loeb, Production of energy from concentrated brines by pressure-retarded osmosis: I. Preliminary technical and economical correlations, J. Memb. Sci 1 (1976) 49–63.
[61] T. Thorsen, T. Holt, The potential for power production from salinity gradients by pressure retarted osmosis, J. Memb. Sci. 335 (2009) 103–110.
[62] R. Semiat, J. Sapoznik, D. Hasson, Energy aspects in osmotic processes, Desal. Water Treat. 15 (2010) 228–235.
[63] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: principles, applications, and recent developments, J. Memb. Sci. 281 (2006) 70–87.
[64] D.L. Shaffer, N.Y. Yip, J. Gilron, M. Elimelech, Seawater desalination for agriculture by integrated forward and reverse osmosis: improved product water quality for potentially less energy, J. Memb. Sci. 415–416 (2012) 1–8.
[65] M.C. Porter, Concentration polarization with membrane ultrafiltration, Ind. Eng. Chem. Prod. Res. Dev. 11 (1972) 234–248.
[66] Th.A. Peters, Purification of landfill leachate with reverse osmosis and D-T module, in: A. Caetano (Ed.), Membrane Technology: Applications to Industrial Wastewater Treatment, Kluwer Academic Publishers, Boston, MA, 1995, p. 175.
[67] K. Scott, J. Lobato, Mass transfer characteristics of cross-corrugated membranes, Desalination 146 (2002) 255–258.
[68] A.I. Schafer, N. Andritsos, A.J. Karabelas, E.M.V. Hoek, R. Schneider, M. Nystrom, Fouling in nanofiltration, in: A.J. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 169–240.
[69] H.-C. Flemming, Mechanistic aspects of reverse osmosis membrane biofouling and prevention, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 163–209.
[70] C. Jonsson, A.-S. Jonsson, Influence of the membrane material on the adsorptive fouling of ultrafiltration membranes, J. Memb. Sci. 108 (1995) 79–87.
[71] M. Mulder, Nature of Membranes, in: J.A. Howell, V. Sanchez, R.W. Field (Eds.), Membranes in Bioprocessing, Chapman & Hall, London, UK, 1993.
[72] R.H. Sedath, D.R. Taylor, N.N. Li, Reduced fouling of ultrafiltration membranes via surface fluorination, Sep. Sci. Technol. 28 (1993) 255–262.
[73] D. Mukerjee, A. Kulkarni, W.N. Gill, Flux enhancement of reverse osmosis membranes by chemical surface modification, J. Memb. Sci. 97 (1994) 231–249.
[74] S.P. Nunes, L.S. Mauricio, K.-V.J. Peinemann, Dense hydrophilic composite membranes for ultrafiltration, J. Memb. Sci. 106 (1995) 49–56.
[75] S. Akhtar, C. Hawes, L. Dudley, I. Reed, P.J. Stratford, Coatings reduce the fouling of microfiltration membranes, J. Memb. Sci. 107 (1995) 209–218.
[76] D.J. Miller, X. Huang, H. Li, S. Kasemset, A. Lee, D. Agnihotri, et al., Fouling-resistant membranes for the treatment of flowback water from hydraulic shale fracturing: a pilot study, J. Memb. Sci. 437 (2013) 265–275.
[77] R.P. Castro, Y. Cohen, Y.G. Monbouquette, Proceedings of the National Conference on Environmental Engineering, Boulder, CO, American Society of Civil Engineers, New York, 1994.
[78] T. Matsuura, A. Fane, New directions in desalination, Desalination 308 (2013) 1.
[79] Cross-flow membrane market to exceed $10.4 billion, Filtration + Separation.com, 29 April 2013.
[80] W.J. Koros, R.J. Lively, Water and beyond: expanding the spectrum of large-scale energy efficient separation processes, AIChE J. 58 (9) (2012) 2624–2633.
[81] R. Singh, Worldwide water crisis, J. Memb. Sci. 313 (2008) 353–354.

CHAPTER 2

Water and Membrane Treatment

> *"Whisky is for drinking, water is for fighting over."*
>
> ***— Mark Twain***

2.1 PRICELESS WATER

Current shortages of potable water around the world and the looming water scarcity, especially in the developing countries, is the greatest crisis facing humanity in the twenty-first century and possibly beyond [1–3]. According to the UN, 1.2 billion people do not have access to clean drinking water, and half of the world's population lacks adequate water purification. By 2025, 1.8 billion people will be living in areas likely to experience absolute water scarcity [1]. One-third of the world's population that currently lives in water-stressed countries is expected to rise to two-thirds by 2025. By the year 2050, between 2 and 7 billion people will face water shortages. Inadequate supply of potable water, coupled with higher water demand in developing countries due to rapid population growth and industrialisation, are among the major reasons for the worsening water situation.

Nearly 60% of illness around the world is due to contaminated water and lack of sewer treatment. According to the World Health Organisation (WHO), about 2.4 billion people do not have access to basic sanitation facilities, and more than one billion people do not have access to safe drinking water. Unclean water causes diarrhoea, cholera, dysentery, guinea worm infection, typhoid, intestinal worm infection and trachoma [3]. According to the WHO, four billion people get diarrhoea every year that kills nearly 1.8 million people of which 90% are children under the age of five.

Although water is the most common substance in the world, only 3% is fresh water (97% is seawater), and only 1% is available for human consumption. According to many experts even 1% is adequate since fresh water supply is infinite because of the natural water cycle [1,3]. However, the availability and application of water is uneven around the world; in water-stressed countries such as India, China as well as in countries in South-East Asia, Northern Africa and North-East Africa, the situation is especially acute. In India, for example, groundwater from aquifers is being pumped at nearly twice the rate of aquifer recharge from rainfall, while both the demand for water and the country's population is expected to increase at least 50% by 2050 [4].

Further, the quality of available or useable water is decreasing due to increasing water pollution from industrial, agricultural and other human activity. In fact, it is becoming a major environmental problem today. For example, due to excessive use of fertilisers in India's bread-basket state of Punjab during the last 40 years, the nitrate level in groundwater has exceeded the carcinogenic level of 50 parts per million (ppm) in many areas [4]. Nitrates are a health concern because they are converted to nitrites which interfere with hemoglobins to exchange oxygen in blood. This can cause serious problems especially for fetus and children. Nitrate residues also accelerate eutrophication – enrichment of ponds and lakes by nutrients that results in oxygen depletion – of water bodies. Another major source of water pollution is chlorine, which is used in pulp and paper bleaching, metal processing, pharmaceutical manufacturing, textile dyeing and cleaning, corrosion control, photography and water treatment [3]. Arsenic, a carcinogen at concentrations greater than 10 parts per billion (ppb), occurs naturally in groundwater in several countries. The problem is especially acute in Bangladesh where 60 million people are seriously affected by arsenic in natural drinking water. Similarly, endocrine-disrupting compounds in wastewaters from pharmaceutical, cosmetic and food processing plants in even trace amounts (ng/l) are carcinogenic, and pose a problem due to incomplete removal by conventional primary and secondary treatment processes. Prominent among the endocrine disrupting contaminants are steroid hormones that are continuously excreted by humans and animals.

Scarcity of water resources is also often the limiting factor for economic and social development. Water is needed not just for drinking, household purposes and for agriculture, but also for manufacturing goods, food processing and power generation. Industrial water purification has been growing in the US at approximately twice the GNP, according to the American Society of Testing Materials. Highly purified water plays a critical role in the manufacture and use of advanced materials such as biotechnology, quenching of turbine forgings, final rinsing of fluorinated polymer films, manufacture of new glass laminates, and the use of ultrahigh purity (resistivity ≥ 18.2 M**Ω**-cm) water in the production of graphite fibres and microchips. Current and looming water scarcity and the effects of environmental pollution, groundwater degradation and global warming on water availability can have severe and adverse effects on the world economy, especially developing countries. This may lead to human displacement at an unprecedented scale. It is imperative, therefore, that existing water resources are preserved and advanced treatment processes are deployed to provide potable water.

Water demands and its quality depend on its usage, which varies from region to region. Water shortages have been attributed to varied reasons such as nearly 50% loss due to leaks in piped water systems and inefficient usage of water (70–90% of available water) for agricultural irrigation. For example, intensive and indiscriminate pumping of groundwater is depleting the huge Ogallala aquifer in middle America eight times faster than it is being replenished. Similarly, excessive use of water required for high-yielding grain crops is depleting groundwater in the Punjab region of India [4]. Water scarcity problems, however, can be solved by a combination of water conservation, reclamation, recycling and desalination, as discussed in Chapter 3.

Industrial water management relies heavily on separation science, e.g. coagulation and flocculation are used to separate or remove suspended solids from water for clarification by accelerating their settlement rates during conventional treatment. Membrane filtration processes – ultrafiltration (UF) and microfiltration (MF) – are being used for treating waste water in lieu of coagulants such as aluminium sulphate (alum) and polymers, thereby eliminating the production of sludge and its disposal (see Figure 3.47). Separation techniques such as adsorption, ion-exchange, membrane separation and chemical coagulation and precipitation are being deployed for removing arsenic from groundwater.

RO membrane separation has been traditionally used for seawater and brackish water desalination, and production of high-purity water for food, pharmaceutical processing and industrial waste treatment, as discussed in Chapter 1. The development of nanofiltration (NF) membranes has opened up many areas of application including water softening, removal of disinfection by-product precursors (trihalomethanes), removal of total organic carbon (TOC), food processing and industrial water treatment [5].

Low-pressure membrane filtration using MF and UF membranes is becoming the separation processes of choice for municipalities for removing turbidity and pathogens [6,7]; membrane filtration has proven to be very effective and reliable in removing microbiological parasites, *Giardia* and *Cryptosporidium*, since first used in this application in 1995. Increasingly integrated UF/MF-RO membrane systems are being used for the reclamation of industrial and municipal water where UF or MF replaces conventional filtration for treating RO feed water, e.g. treating secondary treatment effluent with membrane filtration followed by RO membrane treatment for producing water for industrial use and aquifer recharge, and RO seawater desalination pre-treatment [8]. Several case studies of integrated membrane systems used in water treatment are discussed in Chapter 3.

The reasons why membrane filtration is becoming the preferred technology for water treatment complementing RO or NF membrane systems are detailed below:

- Development of high-frequency backwashed UF and MF processes for combating membrane fouling using high integrity hollow fibre membranes.
- Application of dead-end MF/UF systems, well-suited for municipal raw water treatment because of low particle count.
- Reliable and consistent high-quality product water including removal of parasites and pathogens.
- Minimal use of chemicals thereby meeting stringent water pollution standards with ease.
- Reliable and well-established membrane plant operation.
- Automated control of systems resulting in reduced operating labour costs.
- Small footprint and modular design allowing for easy future expansion.
- Increasingly cost-competitive; the cost of RO membranes dropped substantially in the last two decades while the permeate production has increased threefolds [9].

- Proven integrity of membranes albeit with a limited life span of 3–5 years for polymeric membranes. Ceramic membranes, which last longer, are also being deployed but are expensive.

2.2 WATER TREATMENT

The types of impurities depend on the water source. The feed water could be ground water, well water, surface water, seawater, brackish water, or municipal wastewater. Water composition of some typical waters is given in Table 2.1. Surface water usually contains suspended solids, colloids and organics including high bacteria count, and has significant variable quality during the year. Ground water and well water usually have low amounts of suspended matter but may contain iron, manganese and hardness ions of calcium and magnesium [10]. Industrial wastewaters are regulated for suspended solids,

Table 2.1 Composition of typical feed waters

Item/ion	River[a]	Lake[b]	Well[c]	Brackish[d]	Seawater
Cations					
Calcium	50[e] (125[f])	38	114	129	400
Magnesium	14 (57.4)	8	19	89	1252
Sodium	35 (76.3)	11	–	521	10,561
Anions					
Bicarbonate	158 (129.5)	117	170	161	140
Carbonate	1.2 (2)	–	–	–	–
Hydroxyl	–	–	–	–	–
Sulphate	97 (100.9)	26	29	1260	2650
Chloride	16 (22.6)	18	76	262	18,980
Nitrate	4.6 (3.7)	1.8	–	–	1.5
Fluoride	–	–	0.1	–	1.4
Boron	–	–	–	2.8	4
Other					
Silica	13 (2.1)	12	10	49	–
Iron	0.1 (0.01)	3.5	Trace	1.2	–
Manganese	–	0	0.01	–	–
pH	7.9	6.8	7.5–8.4	7.7	–
Turbidity	58	0–20	0	–	–
TDS	–	–	–	2478	33,990
Alkalinity[f]	132	96	140	133	115
Hardness[f]	183	128	363	692	6133

[a] Mississippi.
[b] Lake Erie.
[c] West Virginia.
[d] Coalinga, California.
[e] Ion as mg/l.
[f] Ion as $CaCO_3$.

free oil and grease, pH and biochemical oxygen demand (BOD) and heavy metals, and often contains mineral acidity, detergent compounds and trace amount of chemicals and heavy metals due to industrial pollutants. Membrane separation processes are also used to treat these waters for environmental pollution control [11].

Once the feed water source has been determined, analysis of the feed water composition is necessary before a treatment system can be designed. Feed water constituents that must be analysed prior to designing a RO/NF membrane system as per ASTM Designation D4195-88 "Standard Guide for Water Analysis for Reverse-Osmosis Applications" are discussed in Chapter 6. Typical water treatment methods are summarised in Table 2.2.

In the case of municipal wastewater for reclamation, secondary treatment effluent is often the feed water for membrane plants. Preliminary and primary treatment remove heavy solids, fine suspensions, grease and fats. Sometimes raw water is chlorinated for odour control. In the case of raw municipal wastewater, primary treatment removes 30–50% of suspended solids. The remaining organic matter is removed in biological secondary treatment [12,13]. Typically, RO/NF feed water is primary treatment effluent except when the feed water source is brackish water or seawater. RO/NF pretreatment is used to remove (a) certain dissolved solids and minerals, (b) organics, (c) virus and pathogens, (d) trace metals, (e) nutrients, and (f) removing remaining suspended solids in order to minimise fouling and scaling. The water treatment unit operations (UOPs) discussed include [10,12,14]:

- Coagulation
- Softening
- Granular media filtration
- Activated carbon filtration
- Membrane filtration
- Deaeration-Decarbonation
- Chemical oxidation
- Disinfection
- Electrocoagulation
- Ion exchange (IX)

When RO product water needs to be polished to produce higher grade water, several or all of UOPs listed below are also required. These UOPs remove trace amounts of contaminants such as ions, gases, particles, microorganisms and organic compounds:

- Mixed-bed IX
- Electrodeionisation (EDI)
- Membrane degasification
- TOC ultraviolet radiation

Besides feed water characteristics and product water quality, capital costs (CAPEX) and operating costs (OPEX), manpower, space availability, and future expansion requirements, and

Table 2.2 Water constituents and treatment methods

Constituent	Chemical formula	Effect/problem	Treatment
Turbidity	None (expressed as Jackson Turbidity Units, JTU)	Imparts unsightly appearance to water. Deposits in water lines and process equipment. Interferes with most process uses	Coagulation, settling and filtration
Colour	N/A	May cause foaming in boilers	Coagulation, and filtration, chlorination, activated carbon, anion exchange, NF
Hardness	Ca^{2+} and Mg^{2+} salts expressed as $CaCO_3$	Chief source of scale in heat-exchange equipment, boilers and pipelines. Forms curds with soap, interferes with dyeing	Softening, demineralisation, surface-active agents, NF, RO, ED
Alkalinity	HCO_3^- CO_3^{-2} and OH^- expressed as $CaCO_3$	Foaming and carryover of solids with steam. Embrittlement of boiler steel. Bicarbonate and carbonate produce CO_2 in steam, a source of corrosion in condensate lines	Lime and lime-soda softening, acid treatment, hydrogen zeolite softening, demineralisation, dealkalisation by anion exchange, degasification
Free mineral acids	H_2SO_4, HCl, etc. expressed as $CaCO_3$	Causes corrosion	Neutralisation with alkalies
Carbon dioxide	CO_2	Causes corrosion in water lines, particularly steam and condensate lines	Aeration, deaeration, membrane contactors, neutralisation with alkalies
pH	Hydrogen ion concentration defined as: $pH = \log (1/H^+)$	pH varies according to acidic or alkaline solids in water. Most natural waters have a pH 6.0–8.0	pH can be increased by alkalies and decreased by acids
Conductivity	None (expressed as microSiemens/cm)	High conductivity can increase the corrosive characteristics of water	Demineralisation, lime softening, RO, ED, NF

Nitrate	NO_3^-	Adds to solids content. Useful for control of boiler-metal embrittlement	Demineralisation, distillation, RO, ED
Silica	SiO_2	Causes scale in boilers and cooling water systems, which forms insoluble turbine blade deposits	Hot-process removal with magnesium salts, adsorption by highly basic anion-exchange resins, in conjunction with demineralisation
Sodium	Na^+	Adds to solids content of water. When combined with OH^-, causes corrosion under certain conditions	Demineralisation, RO, ED, distillation
Aluminium	Al^{+3}	Usually present as a result of floc carryover from clarifier; can cause operation deposits and contribute to scaling	Improved clarification and filtration
Iron	Fe^{+2} (ferrous) Fe^{+3} (ferric)	Discolours water on precipitation. Source of deposits in water lines, and boilers. Interferes with dyeing, tanning and papermaking	Aeration; coagulation and filtration, lime softening; cation exchange; contact filtration, surface-active agents for iron retention, greensand filtration
Manganese	Mn^{+2}	Same as iron	Same as iron
Oxygen	O_2	Causes corrosion of water lines, heat exchange equipment, boilers and return lines	Deaeration, membrane contactors, sodium sulphite, corrosion inhibitors
Hydrogen sulphide	H_2S	Causes of "rotten egg" odour and corrosion	Aeration, chlorination, strong basic anion exchange
Ammonia	NH_3	Corrosion of copper and zinc alloys by formation of complex soluble ions	Cation exchange with hydrogen zeolites, chlorination, deaeration

Source: Branan, Gulf Publishing Co., 1998.

the efficacy of the specific techniques are considered in developing a water treatment system for a given application.

2.2.1 Coagulation

Coagulation is a chemical process for removing particles in suspended or colloidal form. These particles do not settle on standing and cannot be removed by conventional physical treatment processes. The settling time for silt, for example is about 3 h as compared to 3 years for colloids. Suspended solids and colloids resist agglomeration because of the similar electrical charge (usually negative charge) on their surfaces that creates a mutually repellant force. The charge repellant behaviour is depicted in Figure 2.1 and is explained by the concept of "Zeta Potential" in Chapter 6.

Colloids are particles in the size range of 0.1 (10^{-8} cm) to 1 nm (10^{-7} cm). They are either hydrophobic (e.g. clays) or hydrophilic (e.g. poorly ionised organic acids). High-valence cation (Mg^{2+}, Al^{3+}) coagulants neutralise the negative charges thereby allowing the particles to come together or coalesce; the larger particles then precipitate and removed via sedimentation or filtration. A clarifier used for both coagulation and settling is shown in Figure 2.2. Chemical coagulants include aluminium sulphate (alum), ferric chloride, lime and polymers (see Table 6.8). Low-molecular-weight cationic polymers and inorganic aluminium and iron salt (e.g., alum and ferric sulphate) are the most commonly used positively charged coagulants [10,12,14].

Coagulation is a two-step process: first, the zeta potential is reduced to a level below the van der Waal's attractive forces, and second, the micelles aggregate to form clumps that agglomerate the colloidal particles [10,12,13]. The mechanism of the coagulation process is shown in Figure 2.3. For an effective coagulation, alkalinity should be added first (bicarbonate provides alkalinity without raising the pH), alum or ferric salts are added next, and coagulant aids such as activated silica and/or polyelectrolyte for floc build-up and zeta potential control are added last. Activated silica is a short chain polymer that binds together particles of microfine aluminium hydrate. Polyelectrolytes are high-molecular weight polymers capable of forming bridges between particles or charge flocs. Large flocs (0.3–1 mm) are created when small dosages are added with alum or ferric chloride.

The reaction of alum $[Al_2(SO_4)_3 \cdot 18H_2O]$ when added to water in the presence of alkalinity is:

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Ca(OH)_2 \rightarrow 3CaSO_4 + 2Al(OH)_3 + 18H_2O \tag{2.1}$$

The alum floc is least soluble at a pH of about 7.0; the floc charge is positive below pH 7.6 and negative above pH 8.2. Aluminium hydroxide is amphoteric and acts as either an acid or a base.

There are three types of polyelectrolytes: cationic, anionic and non-ionic. Sometimes cationic polymers are added as a coagulant. The polymers bring the system to the isoelectric

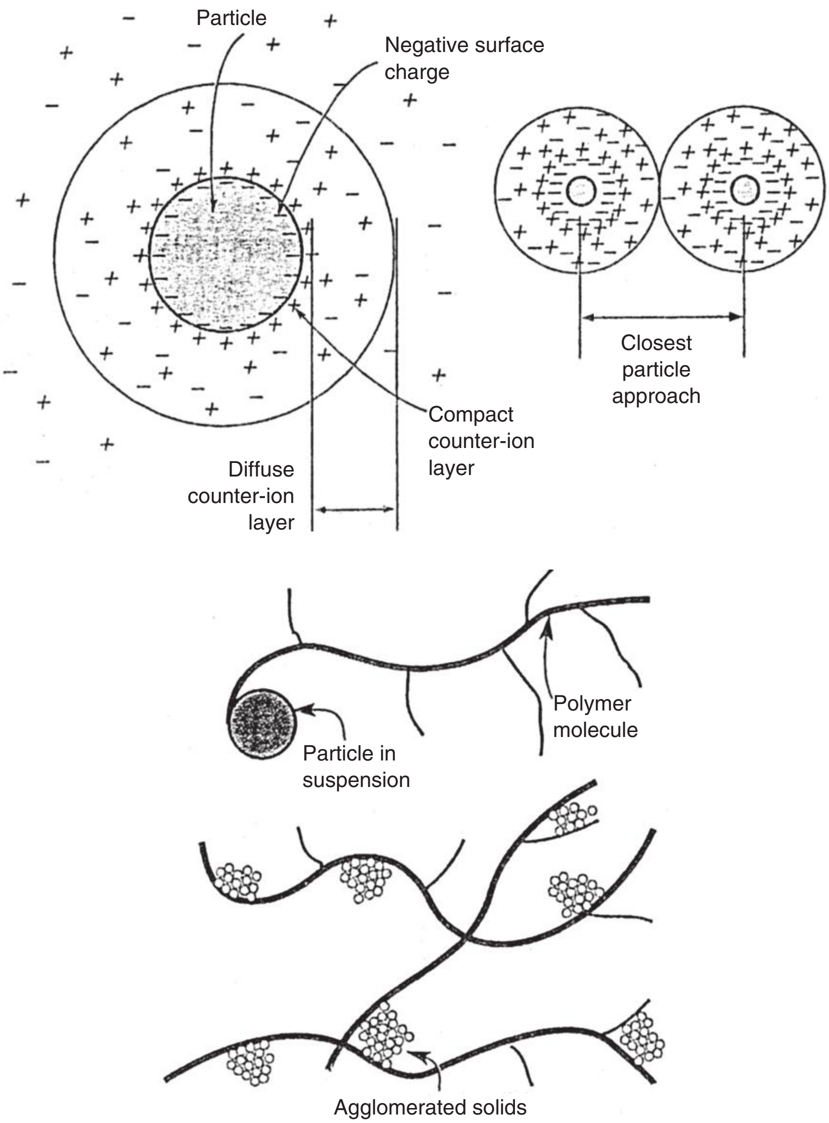


Figure 2.1 Repulsive force between suspended particles limiting or preventing agglomeration due to natural electric surface charge (top). Polymers attach to floc sites and enhance growth by chemical bridging (bottom). Chemical coagulants neutralise the charge reducing the potential barrier and facilitating coalescence into floc.

point without a change in pH. Although polymers are many times more effective than alum, they are quite expensive. The dosage range for a cationic polymer is 2–5 mg/l vs. 75–250 mg/l for alum. The dosage range for anionic and non-ionic polymers is 0.25–1.0 mg/l.

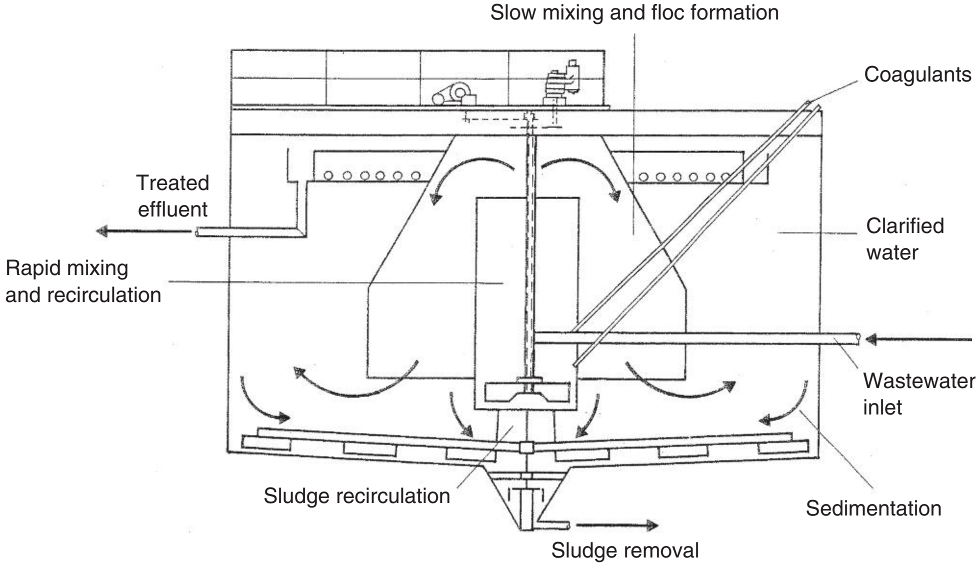


Figure 2.2 A reactor/clarifier designed for both coagulation and settling. *Source: Eckenfelder, Reproduced with permission from McGraw-Hill.*

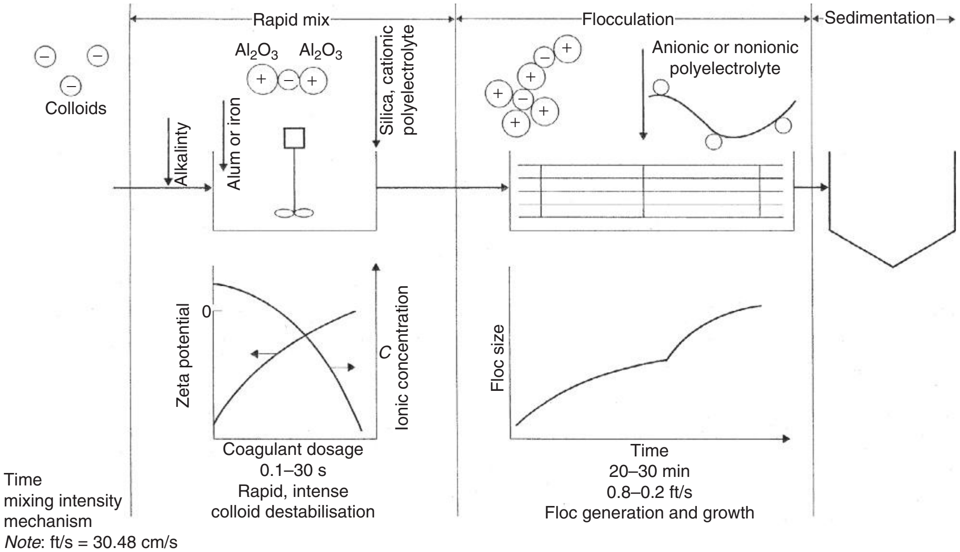


Figure 2.3 Mechanism of coagulation. *Source: Eckenfelder, Reproduced with permission from McGraw-Hill.*

Some clarification systems concentrate on producing only a fine or pin floc, which is then removed by in-line coagulation (coagulants are typically fed to the influent side of a media filter and allowed to mix in-line with the aid of an in-line mixer). In-line coagulation increases particle size and, therefore, filterability of solids that have carried over. Typical coagulant feed rates range from 0.5 to 20 mg/l, with dosage for inorganic coagulants generally higher than polymeric coagulants. This process eliminates the large settling clarifier and produces high clarity water more quickly in smaller equipment.

2.2.2 Softening

Softening refers to removing calcium and magnesium hardness by chemicals. However, silica, alkalinity and other constituents are also removed during lime softening. Other water softening methods include ion exchange and NF membrane separation.

Lime softening

Lime, sodium carbonate (soda ash), and/or sodium hydroxide (caustic soda) are added to water to convert soluble calcium and magnesium hardness to insoluble calcium carbonate and magnesium hydroxide in a contact vessel for 60–90 min [10,12,14]. Lime is not a true coagulant but reacts with bicarbonate alkalinity to precipitate calcium carbonate. Magnesium hydroxide precipitates at high pH levels. The solids are collected as sludge from the bottom of the settling basin. The sludge-free water is clarified by filtration to remove any turbidity and remaining solids thereby ensuring there is no carryover.

Calcium and magnesium occur as bicarbonates primarily. Lime and caustic soda break down the bicarbonate ions $(HCO_3)^-$ into water molecules and insoluble carbonate ions $(CO_3)^{2-}$ as follows:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O \tag{2.2}$$

$$2NaOH + Ca(HCO_3)_2 + Ca^{2+} \rightarrow 2CaCO_3 \downarrow + 2H_2O + 2Na^+ \tag{2.3}$$

Similarly, lime or caustic soda are used to provide hydroxide for precipitation of magnesium hardness as $Mg(OH)_2$. Hardness may also be present in non-carbonate form as sulphate, chloride, or nitrate. In the case of non-carbonate calcium compounds, carbonate for precipitation is provided by adding sodium carbonate (soda ash):

$$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3 \downarrow \tag{2.4}$$

Cold lime softening is never complete because calcium carbonate and magnesium hydroxide are slightly soluble in water. Hot lime softening (HLS) with water heated to 100°C, on the other hand, significantly reduces silica in addition to hardness and alkalinity. Heating aids in the completion of the softening reaction, which in turn increases the efficacy of silica removal by providing more solids, particularly magnesium hydroxide that absorbs silica. HLS is not, however, used for potable water applications.

Lime softening is followed by filtration to remove any turbidity and solids. Inorganic coagulants are typically used to minimise carryover in cold process softening, whereas anionic polymers are used with hot process softening. Effluent hardness from a cold process softener ranges from 35 to 80 mg/l; effluent hardness from a hot process softener is as low as 10–40 mg/l. In order to reduce the hardness further (1 mg/l), ion-exchange softening is required.

Coagulants are often added in conjunction with lime to increase the settling rate of calcium carbonate and magnesium hydroxide. Most of these coagulants are acidic in nature and react with the alkalinity of the water. Commonly used coagulants include aluminium sulphate (alum), sodium aluminate, ferric sulphate and ferrous sulphate (Table 6.8). Alum reacts with natural alkalinity in water to form aluminium hydroxide floc (Equations 2.5–2.8) [14]. About 1 ppm of alum decreases water alkalinity by 0.5 ppm and produces 0.44 ppm of CO_2:

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Ca(HCO_3)_2 \Leftrightarrow 2Al(OH)_3 + 3CaSO_4 + 18H_2O + 6CO_2 \quad (2.5)$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Mg(HCO_3)_2 \Leftrightarrow 2Al(OH)_3 + 3MgSO_4 + 18H_2O + 6CO_2 \quad (2.6)$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 6Na(HCO_3)_2 \Leftrightarrow 2Al(OH)_3 + 3Na_2SO_4 + 18H_2O + 6CO_2 \quad (2.7)$$

$$Al_2(SO_4)_3 \cdot 18H_2O + 3Na_2CO_3 \Leftrightarrow 2Al(OH)_3 + 3Na_2SO_4 + 15H_2O + 3CO_2 \quad (2.8)$$

Ion-exchange softening

Water softening by ion exchange (IX) uses strong acid cation (SAC) resins in the sodium form ($-SO_3Na$) to remove scale-forming cations from water [10,12,14,15]. Ion-exchange softening involves the exchange of hardness ions such as calcium, magnesium, strontium and barium for sodium ions to yield low hardness, or “soft” water (the softened water has a higher total dissolved solids (TDS)), as shown in Equation (2.9), where a cation resin (R) selectively removes calcium ions by the following reaction:

$$R - 2Na + Ca^{2+} \rightarrow R - Ca + 2Na^{+} \quad (2.9)$$

IX softening is typically used when the hardness is in the range of 50–500 mg/l [16], and for feed water flow rates of up to 60 m^3/h (see also Chapter 6).

The exhausted resin is regenerated with a dilute NaCl (brine) solution. This removes calcium and magnesium in the form of their soluble chlorides and at the same time restores the resin to its original sodium form. The bed is rinsed free of undesirable salts and returned to service. The regeneration reaction may be written as:

$$Ca/Mg - R + 2NaCl \rightarrow Na_2R + CaCl_2/MgCl_2 \quad (2.10)$$

The IX softeners normally operate at linear velocities of 14–20 m/h. About 8.5 lb (3.9 kg) of salt (NaCl) is required to regenerate 1 ft^3 (0.3 m^3) of resin, and remove approximately 4 lb (1.8 kg) of hardness. Hardness is given in grains/gallon or in ppm as $CaCO_3$. The reduction is directly related to the amount of cations present in raw water and the amount of salt used to regenerate the resin bed. Typically, 6 lb of NaCl/ft^3 of resin is used for regenerating SAC resins.

Ion-exchange dealkalisation usually employs weak acid cation (WAC) carboxylic acid resins operating on the hydrogen cycle. Dealkalisation and alkaline hardness removal are synonymous terms that mean the water is only partially softened after such a treatment. Complete softening may be achieved by treating it further in the conventional sodium cycle to remove the remaining permanent hardness. The high selectivity for divalent ions such as calcium and magnesium over monovalent sodium ions results in the preferential exchange of calcium and magnesium ions (denoted M^{2+}) [15]:

$$2R-COOH+M^{2+} \rightarrow (RCOO)_2M+2H^+ \tag{2.11}$$

In the presence of hydrogen ions, the above exchange does not occur. However, if alkaline hardness (bicarbonate) is present, the exchanged hydrogen ions are immediately neutralised by the basic bicarbonate and carbonate anions to give carbon dioxide, which dissolves in water as weak carbonic acid:

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \tag{2.12}$$

$$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2 \tag{2.13}$$

The exchange of calcium and magnesium ions continues until all basic anions are neutralised after which time no further exchange can occur. Hence, the extent of hardness removed is equivalent to the alkaline hardness of the water. The resins are regenerated with either dilute hydrochloric acid or dilute sulphuric acid over a period of 30 min. The weak acid resin is regenerated at virtually 100% efficiency. Weak base anion (WBA) resins are also effective in removing strong mineral acid anions such as sulphates, chlorides, and nitrates. Hence, as in the case of IX softeners, WBA are sometimes used to treat RO feed water, thereby, reducing the potential of mineral scaling of RO membrane surface. The exhausted bed is regenerated with sodium hydroxide (caustic soda).

NF softening

Membrane softening by NF is a relatively new application as discussed in Chapter 1. NF membranes (“loose RO”) operate at a lower feed pressure than RO membranes, and have a high rejection (99%) of divalent hardness ions. It is a more attractive alternate to lime softening and IX softening because not only is it a reliable process, no regeneration is required and, thus, there is no chemical wastewater. NF separation like RO is a continuous process and is independent of the plant capacity (flow rate) and feed water hardness. It reduces both the hardness and the TDS to a much greater degree than IX and lime softening [5].

2.2.3 Granular media filtration

Granular media filtration (GMF) is a process for removing suspended or colloidal particles; for example removing suspended solids remaining after sedimentation clarification. It reduces turbidity and improves clarity by removing various sized particles, from coarse sediment down to 10.0 μm [10,12]. Filtration protects IX resin beds and RO/NF membranes elements downstream from particulate fouling. Media filters have different size exclusion ratings, from 10 to 100 μm, depending upon the size of particles to be removed. In general, the removal of suspended and colloidal particles can be done by GMF, dead-end MF and cross-flow MF when the water Silt Density Index (SDI) is about 5. For raw waters containing high concentration of colloidal matter ($SDI > 5$), coagulation and flocculation is required before media filtration.

Granular multimedia filters feature layered beds of anthracite coal (0.8–1.2 mm size), sand (0.5–0.8 mm), finely crushed garnet (0.4–0.6 mm) and magnetite (0.3–0.4 mm) or other materials, as shown in Figure 2.4. The top layer of the bed consists of the lightest and most coarsely graded material, e.g. anthracite coal, whereas the heaviest and most finely graded material, e.g. garnet or magnetite, is the bottom layer. The intermediate layer is silica sand. The specific gravity of anthracite is one-half that of silica sand. A typical bed is 1 m in depth. The principle is "filtration in depth" – larger particles are removed at the top layers, and smaller ones are removed deeper in the filter media, i.e. the entire bed acts as a filter rather than the top few centimetres.

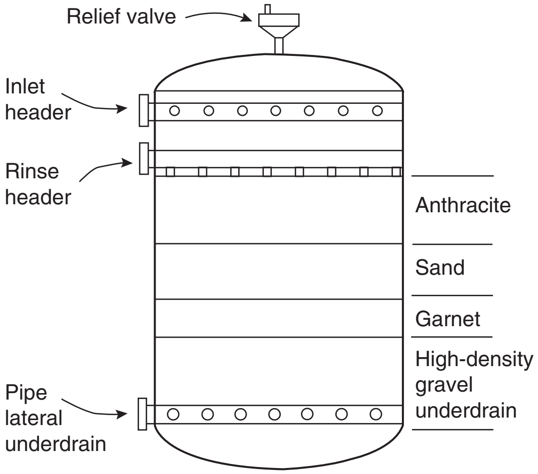


Figure 2.4 A granular media filter with multimedia layers.

During service flow water typically flows downwards from top to bottom under pressure. Typical service superficial flow velocities (flow rates/bed cross-section area) are 7–12 m/h for single-media gravity and pressure filters, 14–20 m/h for multimedia gravity and pressure filters and 12–24 m/h for up-flow filters. Filter operation must avoid channeling and "leakage" of suspended solids; otherwise, the RO membranes will get fouled. Water space above the bed (50–100% freeboard) is provided to allow for bed expansion during backwashing.

Since suspended solids are collected on the media, regular cleaning (backwashing) is required. The rejected particles form a layer on the surface of the media and contribute to blockage of the pores in the filter medium resulting in an increase in the pressure drop (ΔP). Typically, when ΔP reaches 1 bar, the filter is backwashed. During backwashing water flow direction is reversed; it enters the bed through the bottom and flows upwards. This fluidises the bed, which along with the reversed flow, dislodges the silt and carries it to waste. The typical backwash flow rate is 24–36 m/h depending on the temperature, high enough to expand the media bed by at least 50%. The backwash cycle lasts 10–15 min and is followed by a rinse cycle that is accomplished by passing water in a down-flow direction for 5–10 min.

Sometimes coagulants are injected in the feed water line upstream of granular media filters to remove suspended matter of colloidal nature when the particulate matter is either too small or electrostatically repelled from the media. Polymeric coagulants are added in low dosages (<10 mg/l) to remove particles down to 0.5 μm particle size as compared to 10 μm without the coagulant. Anionic coagulants have been shown to reduce the turbidity of raw water to less than 0.5 NTU at a nominal dosage of 1–2 mg/l.

2.2.4 Activated carbon filtration

Activated carbon filtration (ACF) is one of the most effective methods for removing non-polar organic compounds (low, medium and high molecular weight), precipitated iron and chlorine from water [10,12,13]. Activated carbon is a micro-crystalline, non-graphitic form of carbon, e.g. bituminous form of coal that has been processed to develop internal porosity. Activated carbon has the highest volume of adsorptive porosity of any material known to man. Because of its large surface area (1 l of granules has a surface area of 50 ha), activated carbon has a great ability to adsorb organic molecules of liquids or vapours. During feed processing, an organic molecule in the feed enters a surface pore and diffuses to a micropore where it is adsorbed on the carbon surface by physical attraction due to van der Waal's forces. Up to 95% of organics can be reduced. The organic loading is 2–6 kg per 50 kg of carbon. Aromatic compounds are removed more effectively than aliphatic compounds, and non-polar organic compounds are better removed than polar compounds. In addition, some trace inorganics can be removed when chelated with organic compounds.

Activated carbons have specific properties depending on the material source and the mode of operation. Generally speaking, carbons from bituminous coal have a smaller pore size, a larger surface area and a higher bulk density as compared to lignite carbon. A typical surface area range is from 850 to 3000 m^2/g. Bituminous coal also has a lower "peroxide number" than lignite. Peroxide number is an indicator of catalytic activity of carbon; the lower the number, the higher is the catalytic activity. Property standards used for specifying carbons for a specific application are defined below:

- The Phenol Number is used as an index of carbon's ability to remove taste-and-odour compounds.
- The Iodine Number relates to the ability of activated carbon to adsorb low molecular weight substances (micropores have an effective radius of less than 2.0 μm).
- The Molasses Number relates to the carbon's ability to adsorb high-molecular weight substances (pore size ranges from 1 to 50 μm).

Activated carbon is also used for removing chlorine. Chlorine manifests itself mostly as hypochlorous acid (HOCl) and hypochlorite ion (OCl^-). Hypochlorous acid is the primary disinfectant, and hypochlorite ions are less effective. Hypochlorous acid is removed by reduction with carbon as per the following reaction:

$$C + 2HOCl \rightarrow CO_2 + 2HCl \tag{2.14}$$

Chlorine is adsorbed by carbon in the top 5–10 cm of the bed. The bed depth is typically 1 m. Since chlorine is consumed within the top few cm of the carbon bed, the media is susceptible to bacterial growth when the water temperature is greater than 12°C. A pH range of 6.5–7.5 and water temperature between 12 and 27°C provide the best environment for chlorine removal by activated carbon.

During normal service feed water flows downwards through the bed from top to bottom as in the case of GMF under pressure. The linear flow velocity is 5–10 m/h. The flow is reversed during backwash. The beds are backwashed at 7–12 m/h based on service run time or when the pressure drop across the filter bed exceeds 1 bar. The backwash cycle is followed by a downward flow rinse cycle before the bed is returned to service. Backwashing only removes the material collected on the surface of the media, and not what is adsorbed in the pores. Once the pores are filled with organics, carbon can be either regenerated or reactivated. The modes of regeneration are thermal, steam, solvent extraction, acid or base treatment, and chemical oxidation. In water treatment, thermal regeneration is usually done but weight losses and a loss of capacity result from regeneration.

2.2.5 Membrane filtration

Membrane filtration encompasses UF and MF and should not be confused with RO and NF.

In the last 15–20 years semicontinuous, semicontinuous dead-end MF/UF has emerged as a viable process for treating municipal waters and seawater prior to RO desalination [6–9].

Membrane filtration is used for treating high-turbidity waters, surface waters high in TOC and for tertiary water treatment, and provides a more stable and superior water quality than coagulation–sedimentation and media filtration. It is a simple and cost-effective alternative to conventional water treatment operations.

Membrane filtration is a highly effective barrier to particles such as suspended solids, colloidal particles, cysts and bacteria producing treated water with very low turbidity (0.1 NTU) and consistent quality irrespective of the feed source. It has proven to be very effective and reliable in removing microbiological parasites, *Giardia* and *Cryptosporidium*, since these systems were first deployed in 1995. The application has increased dramatically due to its ability to produce high-quality potable water, small footprint and relatively low cost. These systems operate at very low feed pressures (<1–2 bar) and at relatively low trans-membrane pressure (TMP).

The UF/MF market for municipal water treatment was worth $300 M in 2006 and is projected to double by 2014 [8,17]. This market is broadly divided into three categories: (i) drinking/potable water, (ii) seawater RO/NF pretreatment and (iii) wastewater reuse. Increasingly, UF/MF systems are being used for RO/NF pretreatment instead of conventional pretreatment (coagulation, sedimentation, media filtration). High-pressure membrane systems (RO/NF) operating on UF/MF treated water are less prone to fouling, require minimal chemical treatment and have higher on-stream line. The overall result is a higher RO system throughput and longer RO membrane life.

Membrane filtration like other membrane processes is prone to severe fouling. To a large measure membrane fouling has been addressed by backwashing with water periodically; during backwash the filtered water flows in the reverse direction as shown in Figure 2.5 to dislodge the solids and restore the flux lost as a result of cake build-up on the membrane surface and clogging of the membrane pores [6,9]. However, for more challenging waters, chemical pretreatment is also required [18,19]; for example, addition of coagulants ferric chloride, ferric sulphate, alum, or polyaluminium chloride in low dosages to increase the size of suspended solids and colloidal particles to prevent or minimise colloidal, organic and/or biological fouling (see Table 6.8). Coagulation pretreatment possibly reduces fouling by reducing pore constrictions rather than forming the gel layer since coagulants remove mostly hydrophobic compounds and very little hydrophilic neutral compounds. Coagulant addition is also required to remove TOC and tri-halomethane (THM) precursors. In the treatment of secondary effluent, both coagulation and activated carbon adsorption are effective in removing dissolved organic carbon; carbon adsorption removes both small and large organic compounds whereas coagulation removes predominantly larger molecules including biopolymers and humic substances.

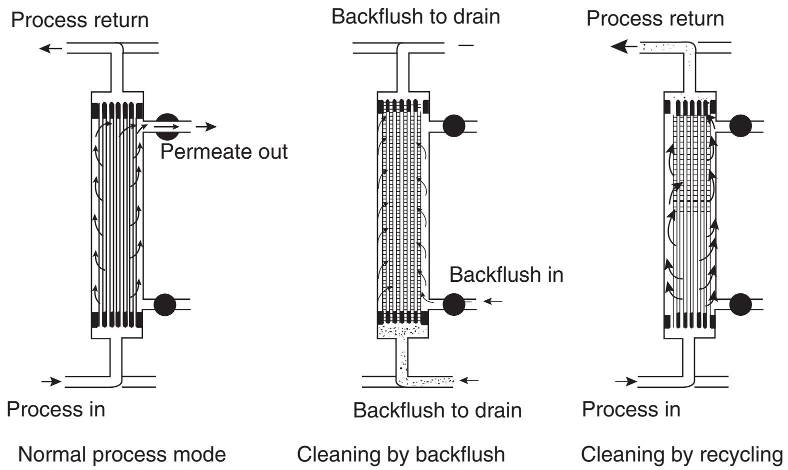


Figure 2.5 Periodic backwashing and co-current permeate flow schemes. *Source: Lonsdale, J. Memb. Sci. 10 (1982), 81–181.*

Continuous cross-flow filtration

Cross-flow UF and MF systems are mainly used for applications in biotechnology, dairy, colour removal from groundwater and industrial wastewater. Industrial wastewater treatment includes electroplating rinse water processing for paint recovery, treatment of oil/water emulsions, processing wastewater containing heavy metals, oil and grease prior to effluent discharge, textile wastewater, and pulp and paper wastewater. Cross-flow UF and MF systems – mostly tubular and hollow-fibre membranes – operate in continuous mode. The feed flow is inside out, i.e. the feed flows in the tube side and the permeate flows radially out of the tube wall. Ninety percent of the reject is typically recycled back to the feed tank at a high velocity of ~ 4–5 m/s. Because of the large i.d. as is the case with tubular membranes, the membrane elements can handle feeds with solid levels of up to 5%. The process is facilitated by operating in a turbulent regime to reduce the build-up of solute cake on the membrane surface. High cross-flow velocity (turbulent flow and surface shear) and large i.d. often eliminates the need for pre-filtration. The permeate flow rate is 10–15% of the cross-flow rate at a flux of ~ 300–500 lmh. Thus, a UF/MF system, designed for 20 m^3/h permeate flow rate, may require a feed/recirculation pump rated for 250 m^3/h at 3–4 bar g feed pressure. Backpulsing with filtered water or permeate reduces the frequency of cleaning cycles. Overall wastewater recoveries of up to 95% are achieved. Cross-flow systems are best suited for relatively small flow systems (up to 100 m^3/h) and special applications. They are not economical for treating large systems such as municipal and seawater treatment because of several drawbacks:

- High cross-flow velocity (high shear rate) means high feed/recycle flow rate resulting in high energy cost of pumping.

- Low surface area and packing density (especially tubular membranes) result in a large footprint.
- Recovery per pass is only 10%.
- Frequent chemical cleaning is required to remove or dissolve the strongly held accumulated particles that are not dislodged with backwashing.
- High Capex and Opex

Semicontinuous dead-end filtration

The most commonly used membranes for municipal water treatment are hollow fibre modules that are supplied in three operating formats: (i) pressure driven inside feed – PDI, (ii) pressure driven outside feed – PDO and (iii) submerged vacuum driven – SUBO [6,9,17]. Classification and specifications of membrane modules are detailed in Table 6.14. These UF/MF systems operate in semicontinuous dead-end mode with intermittent backwash often combined with air scour either during filtration and/or backwash cycles [9]. The flow regime typically is from outside of the fibre (shell side) through the pores in the membrane wall to the lumen side. As the water gets filtered, the solids rejected by the membrane form a layer on the membrane surface. The foulant cake layer is removed by backwashing the membrane elements by air scouring and air-assisted backwash every 30–60 min to maintain the flux (constant flux operation). Over time, chemical cleaning is required to remove traces of foulants that are difficult to dislodge by backwash. Backwashing reduces the frequency of chemical cleaning, thereby, enabling the membrane system to run on feed water with turbidity as high as 500 NTU. The filtrate or product water turbidity is typically $\leq$0.1 NTU. Since the solids content is low ($<$0.5%) in water treatment applications, submerged membranes are now increasingly used instead of pressurised membranes.

Membrane bioreactors

Membrane bioreactors (MBRs) are a special application of membrane filtration and discussed in detail in Chapter 3. It is a novel process that combines a biological stage with a membrane element. In this process, biological degradation of organic pollutants is carried with microorganisms in the bioreactor followed by membrane filtration to separate microorganisms [20,21]. The use of membranes to remove solids from treated wastewater is the main difference between MBRs and conventional biological treatment plants; higher removal efficiency than conventional treatment plants, e.g. the MBR, allows a higher biomass concentration, higher COD removal ($>$90%) and higher separation of solid suspensions (complete retention of the biomass). The MBR process has shown to be more efficient in removing total BOD, turbidity and coliforms. By eliminating the problem of poorly settling flocs when using a MBR system, there is more biological degradation resulting in higher treatment efficiency.

The types of membranes used in MBRs are (i) flat sheet (FS), (ii) hollow fibre (HF) and multitube (MT). There are two types of MBR technologies: (a) external MBR (eMBR) in which the membrane modules are placed outside the bioreactor (MT only), and (b) submerged MBR (sMBR) where the membrane module is placed inside the bioreactor (FS and HF) [20]. The sMBR is more economical and energy efficient: (a) there is no recycle pump since aeration generates a cross-flow across the membrane surface, and (b) the operating conditions are milder because of lower values of TMP and tangential velocity. The TMP values are 1–4 bar for eMBR and 0.5 bar for sMBR systems. The permeate flux for sMBR, however, is lower: 15–50 lmh vs. 50–120 lmh for eMBR. Polymeric MF membranes with a pore size of 0.1–0.4 μm are the main membranes used in sMBR systems while tubular inorganic membranes are generally used in eMBR units. The eMBR units are preferred to sMBR units when treating concentrated effluents or concentrated biomass to avoid membrane fouling; higher shear rate is achieved because of higher recycle flow rate.

For municipal wastewater treatment, MBR systems are economically attractive where space is limited especially in urban areas or when high effluent quality is required for water reuse. Most MBR units use submerged membrane plates or hollow fibres. Fouling by microorganisms as a result of microbial products, concentration and size of particles is one key area of process deficiency. Different strategies have been considered for controlling fouling including backwashing. In addition, there is concern whether oxygen can become the limiting factor during aerobic biological activity [20]. Since the particulate solids content in the wastewaters treated by submerged MBR systems is relatively high (e.g. TSS = 10–15 mg/l) with additional colloids and macrosolutes, bubbled cross-flow is used to minimise concentration polarisation and subsequent fouling [9].

2.2.6 Deaeration-decarbonation

Air stripping is used to remove oxygen, carbon dioxide, ammonia and volatile organic compounds (VOCs) from water. Decarbonation removes alkalinity – carbonate, bicarbonate, carbon dioxide – by acidification and stripping the resulting carbon dioxide. Carbon dioxide is removed from RO product water to reduce the load on ion exchange resins downstream. Stripping of carbon dioxide increases the water pH, and thus reduces the corrosive properties of water. Forced air decarbonation is always used in conjunction with either RO or IX.

Ammonia is easily stripped since it is volatile. When the pH of water is raised above 9.3, the equilibrium point, ammonium ions in water convert to ammonia as per Equation (2.15) given below as the equilibrium shifts to the left. The pH range for stripping ammonia is 10.8–11.5:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{2.15}$$

In the case of stripping VOCs such as halogenated hydrocarbons that are carcinogenic, the process relies on the tendency of moderately soluble organic compounds to vaporise based on Henry's law.

Air stripping requires packed towers for maximum operational efficiency [13]. Water is pumped to the top of a tower packed with media as shown in Figure 2.6. The water is evenly distributed across the media. As it flows down under gravity it forms a film layer on the packing surfaces. Air is blown upwards from the bottom contacting the large surface areas. The blown air enhances the removal of the volatile species by mass transfer. Degasification is

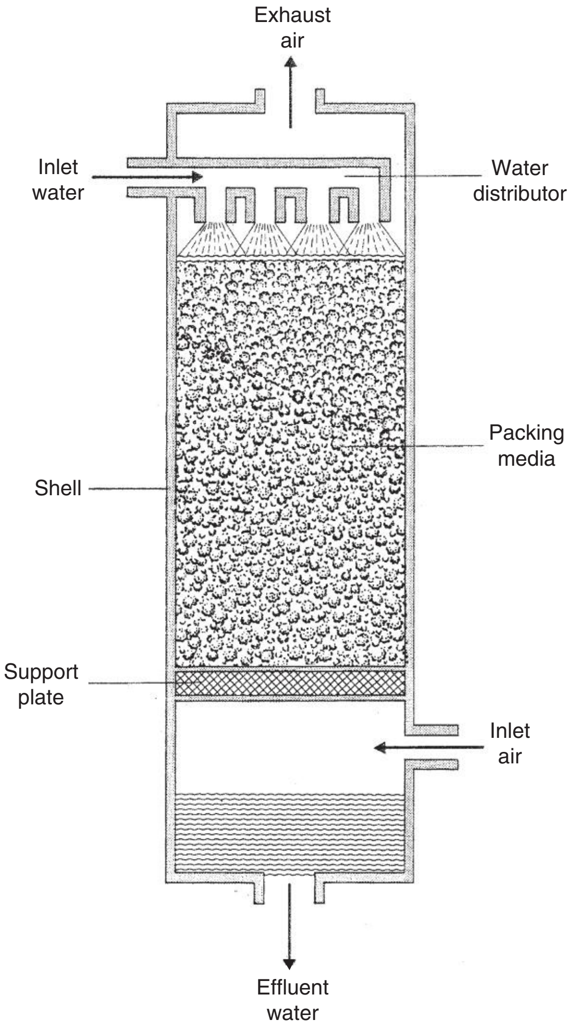


Figure 2.6 Typical packed tower. *Source: Eckenfelder, Reproduced with permission from McGraw-Hill.*

usually not economical if water alkalinity is less than 100 mg/l or 20% of total anions, or if the water flow rate is less than 5–6 m^3/h. The ratio of gas to liquid is in the range of 100–1 (volume basis).

2.2.7 Chemical oxidation

Chemical oxidation is used to control inorganics (manganese, ferrous iron, sulphur, sulphite and cyanide irons) and organics (phenols, amines, humic acids, toxic compounds, bacteria and algae) by converting them to unharmful products [10]. The oxidising agents used include air, oxygen, ozone, hydrogen peroxide, chlorine, chlorine/hypochlorite and chlorine dioxide. Aeration followed by chlorination is very efficient at precipitating sulphur, which can then be removed via filtration. Contact times of 3–4 h can reduce the hydrogen sulphide levels by up to 3 ppm via aeration alone. Hydrogen sulphide is generally found in well water, particularly shallow wells. Chlorination increases the kinetics of precipitation, and at the same time acts as a germicide to minimise the growth of sulphur bacteria, which are the source of hydrogen sulphide. Chlorine, potassium permanganate and ozone are also effective in destroying many odorous compounds.

Manganese greensand oxidation-filtration

Some well waters, usually brackish waters, contain divalent ferrous iron, manganese and sometimes sulphide in the absence of oxygen. When water is exposed to air or is chlorinated, these compounds are oxidised resulting in the formation of insoluble colloidal hydroxides and elemental sulphur as [12,14]:

$$4Fe(HCO_3)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 + 8CO_2 \tag{2.16}$$

$$4Mn(HCO_3)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3 + 8CO_2 \tag{2.17}$$

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \tag{2.18}$$

The manganese greensand filtration (MGF) process employs manganese greensand as the filter medium to remove soluble iron, manganese and hydrogen sulphide by one-step oxidation filtration. The filter bed consists of anthracite filter media over manganese zeolite (greensand). Greensand is processed from glauconite, which is an iron potassium alumino-silicate material of marine origin. The filter-bed material acts as a catalyst for the reaction of iron with oxygen. It can supply the necessary oxygen, which must be replenished with an oxidising regenerant solution such as potassium permanganate ($KMnO_4$).

The most common method of oxidative MGF is known as continuous regeneration. Permanganate solution (1–2%) is injected into the raw water feed water line. Precipitation of iron and manganese occurs in the anthracite bed as per the reaction in Equation (2.19). Heavier precipitates are filtered out in the anthracite bed, and the remaining fines and residual dissolved metal are removed by greensand. The water pH should be about 7.2.

$$\mathrm{Fe(HCO_3)_2 + KMNO_4 \rightarrow Fe(OH)_3\downarrow + MnO_2\downarrow} \tag{2.19}$$

Iron concentrations up to 15 ppm can be effectively removed, although concentrations greater than about 3 ppm require low service flow rates, which results in short runs between the backwash cycles. At low feed water iron concentrations, the flow velocity is 14–20 m/h for up to 36 h between the backwash cycles. Lower flow velocity 4 m/h and shorter service run lengths are advised when the feed water iron concentration is 3–15 ppm.

2.2.8 Disinfection

Disinfection of RO/NF feed water is required to prevent biofouling of the membranes. However, the disinfected water must be treated with reducing agents if the membrane polymer, e.g. polyamide is damaged by oxidants. Disinfection is the selective destruction of pathogenic organisms (bacteria and viruses). Recently, microconstituents such as endocrine disrupting compounds as well as pharmaceutical and personal care products have also come under review. Disinfection is not the same as sterilisation, which implies the destruction of all organisms. Disinfection treatment methods commonly used include (a) chlorination or ozonation chemical means, (b) photochemical means, e.g. ultraviolet disinfection and (c) physical means such as membrane filtration. Parasites such as *Giardia lamblia* and *Cryptosporidium parvum* are resistant to conventional forms of disinfection such as chlorination, but are removed by other methods such as ozone, ultraviolet irradiation, and membrane filtration.

Chlorination

The disinfectant action of chlorine results from its strong oxidising action on bacterial cell's chemical structure that destroys the enzymatic processes required for life [12]. The effectiveness of chlorine disinfection is a function of the product of contact time and chlorine residual. Chlorine gas is soluble in water (7160 mg/l at 20°C and 1 bar), and hydrolyses rapidly to form hypochlorous acid or as the hypochlorites of sodium and calcium:

$$\mathrm{Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-} \tag{2.20}$$

$$\mathrm{NaOCl + H_2O \rightarrow HOCl + NaOH^-} \tag{2.21}$$

$$\mathrm{Ca(OCl)_2 + H_2O \rightarrow 2HOCl + Ca(OH)_2} \tag{2.22}$$

Hypochlorous acid (HOCl) dissociates in water to hydrogen ions and hypochlorite ions (OCl^-). The sum of Cl_2, NaOCl, $Ca(OCl)_2$, HOCl and OCl^- is referred to as "free available" chlorine. The power of free chlorine residual decreases with increasing pH.

Hypochlorous acid concentration at 20°C is 90% at pH 7, 50% at pH 7.6 and 10% at pH 8.6. Almost the reverse is true for hypochlorite ions. Hence, automatic monitoring of residual chlorine and automatic feedback of injection rate is necessary to prevent overdosage or inadequate disinfection. Minimum chlorine residuals for bactericidal disinfection after 60 min of contact vary between 1 ppm at pH 6.0 and 1.8 ppm at pH 8.0. A hypochlorous residual of 0.5–1.0 ppm is effective within 30 min.

In gaseous form chlorine is extremely hazardous. Liquid chlorine is shipped in pressurised steel cylinders. One volume of liquid chlorine yields about 450 times vapour volume. Because of safety concerns liquid chlorine compounds such as sodium hypochlorite are used instead. Sodium hypochlorite (NaOCl) is handled in liquid form at concentrations between 5 and 15% available chlorine. Calcium hypochlorite [$Ca(OCl)_2$] contains about 70% available chlorine.

An alternate technique is on-site generation of NaOCl, which is achieved through electrolysis by applying an electrical current to a solution of salt (preferably food-grade) and water. The electrolytic cell is the heart of the oxidant producing unit. The cell consists of two electrodes placed so that both make contact with the water and brine solution. A by-product of the electrolysis reaction is hydrogen gas, which is safely removed from the cell and the oxidant storage system. On-site generators are used to provide disinfection for swimming pools, cooling towers and sanitation for clean-in-place operations. The largest application of on-site NaOCl generators is for municipal drinking water disinfection.

Ozonation

Ozone is a strong oxidant and disinfectant. It has similar bactericidal properties to chlorine and is at least equal to chlorine in its ability to perform virus inactivation [12]. Ozone is also an option for odour control in reclaimed wastewater treatment. Ozone oxidises organic contaminants via a reaction with molecular ozone (O_3) or through a reaction with the hydroxyl radical ($OH^{\bullet}$), which is formed often in the presence of a catalyst when ozone is added to water. Ozone is generated on-site from air or oxygen zone when a high voltage is imposed on a discharge gap. It is generated on-site because it is a relatively unstable gas with a half-life of about 10 min. When ozone is added to water, it rapidly reverts to oxygen so that no chemical residuals remain in the ozonated water. Chlorine is added for post-disinfection, if required. There are, however, some adverse health effects due to the formation of bromates and aldehydes as by-products. The maximum allowable limit of bromate, a carcinogen, in drinking water is 25 ppb (μg/l).

UV irradiation

Ultraviolet (UV) light represents a band of electromagnetic light in the 100–400 nm range. It is a non-chemical disinfectant process that uses a very short contact time (<5 s). UV light is used to break specific chemical bonds, sometimes by direct photolysis, but usually by the creation of highly reactive hydroxyl (OH-) radicals. Photolysis applications include dechlorination, de-ozonation, removal of TOC and more recently to counter the threats caused by endocrine disruptors and pharmaceutical compounds (both metabolised and un-metabolised).

UV disinfection avoids a major disadvantage of chlorination, i.e. the generation of harmful by-products such as trihalomethanes. UV disinfection ensures that the drinking water is free from pathogens such as *e-Coli*, *Legionella* and *Cryptosporidium*. UV is also extensively used in manufacturing processes such as bottled water, beer, carbonated soft drinks and ultrapure water. Disinfection by UV radiation involves damaging the genetic material of organisms by energy in the form of light of wavelength 254 nm emitted from a low-pressure mercury vapour lamp [12]. This particular wavelength alters the genetic material (DNA) of bacteria, viruses and other microorganisms. With their DNA altered, they are unable to reproduce and die within minutes. The dead bacteria produce TOC.

For microbial destruction, 254 nm UV energy is used, whereas shorter (and more powerful wavelength) electromagnetic radiation, 185 nm UV energy, is used to reduce organic compounds and chlorine destruction. The energy of a light beam is inversely proportional to the wavelength. Thus, 185 nm UV irradiation carries more energy and is more powerful than the 254 nm light; 185-nm energy oxidises total oxidisable carbon (TOC) to form carbon dioxide and water. Most microorganisms are damaged at a UV irradiation dosage level of 10,000–30,000 μW-s/cm^2, whereas the dosage level required for reducing ozone, chlorine and TOC reduction is 90,000 μW-s/cm^2.

UV systems generally consist of a reactor with a number of lamps that emit UV radiation. Each lamp is encased in a quartz tube. As the water flows thorough the lamps, it gets radiated. Polytetrafluoroethylene (PTFE) is also used since PTFE is transparent to UV radiation. UV radiation dosage is determined by residence time in the reactor and the intensity of radiation. The effectiveness of a UV system depends on the hydraulic design of the reactor, absorbance of liquid, presence of particles and transmittance of the lamps and the quartz tubes. Intimate contact between the liquid and the lamps needs to be maintained at all points in the reactor since radiation diminishes with distance. Contact time for radiation exposure is maximised by maintaining plug flow in the reactor and by creating turbulence to cause transverse dispersion. The UV lamp's intensity typically drops to 60% in a year or after 8000 h of use.

2.2.9 Electrocoagulation

Electrocoagulation (EC), a radio frequency technology developed 100 years ago, is a simple and effective technology for treating a wide range of waters including municipal water and industrial wastewaters prior to membrane treatment [22–24]. The EC reactor is an electrochemical cell. EC involves the generation of coagulants in situ by dissolving aluminium or iron electrodes; the generation of metal ions takes place at the anode and hydrogen is generated at the cathode as an electrolysis product. Hydrogen helps to float the flocculated particles out of water. The electrodes are arranged in a mono-polar or bipolar mode. The electrodes are in plate form or in packed form of metal scraps. The reactions occurring in an EC reactor are shown schematically in Figure 2.7.

The electrolytic dissolution of Al anode in water produces:

$$Al \Rightarrow Al^{3+} + 3e^{-}$$

and, water decomposition at the cathode produces hydrogen bubbles:

$$2H_2O + 2e^{-} \Rightarrow H_2 + 2OH^{-}$$

The overall reaction for Al dissolution at the anode is:

$$2Al\,(s) + H_2O\,(l) \Rightarrow 2Al\,(OH)_3 + 5H_2 + O_2 \tag{2.23}$$

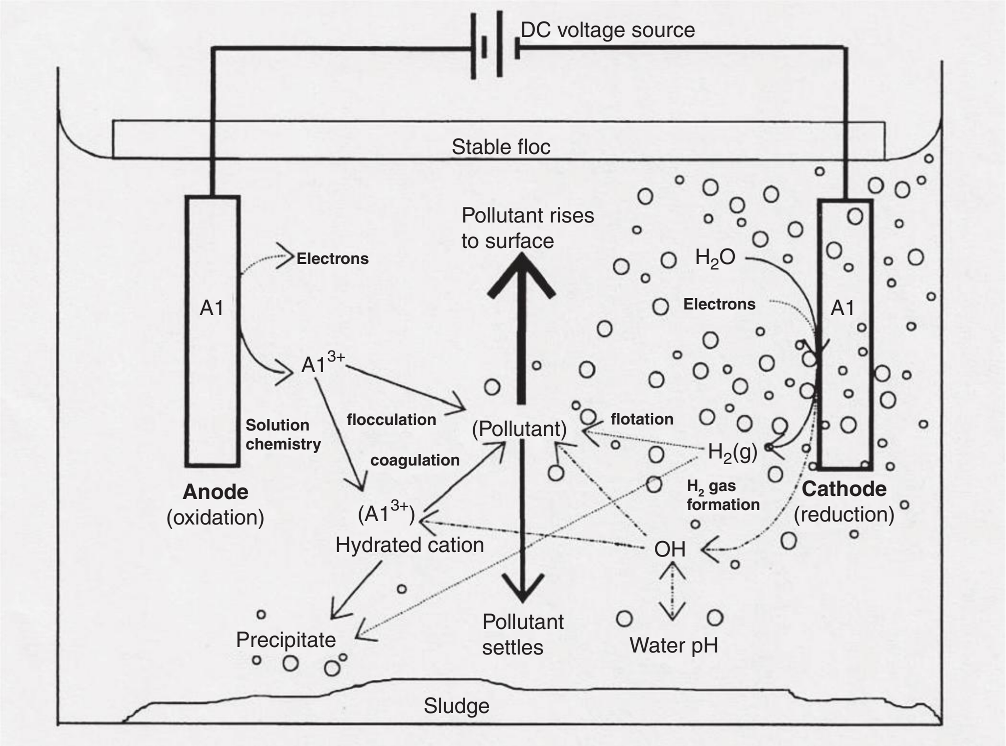


Figure 2.7 Interactions occurring within an electrocoagulation reactor. *Source: [22].*

Similarly, the electrolytic dissolution of Fe anode in water produces:

$$\mathrm{Fe} \Rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^-$$

The metal ions, Al^{3+} (or Fe^{2+}), are very efficient coagulants for flocculating particulates. Aluminium is usually used for water treatment and iron for wastewater treatment because iron is relatively cheaper. Faraday's law can be used to calculate the amount of coagulant produced [22]:

$$m = ItM/zF \tag{2.24}$$

where m is the mass of Al generated, F is Faraday's constant (96,486 C/mol), I is the operating current in Amps, t is run time, M is the molecular weight of aluminium in g/mol and z is the number of electrons transferred in the anodic dissolution ($z=3$ for Al).

Operating parameters

The quality of treated water depends on the amount of ions produced (mg) or charge loading (A h), i.e. current and time. The supply of current determines the amount of Al^{3+} (or Fe^{2+}) released from the respective electrodes. A large current means a small EC unit. However, a very high a current usually results in wasting electrical energy in heating water. The optimum current density for EC is 20–25 A/m^2. However, the current density value should take into account other operating parameters such as pH, temperature and flow rate to ensure high current efficiency.

The optimal temperature for operating the system is 60°C resulting in lower energy consumption as a result of higher conductivity than at ambient temperature. Higher water conductivity, for example, with the addition of table salt (NaCl), is beneficial as it results in reduced power consumption. Besides its ionic contribution in carrying the electric charge, chloride ions can significantly reduce the adverse effects of bicarbonate and sulphate ions; HCO_3^- and SO_4^{2-} ions can result in the precipitation of Ca^{2+} and Mg^{2+} ions forming an insulating layer on the surface of the electrodes resulting in reduced current efficiency [23]. Further, electrochemically generated chlorine is effective in water disinfection.

Treated waters

EC is effective in water treatment for drinking water supply, membrane pre-treatment, marine operation, and boiler water supply for small systems. It is very effective in treating colloids found in natural water by reducing turbidity and colour as well as removing suspended solids, oil and grease, iron, silicates, humus and microorganisms. A comprehensive summary of pollutants removed by EC is given in [24].

2.2.10 Ion exchange

The primary function of the ion-exchange (IX) operation is to remove ions from a dilute solution and concentrate these into a relatively small volume. An IX reaction may be defined as the reversible inter-change of ions between a solid phase (the ion exchanger) and a solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out [15]. IX resins remove undesirable ions by replacing them with an equivalent number of desirable ones. For example, a cation resin (R) selectively removes calcium ions by the following reaction:

$$R - 2Na + Ca^{2+} \rightarrow R - Ca + 2Na^{+} \qquad (2.25)$$

The reaction is reversible; when the resin becomes saturated with calcium it can be regenerated with a concentrated solution of sodium chloride. This is known as sodium-cycle cation exchange.

IX resins

Most IX resins are based on a styrene-divinylbenzene copolymer, which is appropriately treated to graft on ionic or functional groups. For example, sulphonation produces a cation resin, while amination produces an anion resin [15].

Strongly acidic cation resins

These resins have a sulphonic acid ($-SO_3$) functional group as shown in Figure 2.8. The ones in the H-form ($-SO_3H$) are capable of removing all cations from water. For most deionisation applications, SAC resin with an 8% divinylbenzene (DVB) content are used.

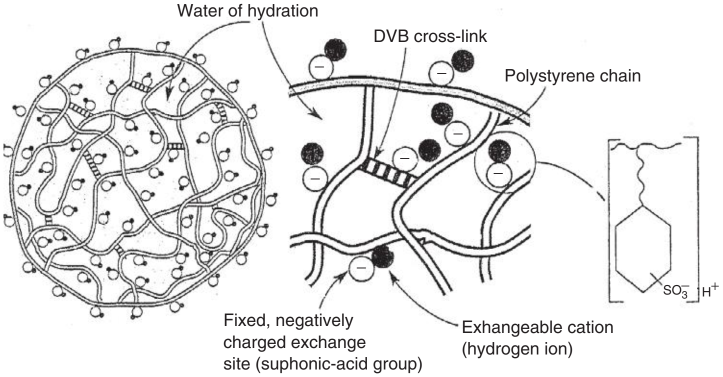


Figure 2.8 Schematic of a cationic ion-exchange resin bead. Strongly acidic cationic exchange resin with fixed, negatively charged sites (sulphonic acid groups) and mobile hydrogen (positive) ions attached for the IX resin in the hydrogen form.

Generally, they show maximum selectivity for trivalent ions, followed by divalent and monovalent ions. They are regenerated with strong acids, usually HCl or H_2SO_4, and require 200–300% of the theoretical stoichiometric quantity. When used in the hydrogen cycle, the effluent is acidic. The maximum operating temperature of the resin is 135°C.

Weak acid cation resins

This class of cation-exchange resin is typified by the carboxylic acid (–COOH) functional group, which in its acid form is only very weakly ionised, e.g. methacrylic-divinylbenzene, $-R'C(CH_3)COOH$. The degree to which dissociation occurs is highly pH dependent, increasing with increasing external pH. The resins are used for removing alkaline hardness as discussed under "softening."

Strongly basic anion resins

There are two types of strongly basic anion (SBA) resins: Type I and Type II. Type I resin has the highest basicity, and, therefore gives the optimum effluent quality. Type II has a lower basicity and, therefore, requires less caustic for regeneration. In general, Type II resin is used where silica effluent quality is not critical. Both resins are usually based on styrene DVB; however, recent resins now include acrylic materials. The functional group in Type I is quaternary benzyltrimethyl ammonium chloride, $RCH_2N \cdot (CH_3)_3^+ \cdot Cl^-$, and the functional group in Type II class is $RCH_2N \cdot (CH_3)_2(C_2H_4OH)^+ \cdot Cl^-$. These resins are capable of removing all anions from water. Selectivity is maximum for divalent ions. SBA resins are regenerated with a strong alkali such as caustic soda. The maximum operating temperature of SBA resin is 60°C (OH^- form) and 77°C (Cl^- form).

Weak base anion resins

The WBA resins come in two forms: free base form, $CH_2N(CH_3)_2$, and chloride form – $CH_2N(CH_3)_2\ {}^+Cl^-$. WBA resins operate essentially as acid absorbers. They are more efficient than strong base anion resins for removing free mineral acids (FMAs) such as HCl, H_2SO_4 and HNO_3, but are not effective at removing carbon dioxide or silica.

Resins selection

Other than the selection of appropriate resin type (cation or anion) and its strength (strong or weak) there are no firm rules, and experience outweighs all other considerations. Guidelines concerning the options related to matrix, structure and particle size grading are provided by resin manufacturers. Cost is also a major factor. Matrix-modified resins (acrylic) and structure modified materials (macroporous) can increase resin cost between 20 and 150% compared with standard gel styrenic products when comparing anion or cation resins, respectively.

Physical characteristics

The size and range (0.3–2 mm) of resin beads is an important consideration vis-à-vis performance. Uniform beads have been developed to produce stronger resins that resist attrition and eliminate cross-contamination of the resins during backwashing in mixed-bed systems. Uniform size is important since it imparts [10,15,16]:

- Higher operating capacity
- Lower ionic leakage
- Cleaner separation of resins during mixed-bed regeneration
- Faster rinsing

Diffusion of ions into and out of a large bead limits its performance. Hence, the diffusional path length should be as short as possible to achieve:

- Increased utilisation of the functional sites located within the bead
- Higher efficiency with which regenerating solution chemicals get into and out of the bead

Limitations

The basic limitation of an IX resin to remove and exchange ions and concentrate them within its structure is determined by the "selectivity" and the "capacity" of the resin. The ions being exchanged compete for the exchange sites with the resins having a different affinity for each type of ion. Note that since IX resins are primarily designed for removing soluble ionic species, they cannot be expected to absorb macro- or colloidal ionic species except at the surface of the particle.

Demineralisation

There are two types of resins involved in deionisation water treatment applications. These are strongly acidic cation-exchange resins and strongly basic anion-exchange resins. If the regenerating solution was a strong acid, such as hydrochloric or sulphuric acid, instead of a salt, the metallic ions would be replaced with hydrogen, and the resin would then remove cations, replacing them with hydrogen ions. This is called hydrogen-cycle cation-exchange. Thus,

$$\mathrm{R-2H+Ca^{2+}\rightarrow R-Ca+2H^{+}} \tag{2.26}$$

Anions are exchanged in a similar fashion. Anion resins usually operate in either the hydroxide cycle (regenerated with a strong alkali) or the chloride cycle (regenerated with sodium chloride):

$$\mathrm{R-2OH+SO_4{}^{2-}\rightarrow R-SO_4+2OH^{-}} \tag{2.27}$$

By using hydrogen-cation and hydroxide-anion resins in series, all cations are replaced with H^+ ions and all anions with OH^- ions; the result is pure water. This process is called deionisation or demineralisation.

Dual-bed demineralisation

In a two-stage or dual-bed IX demineralisation process, raw water is first passed through a SAC exchange resin bed in the hydrogen form. The effluent from the cation column is then passed through a strongly basic anion-exchange resin bed in the hydroxide form. Across the cation exchanger, all cations exchange for hydrogen ions to give a dilute acidic effluent ("free mineral acids" or FMAs) made up of acid sulphates, nitrates, and chlorides together with dissolved carbon dioxide. Upon passing through the anion exchanger, neutralisation of the FMAs occurs through the exchange of all anions for hydroxide to give deionised water. A typical IX vessel is shown in Figure 2.9 (left). Dual-bed sample design calculations are given in Chapter 6.

Mixed-bed ion exchange

A mixed-bed (MB) contains a uniform mixture of strong acid and strong base (Type I) resins in the H^+ and OH^- forms, respectively. Demineralisation occurs through simultaneous exchange of cation and anions in a single vessel. In effect, this is equivalent to

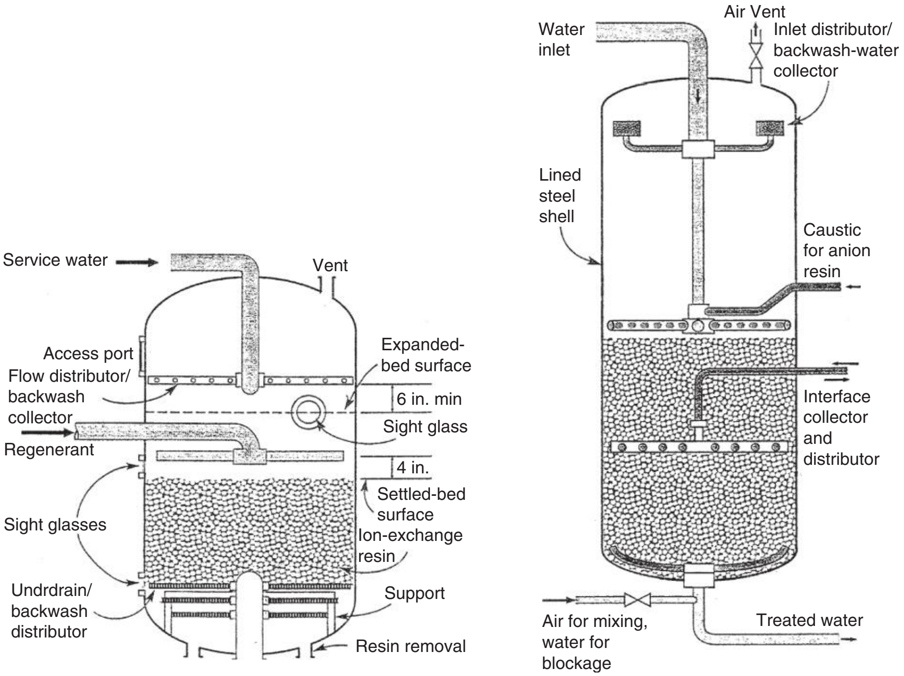


Figure 2.9 A single-resin demineraliser vessel (left) and a mixed-bed demineraliser vessel (right). The mixed resin bed separates into lighter anion (top) and heavier cation (bottom) resin beds during backwashing. Acid is used to regenerate the cation resin, and caustic soda is used for regenerating the anion resin. Acid inlet at the bottom of the vessel is not shown.

having an infinite series of two-bed demineralisers in series. Every anion bead reacts instantly with the acid produced by a neighbouring cation bead, removing the acid as it forms and driving the reaction to complete demineralisation. A pictorial drawing of a MB vessel is shown in Figure 2.9 (right).

The development of the MB-IX system is considered to be the most important contribution to the application of IX technology since the development of IX resins. The key to the successful operation of the mixed-bed is the ability to separate the two resins after the service cycle so that they can be regenerated separately. Uniform beads have been developed to produce stronger resins that resist attrition and eliminate cross-contamination in separation of the resins from one another during backwashing. Not only is cross-contamination of the resins undesirable from the obvious loss of capacity, but it can also reduce the quality of water. One way to reduce cross-contamination occurring at the interface distributor is by the use of an inert resin. The inert resin has a specific gravity intermediate between those of the anion and cation resins that, hydraulically, classifies between the anion and cation resins when backwashed. The quantity of the inert resin (10–15% of total resin volume) should be enough to cover the interface distributor, thereby, effectively reducing the cross-contamination problem.

Normal operation

An IX vessel is designed to distribute influent water evenly over the resin bed so that it passes through the bed uniformly. This ensures that the bed remains in a packed condition. Disruption of the bed during service would increase the amount of impurity allowed through (called slippage), and reduce the resin bed's operating capacity. In down-flow service, those ions for which the resins have the strongest affinity or selectivity are held at the top of the bed, i.e. those with the lowest selectivity are displaced from the exchange sites by other ions and move down the bed. When the exchange front eventually reaches the bottom of the bed as shown in Figure 2.10, the vessel is taken off line for regenerating the resins. The first sign of column breakthrough or ionic leakage is indicated by the most loosely held ions, silica ($HSiO_2^-$) for anion resins and sodium (Na^+) for cation resins.

The operation of a MB is similar to a single-bed IX operation. The regeneration cycle shown in Figure 2.11 is, however, complex. Backwashing, in addition to cleaning as discussed above, helps to classify the resin: the lighter anion beads rise to the top of the bed, the heavier cation beads dropping to the bottom. An inert resin bed with intermediate density forms a layer between the two resins helping to separate them during regeneration and reduces likely cross-contamination of resins. Acid solution flows through the bottom and upward through the cation resin bed and out through the interface collector. Caustic soda solution is introduced above the bed level and flows down through the anion resin bed and out through the interface collector. The resins are then rinsed as described above

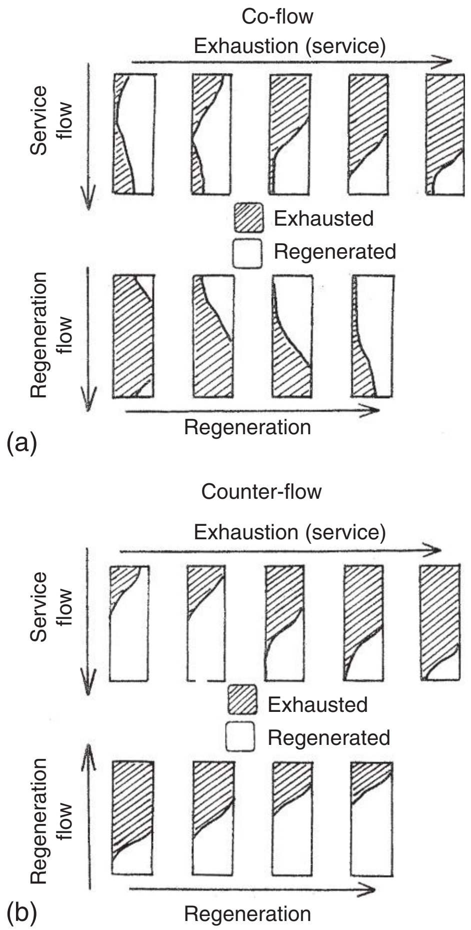


Figure 2.10 Resin bed loading distribution profiles. Ion leakage is indicated when the exhausted bed touches the bottom. *Source: Harland.*

and mixed with air or nitrogen before returning to service. The regeneration process is described in detail in Chapter 4.

Regeneration

Step I – Backwashing. This is accomplished by passing water upward through the bed for 10–20 min at a velocity of 7–15 m/h sufficient to expand the bed by 50–100%. Backwashing removes particulate matter, relieves any bed compression, and allows trapped gases to escape.

Step II – Chemical regeneration. Regeneration displaces the ions that were exchanged during the service run, returning the resin to the original ionic form. This is accomplished

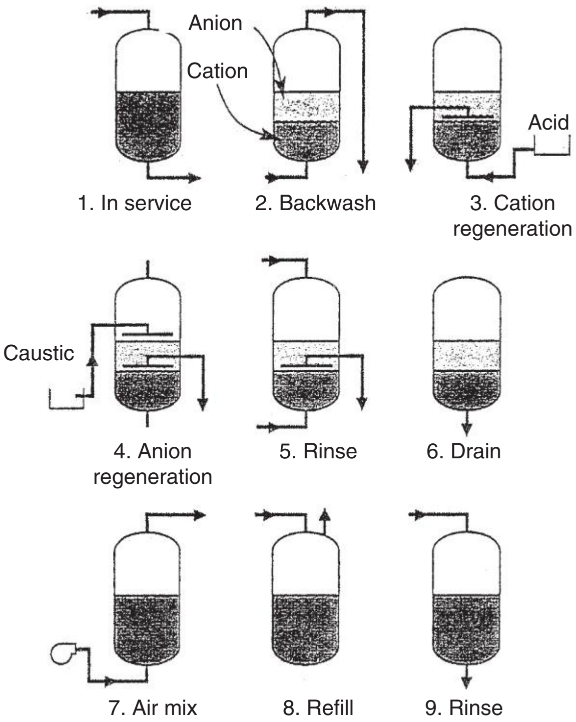


Figure 2.11 Regeneration process of mixed-bed resins.

by using solutions of sufficient strength (e.g. 8–10% NaCl for softener cation resin) to drive the equilibrium established during operation in the reverse direction. Cation-exchanger resins are regenerated with strong acids such as H_2SO_4 and HCl. Regeneration with H_2SO_4 is usually done at two different concentrations; initially at 2–3% acid followed by 5–6% dilute acid. Anion-exchanger resins are regenerated with NaOH at 4–5% dilute caustic soda solution.

The regenerating solution flow rate is low enough (2–4 $m^3/h\ m^3$ of resin) to allow the chemical to diffuse into the resin and to allow the largest impurity ions to migrate out of the resin. Regeneration efficiency can sometimes be improved, significantly, by heating the regenerating solution. Heating caustic soda to 49°C aids in removing polymerised silica from SBA resins.

Step III – Rinsing. Excess regenerating chemicals from the resin bed are flushed by a two-step rinsing process. The first step is a displacement (slow) rinse, in which the flow rate is the same as that used for adding the regenerant solutions (typically replacement of two bed volumes). This ensures that the chemicals are fully utilised. The second step is a fast rinse, typically 10 min. The high flow rate of water during rinsing flushes out any traces of the regenerant solution.

2.2.11 Non-DI water ion-exchange applications

Besides DI water treatment and oxygen removal, there are several other applications where IX is used. Some of these applications are reviewed briefly.

Organics removal

Organic matter in surface water is supposed to behave as a colloid, and is often complexed with silica and heavy metal ions such as iron, aluminium and manganese. In order to minimise the risk of organic fouling, SBA resins operating on a co-flow chloride cycle are often employed. It is not essential that the resin has a high ion-exchange capacity. Rather, it is more desirable that they possess greater porosity even at the expense of capacity. Typically, 50–70% of organics are removable.

Nitrates removal

Biological denitrification and IX are the processes used for removing nitrates from contaminated groundwaters when present in carcinogneic concentrations (>50 mg/l). Ion exchange is the easiest and most economic. The process uses SBA resin bed in either co-flow or counter-flow arrangement. To ensure reliable operation nitrate-selective resins have been developed. Regeneration is carried out using NaCl solutions.

Industrial wastewater treatment

SAC and SBA resins are typically used to treat wastewater effluents from metal finishing processes such as plating and anodising, pulp and paper manufacture, chemical leaching, zinc smelting, metal pickling and photographic processing plants. For example, in metal pickling where hydrochloric acid is used in the steel galvanising process, cation is removed as a complex anion. Strong base anion resins in the chloride form readily take up the chloro-complex ions ($Fe^{3+}\,Cl_4^-$ and $Zn^{2+}\,Cl_4^-$), thereby rejuvenating hydrochloric acid. Similarly, SBA resins and sometimes chelating resins are used for recovering heavy metals from various process streams.

Carbohydrate refining

IX processes in carbohydrate treatment are used for the purification of juices and syrups from cane sugar, beet sugar and corn starch hydrolysates. The main operations are decalcification (softening), deashing (demineralising) and decolourising (removal of organic colour bodies). These processes improve the yield and quality of the final recrystallised sugar or concentrated syrup. One interesting application is the inversion of sucrose to invert sugar (fructose + glucose) using SAC resins in the hydrogen form. Since raw sugar processes yields a fairly viscous syrup, macroporous resins are often used in sugar refining. Decolourising is usually done with macroporous WBA resins.

Pharmaceutical processing

IX is widely used to concentrate and recover antibiotics and vitamins from fermentation broths. For example, streptomycin molecule, which is moderately basic, is very favourably exchanged by the sodium form of macroporous WAC resins. General categories of biological compounds that are recovered and purified by IX include antibiotics, vitamins, nucleotides, amino acids, proteins, enzymes and viruses.

2.2.12 Membrane degasification

Membrane contactor (MC) is a new type of phase-contacting device for use in gas transfer and liquid/liquid extraction processes, as discussed in Chapter 1. MCs are used for stripping (degassing) dissolved gases including oxygen and carbon dioxide from deionised water and many high-purity water industrial applications where deaeration towers are not suitable because of possible contamination [25]. The CO_2 level is reduced to 1–5 ppm. Because of their compact size, MC systems are easily integrated with a separation process such as RO or IX, providing a highly efficient hybrid system. They can also be used in aerobic wastewater treatment without bubble formation. The process flow sheet of a MC unit with typical operating conditions for removing O_2 is shown in Figure 2.12.

Because of the large surface area of the fibres, a MC module can provide a large number of separation stages in a relatively short length of the module; the size of an MC is more than an order of magnitude smaller than a vacuum tower degasifier with comparable capacity. In general, it is the large surface area per module and not the enhanced mass transfer that makes the process more attractive than conventional contactors. In addition to being very compact in size, MC can be operated over a wide range of flow rates and outlet oxygen specifications. Because of its modular design, a membrane degasifier system can be expanded by adding MC modules in either series or in parallel. Adding more in series allows for lower oxygen concentration in water\outlet values, while additional units in parallel allows for higher flow rates.

For a given MC, the performance can be described as a function of liquid flow rate. The performance of an MC is based on the percentage of oxygen removal (OR) defined as:

$$\text{OR } (\%) = \frac{\text{inlet concentration} - \text{outlet concentration}}{\text{inlet concentration}} \times 100$$

2.2.13 Electrodeionisation

Electrodeionisation can be referred to as "electrodialysis moderated ion exchange." An EDI cell consists of MBIX resins sandwiched between an anion-exchange membrane (AEM) on one side and a cation-exchange membrane (CEM) on the other side, as shown in Figure 2.13 [26]. Electrodialysis (ED) is generally used to reduce the salt level from 1000–10,000 mg/l to a few hundred mg/l, whereas EDI is used to purify solutions containing 10–100 mg/l down to <1 mg/l. In the production of high-purity water, salt

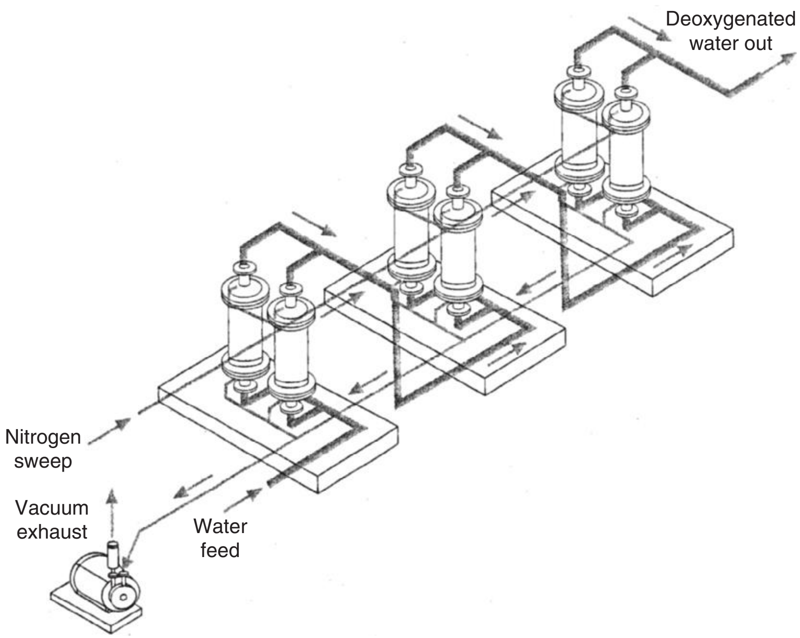


Figure 2.12 Membrane contactors (MC) system for degasification. Typical operating conditions: water flow rate 55 m^3/h at 25°C; feed and outlet O_2 concentration is 5 ppm and <10 ppb; MC 25 cm diameter × 70 cm long; 3 series × 2 parallel array; vacuum 700 mm Hg; N_2 sweep-flow rate 1900 cm^2/min. *Source: Hoecht-Celanese brochure.*

concentration in product water has to be reduced to the ppb (μg/l) range. This is not possible with ED because of the low conductivity of very dilute feed stream. This limitation is overcome by filling the diluate chambers with MBIX resin beads. The ions in the chamber partition into the IX resin beads and get concentrated several times so that ions and current flow through the beads, resulting in much lower resistance of the cell than in a normal cell operating with the same very diluate feed.

An EDI module consists of multiple cell pairs (up to 240 cell pairs) stacked end-to-end. The resin spacers in thick cells are 8–10 mm and 3 mm in thin cells. DC power is applied to a positive electrode (anode) located on one end of the module and to a negative electrode (cathode), located on the other end. The IX membrane is ion selective, which means that the CEM allows only cations to pass through, and AEM allows only anions to pass through. Since the polymer is hydrophobic, it is not permeable to water. Feed water enters the product compartments in parallel, and flows from top to bottom. The product stream flow rate may be increased or decreased within the range given in the specifications to meet the changing usage requirements. Increasing the product water flow rate above the specified range decreases the product water quality. There are two modes of operation: constant voltage and constant current.

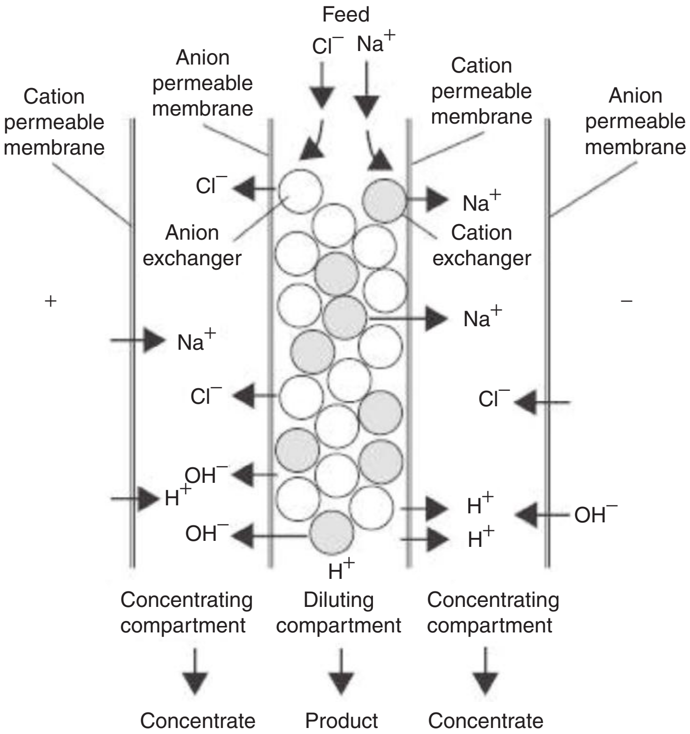


Figure 2.13 Schematic diagram of an EDI cell.

Because of the direct current that is applied perpendicular to the flow by the electrodes, the anions are driven toward the anode through the selectively permeable AEM. Similarly, the cations are driven toward the cathode through the CEM. The ions in the reject compartment are swept out of the module and sent to drain. As the water travels through the product compartments, it becomes increasingly pure. The DC voltage causes some of the deionised water towards the bottom of the product compartments to "split," i.e. the water molecules are broken down into hydrogen (H^+) and hydroxyl (OH^-) ions. The H^+ and OH^- ions react to regenerate the mixed-bed resins at the bottom of the compartments continuously, thus, producing highly pure water. As a result, the EDI system has the advantage of being environmentally friendly because chemicals are not needed to regenerate the resin. Further, EDI is more effective than MBIX for removing weakly ionised ions boron and silica.

EDI units are designed to operate with little or no downtime. EDI produces a consistent quality water without the problems and costs of regenerating IX resins and waste neutralisation [25,26]. High-purity water of up to 16.0 MΩ-cm resistivity can be produced with an EDI system using RO permeate of conductivity 1.0 μS/cm as feed water with product water recoveries in the 90–95% range. The following operational parameters can help to maximise the recovery of EDI units [27]:

- Use sodium cycle IX softeners instead of anti-scalants for RO pre-treatment; lower hardness leakage through the RO and less chance for upsets allows the operation at higher recovery.
- Lower alkalinity and CO_2 loading to the EDI by operating the RO at high pH (>9.0). This requires softened feed water to prevent scaling of RO membranes.
- CO_2 is not rejected by membranes and is transferred to the EDI reject. When the reject is recycled to the RO inlet, the pH of RO feed water is raised to >9.0 with caustic soda required to convert CO_2 to sodium bicarbonate, which is rejected by the RO membrane.
- If CO_2 concentration is >5.0 ppm, the feed water should be degasified using MCs to prevent build-up of CO_2 in the system, which lowers product water recovery and efficiency. Alternately, raise the pH of RO feed water to >9.0.

Feed water temperature, hardness, alkalinity, free chlorine and pH must meet the EDI quality requirements given in Table 2.3. RO pre-treatment is essential. In critical applications where bacteria control is important, a bacteria destruct 254 nm UV light is installed to reduce the bacteria count in EDI feed water. EDI modules are sanitised with chemicals or preferably hot water at 80°C.

Electrodeionisation has made major advances since it was introduced 25 years ago. It has captured a niche market for polishing RO product water in high-purity water applications. There are several thousand EDI systems in commercial operation for the production of high

Table 2.3 EDI process feed water requirements[a]

Item	Process condition
Pressure	
Minimum	2 bar g
Maximum	7 bar g
Temperature	
Minimum	10 °C
Maximum	45 °C
pH	4–10
Free chlorine	<0.02 mg/l (intermittent)
Iron, manganese, sulphide	<0.01 mg/l
Silica	<2.5 mg/l at 90% recovery
Total hardness	Depends on alkalinity and recovery; <1.0 mg/l at 90% recovery

[a] The total hardness, CO_2 and alkalinity of feed water determine the maximum recovery (yield) at which the EDI unit may be safely operated without damage to the module.

Source: USFilter/Ionpure.

purity water ranging from <0.1 to $>1500\ \mathrm{m^3/h}$. Commercially available devices are produced in two main configurations, plate-and-frame and spiral-wound [25,27]. More than 90% of installed EDI systems are plate-and-frame type. The plate-type devices are similar in concept to a plate-and-frame heat exchanger, with multiple fluid compartments sandwiched between a set of endplates (and electrodes) that are held in compression by bolts or threaded rods. The spiral EDI devices are analogous to a spiral-wound RO element, but with the ion-exchange membrane, resins and spacers wound spirally around a centre electrode rather than a permeate tube [25,27].

Newer EDI designs based on fully-filled compartments – electrode, diluting and concentrating compartments filled with MBIX resins – have been studied [28,29]. In order to increase the removal of weak acids and bases such as boric or silicic acid, alternate module design using bipolar membranes and separate compartments for anion-exchange and cation-exchange resins as shown in Figure 2.6 have also been investigated [29]. While EDI with separate IX resin beds and bipolar membranes leads to an effective removal of weakly dissociated acids, there is still a problem with contamination of the product water by diffusion of cations from the concentrate through the AEM into the diluate when the AEM are not completely permselective. This limitation can be overcome by including a "protection compartment" filled with an anion-exchange resin and rinsed with a small portion of the diluate [29].

2.2.14 Post-treatment of desalinated water

Desalinated water (RO permeate) is generally acidic (pH ~ 6.0), chemically unstable, low in mineral constant and corrosive. Water that contains no hardness is considered unhealthy for potable use, and water that contains no dissolved oxygen may taste flat. Hence, remineralisation is necessary to equilibrate the water to prevent corrosion in pipelines and to re-introduce some ions essential for human health. The permeate can be remineralised in several ways: calcite contactors, lime coupled with carbonic acid solution, sodium hydroxide and blended phosphate corrosion inhibitor, and permeate blended with raw groundwater [30].

Calcite treatment is simpler and cheaper than dosing with sodium hydroxide. RO permeate passes through a packed calcite bed and the medium slowly dissolves over time. Calcite dissolution is produced according to equation:

$$\mathrm{CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2\,HCO_3^-} \tag{2.28}$$

The dissolution increases alkalinity (HCO_3^-) with the added benefit of increasing an equivalent amount of hardness (Ca^{2+}). Limestone is a sedimentary rock primarily composed of calcite, aragonite and vaterite. Calcite can be pure in composition ($CaCO_3$) or can contain low concentrations of magnesium-forming magnesium calcite. Natural limestone can contain minerals or impurities such as dolomite [$CaMg(CO_3)_2$] and quartz (SiO_2).

The remineralised water is disinfected typically with chlorine, sodium hypochlorite or chloramines. It may include fluoride replacement as well.

2.3 MEMBRANE FOULING, SCALING, AND CONTROLS

One of the limitations of membrane processes for liquid separations is severe loss of productivity due to concentration polarisation and fouling as discussed in Chapter 1. The drop in flux can be as much as 80% in a few minutes or may take days. The loss of productivity is substantial vis-à-vis membrane permeability measured with water. Sources of membrane fouling and scaling are detailed in Table 2.4. Common pre-treatment processes discussed in this chapter are summarised in Tables 2.2 and 5.1.

Scaling is largely due to the deposition of materials in close proximity to the membrane surface that often results in fouling [31,32]. One problem with scaling in membrane systems is that the process introduces a large amount of potential foulants in the system; for example colloidal fouling occurs if total suspended solids (TSS) are too high. Cakes of colloids formed on the membrane surface result in blinding the membranes, reducing the flux drastically in most cases, as shown in Figure 2.14. Thus the efficiency of a membrane system, especially the life of a RO or a NF membrane (RO and NF membranes are less rugged than UF and MF membranes), depends on effective treatment of the membrane system feed water.

Generally speaking, fouling and scaling problems are spread as follows: (a) organic fouling – 50%, (b) colloidal fouling – 30% and (c) mineral scaling – 20%. The effects of these on membrane performance are given in Table 2.5. Organic fouling consists of biofouling, natural organic materials such as humic and fulvic acids and organics added during pre-treatment – coagulants and anti-scalants. Colloidal fouling occurs in almost all membrane systems, and is the most serious of the fouling problems.

Table 2.4 Sources of membrane fouling and scaling

Substance	Extent and/or mechanism
Fe, Mn, Al hydroxides	Severe fouling, rapid kinetics
Mineral salts[a]	Form mineral scales when their solubility is exceeded
Colloids	Electrically charged; SDI[b] and zeta potential determine fouling
Microbiological	Forms a biofilm gel layer
Proteins	Fouling by hydrophobic and charge interactions
Polyelectrolytes	Fouling by charge interaction
Organic acids	Humic and fulvic acids cause severe fouling
Oil and grease	Hydrophobic membrane fouling
Suspended solids[c]	Cannot exceed 0.5 ppm

[a] $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$.
[b] Silt Density Index.
[c] Applicable to RO/NF.

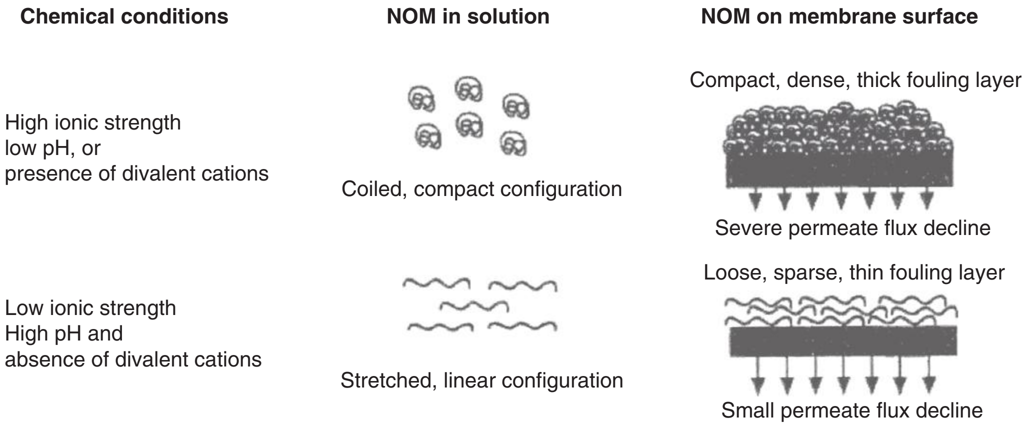


Figure 2.14 Effect of solution chemistry on the deposition of natural organic matter (NOM) on a membrane surface. *Source: Schafer et al.*

Table 2.5 Effect of fouling and scaling on membrane performance

Type of fouling	Permeate flow[a]	Feed pressure	NDP[b]	Solute passage
Organic	Loss	Increases	–	–
Colloidal	Loss	Increases	–	Increases
Scaling	Loss	–	Increases	Increases
Biological	Decreases	Increases[c]	Increases	Increases

[a] Normalised permeate flow.
[b] Net differential pressure across the membrane array.
[c] Due to restrictions in the fouled feed channel Vexar spacer of SW membrane elements.

Measures to prevent or control fouling and scaling include using solution-compatible membranes, i.e. hydrophilic or hydrophobic membranes; using low fouling membranes, e.g. charge compatible membranes; reducing product water recovery; and optimising pre-treatment strategies such as anti-scalants, acidification, water softening and fine filtration and prefiltration in the case of RO and NF systems [32,33]. Several novel techniques for controlling fouling and enhancing flux are given in Table 1.13.

Process parameters – temperature, flow/shear, pressure, feed pH and concentration – influence fouling, for example, the solubility of salts is a function of temperature. Similarly, since protein molecules denature at high temperatures, fouling of UF membranes increases with temperature (30–60°C) due to greater adsorption [34]. Proteins are least soluble at pH 4–5 resulting in maximum fouling in this range. General rules of thumb for preventing or minimising fouling and scaling in RO/NF membrane systems are turbidity less than 1.0 NTU, SDI less than 3.0 and LSI less than zero.

Critical flux operation. Critical flux is defined as the limiting flux below which a flux decline over time does not occur, as discussed in Chapter 1. The pure water flux in pressure-driven processes is directly proportional to the applied hydraulic pressure shown in Figure 1.8. The curves also show that for feed solutions containing solutes, as ΔP increases the flux reaches a plateau (Region III) and becomes independent of pressure [34,35]. This steady-state flux is called the "limiting flux," J_{lm} or gel layer limited flux. In order to reduce the formation of the gel layer and fouling, membrane systems should be operated in the so-called "critical flux" region, Region II in Figure 1.8. The critical flux increases with higher cross-flow velocity (higher Reynolds number) and lower solute concentration, C_{b}. The limiting flux behaviour for various feed waters in RO membrane modules is illustrated in Figure 2.27.

Hydrodynamic fouling control. Advanced membrane processes such as the vibratory shear-enhanced process (VSEP®) have proven to be very effective in reducing fouling and treating difficult waters such as produced waters [36]. The technology uses vibrational energy that creates shear waves at the membrane surface, repelling solids and foulants, as discussed in Chapter 1. The VSEP membrane module uses RO, NF, UF or MF membranes depending on the application.

Hydrodynamic methods applying backwash are a part of the operating cycle of cross-flow and dead-end UF and MF systems [34]; during backwash the filtered water flows in the reverse direction, as shown in Figure 2.5, to dislodge the solids and restore the flux lost as a result of cake build-up on the membrane surface and clogging of the membrane pores. The membrane modules are either tubular (cross-flow only) or hollow fibre. In the case of low-pressure membrane filtration systems operating in semicontinuous dead-end mode the backwash is often combined with air scour either during filtration and/or backwash cycles [6,9]. Air-scouring helps to shear off the layer somewhat acting like tangential velocity in cross-flow systems. Backwashing the membrane elements by air scouring and air-assisted backwashing is done intermittently every 30–60 min. The backwash cycle typically lasts 1–2 min, as discussed in Chapter 4.

Start-up conditions. In the case of high flux UF and MF membranes, it has been shown that if the system is started slowly, fouling is reduced; for example a slow start resulted in 10–25% higher long-term flux than abrupt start-up when processing raw sugar solutions [34]. Maintaining a high permeate back-pressure, ramping up the pump motor speed and reaching the final TMP, minutes or hours after start-up, allow operation below the critical flux for that system.

2.3.1 Scaling and fouling mechanism

Each ionic compound has its own solubility limit, which is the maximum amount of the compound that can remain in solution. This is defined as the solubility product constant, K_{sp}. It is a function of temperature, pressure and pH; slight variations in any of these properties can shift the solubility point and cause scaling. K_{sp} values of various compounds are given in Chapter 6. For this reason, membrane processes are not operated under conditions of solubility limits (unless an anti-scalant is in the feed) because in this zone – metastable region – precipitation can occur when favourable conditions exist [14,32,33].

Phase changes occur at solid (membrane)/liquid interfaces where precipitation occurs easily if there are nucleation sites. Precipitation occurs at a finite rate depending on the number of nucleation sites, the degree of saturation, temperature, pressure and time. Once the process of precipitation starts, the rate is controlled by the size of the solid/liquid interfacial area. If the particles are attached to a membrane surface, they grow in only one direction because the membrane limits access to the adjacent surface. Thus particles grow as a sheet until they form a layer of precipitate on the membrane surface, and the membrane gets fouled. The solute concentration is maximum at the membrane surface and lower in the bulk liquid above the membrane surface; the concentration profile is the reverse of a fluid flow profile in a channel or a tube, as shown in Figure 1.23.

Crystallisation and scaling initially occurs at sites with the greatest amount of available free energy. Most membrane surfaces are relatively low energy surfaces unlike the bulk solution, which has many imperfect solid surfaces such as suspended solids, which are ideal for crystal growth. In the bulk solution there are nucleation sites such as colloidal particles in the feed solution, or are formed by chemical precipitation. Fouling occurs when the number of nucleation sites at the membrane surface is large in comparison to the number of sites away from the membrane surface [36]. Hence, it makes a difference whether the nucleation sites are at the membrane surface or in the bulk solution.

2.3.2 Membrane scaling

Scaling occurs when sparingly soluble salts get concentrated beyond their solubility limits in the reject stream of the membrane element. The process of scaling occurs in multiple stages. During the scaling process, colloids of insoluble mineral salts are formed. Minerals that precipitate and form scale are predominantly divalent metal ions such as calcium, iron, magnesium, barium, strontium and silicon because they are almost insoluble in the presence of sulphate, phosphate and carbonate ions. For example, barium sulphate forms scale when the barium concentration is as low as 0.05 mg/l. As these molecules precipitate they form crystals that start growing at nucleation sites, especially at a liquid/solid interface [32,33]. Monovalent metals such as sodium and potassium, on the other hand, are almost completely soluble. Sparingly soluble salts in the order of decreasing scale formation are [14]:

$$\mathrm{CaCO_3 > CaSO_4 > silica > SrCO_3 > BaSO_4 > SrSO_4 > CaF_2 > CaSiO_4 > MgSiO_3} \\ \mathrm{> MgSiO_3 > Ca_3(PO_4)_2 > Fe(OH)_2}$$

The most common scale found in RO/NF systems is calcium carbonate because it precipitates quickly once concentrated beyond its solubility limit, and also because most natural waters are almost saturated with respect to calcium carbonate (magnesium, barium

Table 2.6 Feed water requirements to minimise scaling

Parameter	Value
LSI (TDS < 10,000 mg/l)	<1.0 w/ antiscalant <0 w/o antiscalant
SDSI (TDS > 10,000 mg/l)	<0.5 w/ antiscalant <0 w/o antiscalant
Barium	<0.05 mg/l
Strontium	<0.1 mg/l
Silica, reactive	60–150 mg/l

and strontium often co-precipitate when calcium and carbonate precipitate). Calcium carbonate chemistry and its scaling potential are discussed in detail in Chapter 6. The scaling potential is evaluated using the Langelier Saturation Index (LSI) for brackish water and the Stiff and Davis Stability Index (S&DSI) for seawater (see Table 2.6).

In the case of brackish waters, $CaCO_3$ and gypsum ($CaSO_4 \cdot 2H_2O$) are the most common scalants. Gypsum is ~50 times more soluble than calcium carbonate based on their K_{sp} values (gypsum, $K_{sp} = 1.9 \times 10^{-4}$ at 25°C; calcium carbonate, $K_{sp} = 8.7 \times 10^{-9}$ at 25°C).

Calcium carbonate, carbon dioxide, calcium and bicarbonate ions are in equilibrium:

$$Ca^{2+} + 2HCO_3^{-} \leftrightarrow CaCO_3 + CO_2 + H_2O \tag{2.29}$$

According to Equation (2.29) calcium carbonate precipitation is favoured by increasing calcium or bicarbonate concentration, decreasing carbon dioxide and increasing temperature or pH. Carbonate – $CaCO_3$, $SrCO_3$, $BaCO_3$ – scaling is prevented by lowering the pH, adding a scale inhibitor, softening (discussed earlier), reducing product water recovery, preventive cleaning, or a combination of all these techniques [14,33]. Scaling compounds such as hydroxides of aluminium, iron and manganese are typically removed during basic pre-treatment.

Process and feed water requirements for minimising mineral scaling in membrane systems are given in Table 2.6. LSI quantifies the scaling potential of $CaCO_3$. The most susceptible elements of an RO/NF system to scaling are the last stages of the membrane array where the reject stream is most concentrated (see Table 2.9). Why does the RO concentrate or reject water come into play? This is discussed below but simply, as the water in the feed/reject stream gets concentrated with the removal of the permeate, sparingly soluble salts can reach their solubility limits and precipitate to form a scale on the membrane surface. Concentration factor, CF, is defined as:

$$CF = 1/(1 - \%recovery) \tag{2.30}$$

where recovery is (permeate flow rate)/(feed flow rate). In other words, when the product water recovery is 75%, the CF is 4, and the salts get concentrated by a factor of 4. A more reliable indicator of scaling used by membrane manufacturers is called the beta factor, β. It quantifies the effect of concentration polarisation, CP. Thus,

$$CF_M = CP/(1 - \%\text{recovery}) \tag{2.31}$$

where CF_M is the modified concentration factor. CP depends on the turbulence of the bulk stream in the feed channel above the membrane surface, and for design purposes β value is in the range of 1.13–1.2 for RO/NF membranes, meaning that the concentration of solutes at the membrane surface is 13–20% higher than in the bulk reject stream. In short, the actual salt concentration at the membrane surface must be accounted for when designing a RO/NF membrane system.

Feed water treatment, therefore, often includes anti-scalant addition and pH adjustment with acid to 6.5–6.8 to maintain the $LSI < 1.8$. Membrane manufacturer's recommendations for salts saturation limits with anti-scalants are as follows: $BaSO_4 = 6000\%$, $SrSO_4 = 800\%$ and $CaSO_4 = 230\%$. Silica solubility can be up to 300 ppm in the presence of a dendrimer anti-scalant supplied by Professional Water Technologies, Vista, California.

2.3.3 Membrane fouling

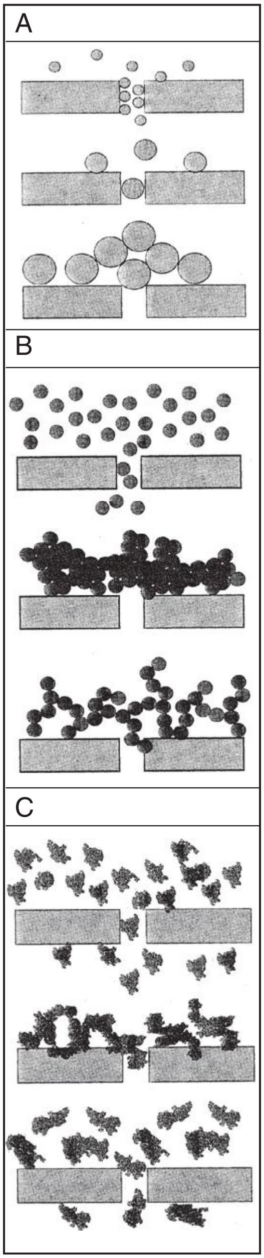
One of the most important issues affecting the development of membrane filtration has been fouling. Membrane foulants can be both inorganic and organic components. The main reasons for membrane fouling listed in Table 2.4 are:

- Organic molecules adsorption (organic fouling, e.g. proteins, humic substances)
- Particulate deposition (colloidal fouling, e.g. clay, iron and alumina silicate)
- Microbial adhesion (biofouling, e.g. bacteria)

Thus, fouling depends on membrane properties and specific interactions between the membrane and solutes in the feed as discussed in Chapter 1 [18,32,34]. Several mechanisms of colloidal and organic fouling are explicitly illustrated in Figure 2.15.

In the case of traditional UF and MF operations (i.e. non-aqueous treatment applications), the problems can be addressed by using or modifying membranes that are compatible with the liquid being processed; for example, positively charged UF membranes are used for recovering anodic paint in electrocoating, whereas negatively charged membranes are used for recovering cathodic paint; otherwise, fouling is severe as shown in Figure 2.16. Backpulsing is used with tubular hollow-fibre UF and MF membranes to control fouling as discussed earlier in this chapter. Pre-treating the feed stream is also an option; for example, in the case of milk processing by UF using polysulphone membranes, fouling occurs due to colloidal calcium phosphate, which is associated with casein micelle [34]. Addition of EDTA or sodium citrate reduced fouling due to a reduction in the calcium–caseinate complex.

In the case of membrane filtration applications in water treatment, there is a rapid and often irreversible loss of flux due to interactions between the membrane and the



Pore versus surface fouling

Pore adsorption ($d_{solute} << d_{pore}$): Colloids or solutes adsorb on the membrane walls, effective pore size is restricted and flux declines

Pore plugging ($d_{solute} \propto d_{pore}$): Colloid or solutes of a similar size to pore diameter block pores completely, reduction in membrane porosity and severe flux decline

Cake formation ($d_{solute} >> d_{pore}$): Colloid or solutes larger than the pores are retained due to sieving effects and form a cake on the membrane surface, depending on pore to particle size ratio flux decline occurs (permeability of the cake layer as well as the cake thickness are important)

Impact of colloid or solute stability

Stable colloids smaller than the pore size are not retained by membrane, unless adsorbed by the membrane material

Tight aggregates are formed by slow coagulation, are retained and form a cake on the membrane. The aggregate structure may collapse depending on forces on the aggregate and the aggregate stability. Flux through the tight aggregates is usually low unless the aggregates deposit as a porous cake of large particles

Loose aggregates are formed by rapid coagulation and are also retained. Such aggregates form a cake on the membrane. The aggregate structure may collapse depending on forces on the aggregate and the stability of the aggregate. Flux through the open aggregates is high if the structure is maintained during filtration

Solute–solute interaction

Colloids < pores and stabilised with organics (for example) are not retained by the membrane, unless adsorbed by the membrane material or destabilised with high salt concentrations

Aggregates with organics adsorbed after aggregation (for example) are fully retained by the membrane, but may penetrate into the upper layer of the membrane. This could also be organics destabilised with multivalent cations

Colloids which are partially aggregated and destabilised such as a variety of solutes that interact with each other in heterogeneous ways in the presence of salts, collids and dissolved organics, form small and diverse aggregates which may block pores

Figure 2.15 Colloidal-organic matter complex membrane fouling mechanism. *Source: Schafer et al.*

components of natural raw water. The most important foulant is small colloidal matter (3–20 nm in diameter). Materials in the colloidal size range such as proteins and macromolecules are known to be the worst foulants. In addition, most of the foulants have a narrow size distribution when dealing with natural surface waters. Scaling by

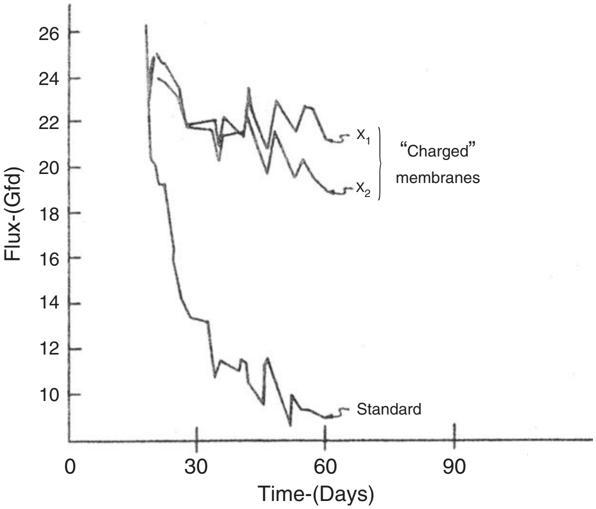


Figure 2.16 Ultrafiltration of cathodic paint using charged membranes (X_1/X_2) and a standard hollow-fibre membrane element. *Source: Romicon.*

Table 2.7 Feed water requirements to minimise fouling

Parameter	Value
SDI_{15}	<5 (some manufacturers require <4)
Turbidity	<1[a] NTU
Iron[b]	<0.05 mg/l
Manganese	<0.5 mg/l
Hydrogen sulphide	<0.1 mg/l
Organics (TOC)	<10 mg/l

[a] Some membrane manufacturers recommend that turbidity be <0.2 NTU.
[b] At pH > 7.0 and 5–10 mg/l dissolved oxygen; at lower pH and lower oxygen levels, slightly higher iron levels can be tolerated.

inorganic deposits also results in fouling because different types of fouling often occur simultaneously and influence each other.

General guidelines to minimise fouling are given in Table 2.7. As the SDI value increases, the potential for fouling increases. Most manufacturers require that the feed water SDI_{15} (the SDI determined by a 15-min test is described in Chapter 6) be less than five, while some require an SDI_{15} less than four. Turbidity specifications must also be satisfied to meet warranty conditions. Note that SDI and turbidity are only directly related. For example, water with low turbidity (less than 0.2 NTU) can still exhibit a SDI greater than five.

Iron and manganese are included as suspended solids since under most operating conditions, iron and manganese that are soluble in RO feed water oxidise (soluble ferrous iron, Fe^{2+} => insoluble ferric iron, Fe^{3+}) and deposit on the surface of the membranes [14]. Furthermore, oxidation of the metal can catalyse the oxidation of the membrane leading to membrane failure. The levels of iron, manganese and nickel in feed water must be less than 0.1 mg/l.

Hydrogen sulphide is considered as a suspended solid because it is readily oxidised to form colloidal sulphur; it reacts instantaneously with chlorine to precipitate sulphur at the pH of typical feed water sources. Hydrogen sulphide is found almost exclusively in well water make-up sources. Reaction with dissolved oxygen in water precipitates sulphur almost as rapidly as exposure to chlorine. Colloidal sulphur is difficult to remove from the membrane surface.

Various techniques can be used to reduce the loading of suspended solids, organics and microbes in feed water. These include physical processes such as media filtration, cartridge microfiltration and chemical treatments. Chemical addition enhances the filterability of the solids such as the addition of coagulants (Table 2.2). Foulants and their control strategies are addressed in Table 2.8. Since any traces of solids and organics get removed in the first membrane modules in RO and NF systems, these materials typically foul the first stages of an RO/NF system (Table 2.9). Once deposited on the membranes,

Table 2.8 Treatment methods for controlling fouling

Foulant	Fouling control
General	Hydrodynamics/shear, operation below critical flux, chemical cleaning
Inorganic (scaling)	Operate below solubility limit, pre-treatment, reduce pH to 4–6 (acid addition), low recovery, additives (anti-scalants) Some metals can be oxidised with oxygen
Organics	Pre-treatment using biological processes, activated carbon, ion exchange (e.g. MIEX), ozone, enhanced coagulation
Colloids (<0.5 μm)	Pre-treatment using coagulation and filtration, MF, UF
Biological solids	Pre-treatment using disinfection (e.g. chlorination/dechlorination), filtration, coagulation, MF, UF

Source: [32].

Table 2.9 Fouling/scaling location

Type of foulant	Most susceptible location[a]
Scaling/silica	Last element of last stage
Metal oxides	First element of first stage
Colloids	First element of first stage
Organic	First element of first stage
Biofouling (rapid)	First element of first stage
Biofouling (slow)	Throughout the whole installation

[a] RO/NF membrane array.
Source: [32].

foulants attract additional solids, thereby accelerating any fouling problem that might already exist. In addition to solids, microbes, and organics, soluble heavy metals (such as iron) can foul RO membranes when oxidised within the membrane modules. Oxidation can occur in any stage of an RO system when the pH and dissolved oxygen concentration are suitable. Microbes, if left untreated, can reproduce and spread, thereby fouling the entire RO system.

Organic fouling

Humic acid and fulvic acid represent up to 80% of the TOC – dissolved organics – of natural waters. Humic substances are weak acidic electrolytes with carboxylic- and phenolic-OH groups with a micelle-like structure and with a molecular weight between 500 (fulvic) and 100,000 (humic). The chemical structure of humic acid is shown in Figure 6.1 [15]. They become hydrophobic as pH decreases, and thus foul hydrophobic membranes more [18]. Humic fouling in the case of natural waters is aggravated by the presence of calcium (Ca^+) by forming a bridge between the membrane and the negatively charged membrane surface, and/or between negatively charged carboxyl groups of the humic acid. Other organic components that foul membranes include microbial slime, polyhydroxy aromatics and polysaccharides. Feed water organic levels measured as TOC should be low to prevent fouling with organic molecules as well as to minimise the potential for microbial fouling since organics provide nutrients that support microbial growth.

Colloidal fouling

Most common colloids found in natural waters are clays, silica, iron and aluminium hydroxides, and organic debris. In the case of industrial process streams, colloids may be paint pigments, proteins, bacterial and yeast cells, and high molecular weight alcohols. Colloidal fouling in a membrane system is caused by the convective deposition of colloids on the membrane surface, and the higher the permeate flux, the higher the rate of colloidal fouling. Membrane systems and operating conditions are designed to reduce the risk of colloidal fouling since it is the most severe [31,32]. These control measures include feed water pre-filtration, reduced recovery, higher cross-flow velocity and frequent chemical cleanings.

Silica fouling

Silica is one of the most common elements, and is present in many natural waters. It is found in waters in the form of (a) reactive silica, (b) colloidal silica, and (c) suspended particles (sand). Reactive silica is called silicon dioxide, and in this form is generally not ionised at normal pH levels of water [33,37]. Colloidal silica is either polymerised silicon with multiple units of silicon dioxide, or silicon that has formed loose bonds with organic compounds or other complex inorganic compounds such as calcium oxide and aluminium silicate. Well waters contain the most silica, from 50 to 100 mg/l. It is mostly reactive silica, a result of dissolving from rock, whereas surface waters contain more colloidal silica even though surface waters contain more reactive silica than colloidal silica. In the case of surface waters, silica chemistry is complex due to biological activity.

Silica has a low solubility of 120 mg/l at pH of 7.0 and 25°C, and silica scale-like barium sulphate scale is difficult to dissolve during cleaning and must be avoided. Silica scaling usually occurs in the last stage of a membrane array (Table 2.9). It is usually associated with iron and alumina (e.g. clays, mullite and feldspars); metal hydroxides adsorb silica to form silica–metal complexes such as aluminium silicates that readily foul the membranes. Iron fouling can be prevented by (a) anti-foulants, or (b) removing iron by oxidation as by greensand filtration or iron filters. Alumina fouling is prevented by (a) pH control and coagulation prior to multimedia filtration, or (b) alumina compatible anti-scalants. If silicates are less than 5 ppm, iron should be less than 0.5 ppm and manganese less than 0.2 ppm, and when the silicates are 30–50 ppm, iron should be less than 0.05 ppm and manganese less than 0.02 ppm. In addition, hardness should be removed and alumina should be less than 0.05 ppm. A dispersant such as high molecular weight polyacrylate scale inhibitor is helpful in silica scale control by slowing agglomeration of silica-scale particles.

The solubility of silica is a function of pH and temperature. Lime softening and lime plus soda ash softening are most effective in removing silica. Other options are process related: (a) run the RO system at reduced recovery, (b) increase the feed water temperature – silica solubility increases with temperature, and (c) use silica inhibitors. Colloidal silica is difficult to remove by IX because it is not ionised, and can foul the resins when the levels are high. Colloidal silica flocculates easily in boundary layers resulting in severe fouling. It can be removed by UF membranes with a MWCO of up to 100,000 Da. Since the solubility of the silica increases below a pH of about 6.0 and above a pH of about 9.0, the actual solubility of silica in the concentrate stream is further affected by the pH of reject water.

Biofouling

Biological fouling by microorganisms has an adverse effect on membrane performance (Table 2.5). A biofilm is difficult to remove because it protects the microorganisms from shear forces and disinfection chemicals. Microorganisms – bacteria, algae, fungi, viruses, and higher organisms – can be regarded as colloidal matter (typical bacteria size is 1–3 μm). Biofouling can be complicated due to mutual interactions between different types of fouling; for example if iron oxide or a biofilm accumulates on the membrane surface it prevents the migration of ions (calcium, sulphate) and other solutes back into the bulk solution, as discussed in Chapter 1, resulting in a supersaturated condition. Thus gypsum (calcium sulphate) scale is formed beneath the primary foulant, and is not easy to remove as compared to the iron scale or the biofilm. The potential for biological fouling is higher with surface water than well water.

Biofouling has been investigated extensively [38,39]. Key characteristics are summarised below:

- Appropriate sampling of biofilms is necessary to identify biofouling. A biofilm has the following characteristics: (a) high content of water and organic matter (70–95%), (b) high numbers of colony-forming units and cells, (c) high contents of carbohydrates and proteins, (d) high content of adenosine triphosphate (ATP), and (e) low content of inorganic matter.
- RO membranes reject bacteria absolutely. However, microorganisms can be found in the permeate due to (a) leakage through O-rings, (b) microscopic imperfections in the membrane surface, (c) microbial contamination of feed water, and (d) growth of microorganisms from contaminated piping.
- Biofilm mode of growth enables microorganisms to survive and multiply even in extremely low nutrient habitats (5–100 ppb TOC).
- Generally biofouling is a slow process.
- The cumulative effects of membrane biofouling are (a) increased cleaning and maintenance costs, (b) a noticeable deterioration of product water quality, and (c) significantly reduced membrane life.
- Biofouling can lead to secondary mechanical deformation ("telescoping") of SW membrane elements.
- Biofouling of membrane surfaces is invariably accompanied by some degree of mineral deposition.
- Biofilm can be considered as a dense gel layer, and dissolved minerals tend to accumulate in this layer and increase concentration polarisation.
- Biofouling causes flow losses due to constriction of the flow channel, increase roughness of the surface, and increase drag because of their viscoelastic properties.
- The first step in biofilm formation prior to microbial adhesion is the irreversible adsorption of macromolecules, which leads to a "conditioning film" (humic substances, lipopolysaccharides, microbial products). This conditioning film alters the effect of the membrane; the electrostatic charge and the critical surface tension may change.
- Primary adhesion is a function of several factors: (a) microorganisms, (b) membrane surface property – charge and hydrophobic/hydrophilic, (c) fluid properties, and (d) bacteria growth phase. Many bacteria have a slight negatively charge, and have to overcome the repulsion barrier when they attach to slightly negatively charged membrane surfaces. Cell hydrophobic property, however, does not seem to be crucial in adhesion to polysulphone (PS) hydrophobic membrane.
- Primary adhesion occurs within a very short time; the highest rate is during the first 1 h followed by a slow plateau after 4–6 h. Dead cells adhere as fast as living cells. This means that destruction of bacteria is not enough, and dead cells must be removed.

- Higher cross-flow velocity provides higher shear forces, and thus, a thinner biofilm. However, the shear forces of the turbulent flow do not "penetrate" the viscous sub-layer and affect the bacterial monolayer. Fluid velocities in SW modules have very little effect on impeding the initial rate of microbial (or colloidal) foulant deposition, although they can reduce the thickness of the fouling layer.
- Surface roughness has a significant effect on biofouling as it: (a) increases the convective transport near the surface, (b) protects small particles from surface shear, and (c) increases the surface area of attachment.
- Polycations from pre-treatment enhance biofouling because of the electrostatic attraction to the slightly negative overall charge of microbial cells.
- A common cause of biofouling is the overdosing of flocculants (used in removing suspended solids during pre-treatment), which provide a suitable habitat for microbial growth.
- Chlorination of seawater has been observed to induce biofouling by degrading humic acid into biologically assimilable material, which supports the growth of a biofilm.

There are several risk factors that are also applicable to non-biofouling membrane operating conditions. These should be kept in mind when operating any membrane system:

- Feed-water characteristics – Temperature >25°C, high amounts of organic and inorganic nutrients, large number of cells ($>10^4$ colony-forming units per ml), and high SDI.
- Operational characteristics – Infrequent monitoring of performance characteristics, use of microbial contaminated pre-treatment chemicals, lower cross-flow velocities, and long storage periods.
- System design – Extended piping runs, dead-legs and disinfected holding tanks.

In most cases, biofouling is assessed based on performance characteristics: (a) flux decline, (b) decrease in salt rejection, or (c) increase in feed-brine pressure drop as given in Table 2.5. These indirect methods, however, are not absolute indicators of biofouling, and cannot be used for any correlation. Common techniques and limitations for controlling biofouling include:

- Removal of the biofilm is essential for effective sanitisation because a biologically deactivated biofilm can cause biofouling.
- Chlorine is a biocide. However, it does not sterilise water, and after chlorination the surviving bacteria can grow especially between 25 and 35°C. Water has to be dechlorinated when using polyamide (PA) membranes.
- Activated carbon used for removing organics is often the source for colonising microorganisms.
- Cartridge filtration using 5.0 μm pore size cartridges are too large for removing bacteria.
- 254 nm UV irradiation is used for disinfecting water. Many types of bacteria are, however, resistant to UV light. Once a biofilm is formed UV light is not able to deactivate

or remove the cells. UV treatment is limited to relatively clean water because of interference by suspended solids in water.

- Regular ozone treatment is effective for sterility, and is used in high-purity water systems.
- Hydrogen peroxide requires long contact times (a few hours), high concentrations (>3%), or high temperatures (>40°C). It is an oxidant and, therefore, not compatible with PA membranes.
- Detergents are effective in inhibiting biofouling in many cases. Alkaline cleaners are quite effective in controlling microbial slime. Biz® bleach is an effective cleaner but is an oxidant.
- Sodium bisulphite is effective in controlling biofouling and colloidal fouling. Typically, 500–1000 mg/l is dosed for 30 min every 24 h to control aerobic bacteria. The permeate contains 1–4% bisulphite during this shock treatment.
- Hot water sanitisation (HWS) is an effective control strategy.
- Preventive sanitisation is much more effective than corrective disinfection because a single attached bacteria is easier to kill and remove than a biofilm. Membrane life is shortened by extensive sanitisation.

2.3.4 In-line chemical treatment

The pre-treatment unit operations discussed in Section 2.2 are the basic essentials for providing acceptable water to RO/NF membrane plants. Additional treatment may be required to further minimise the potential for fouling and scaling to ensure that the RO/NF membrane plants operate from 3 to 6 months without shutdowns for cleaning, unlike MF and UF plants that are usually subject to frequent backwashing and monthly cleaning. For example, synthetic anti-foulants such as Hypersperse™ are used to prevent carbonate and sulphate scaling and to reduce the rate of colloidal fouling [31]. Dosage concentrations of various chemical additives are given in Table 6.7.

In-line coagulation

Polymeric coagulants are sometimes added in low dosages (<10 ppm) to remove particles down to 0.5 μm particle size as compared to 10 μm without the coagulant upstream of a cartridge filter. Even very low amounts of cationic polymeric coagulants in RO/NF feed water can, however, foul negatively charged membranes. In addition, some organic coagulants are not compatible with acrylic-based anti-scalants used in RO/NF systems. Typical coagulant dosage ranges from 0.5 to 20 ppm. Inorganic coagulants generally require a higher dose than polymeric coagulants. The best technique for determining the proper dosage of coagulant is to feed the product in-line and measure the SDI in the filter effluent as a function of coagulation feed rate.

In-line dechlorination

Oxidising agents such as chlorine damage PA membranes by breaking down the polymer backbone as discussed in Chapter 6. The maximum allowable chlorine limit for PA membranes varies between 0 and 1000 ppm h. It is, therefore, mandatory that RO feed water is dechlorinated when using PA membranes. A reducing agent such as sodium metabisulphite ($Na_2S_2O_5$) is used to scavenge any traces of chlorine in carbon filter effluent water. Sodium bisulphite ($NaHSO_3$) is formed when sodium metabisulphite is dissolved in water. $NaHSO_3$ then reduces hypochlorous acid as per the reaction:

$$NaHSO_3 + HOCl \rightarrow NaHSO_4 + 2HCl \tag{2.32}$$

In theory, 1.34 mg of sodium metabisulphite (100%) is required to remove 1.0 mg of free chlorine. In practice, 3.0 mg is used. Similarly, it takes 1.46 ppm of sodium bisulphite and 1.77 ppm of sodium sulphite (Na_2SO_3) to remove 1 ppm of free chlorine. A minimum contact time of 5 s is required. Sodium metabisulphite also helps in reducing dissolved oxygen in water.

In-line pH adjustment

Membrane scaling is linked to system recovery and cross-flow velocity; generally speaking, for recovery up to 70%, and with or no iron present, acidification may be the only chemical pre-treatment necessary to prevent scaling by calcium carbonate. When water recovery is 75–80%, additional processes such as scale inhibitors and/or IX softening instead of acidification is required. The solubility of calcium carbonate depends on the pH of feed water. The equilibrium can be shifted to the right to convert calcium carbonate to soluble calcium bicarbonate [$Ca(HCO_3)_2$] by lowering the pH to 6.0 with sulphuric acid or hydrochloric acid as:

$$CaCO_3 + H \leftrightarrow Ca^{2+} + HCO_3 \tag{2.33}$$

Acid reacts with bicarbonate alkalinity to produce carbon dioxide. RO permeate is often high in anions and always acidic ($pH < 7.0$) due to the presence of dissolved carbon dioxide (carbonic acid). Carbon dioxide concentration can be several hundred ppm when using acidified feed [37]. Dissolved carbon dioxide is removed by tower decarbonation or by membrane degasification to reduce the loading on anion resins when EDI or mixed-bed IX is used for producing DI water. Membrane degasification is preferred in high-purity water systems to prevent contamination. Alternately, IX softening is used to remove calcium ions followed by raising the pH of the softened water to 8.3–8.5 by adding caustic soda. Raising the pH with sodium hydroxide converts the carbon dioxide to sodium bicarbonate, which is easily rejected by RO membrane.

Acid addition is determined by the LSI or SDSI of RO reject water. To control calcium carbonate scaling by acid addition alone, the LSI or SDSI in the concentrate stream must be negative as indicated in Table 2.6. When an anti-scalant (A/S) is used, the LSI can be 1.0. LSI is applicable when the TDS is less than 10,000 mg/l, whereas SDI is applied when the TDS is greater than 10,000 mg/l.

Sulphuric acid is commonly used but hydrochloric acid is preferred when the scaling potential is high due to $CaSO_4$, $SrSO_4$, and $BaSO_4$. Calcium sulphate is more soluble than $BaSO_4$ and $SrSO_4$. However, since calcium ion is present in natural water sources more abundantly than barium and strontium ions, $CaSO_4$ is a greater problem. Nevertheless, $BaSO_4$ and $SrSO_4$ scale is difficult to re-dissolve once precipitated. Hence, overdosing of sulphuric acid must be avoided. Acidification, however, has several limitations:

- Low pH increases fouling by natural organic matter (NOM) such as humic acids.
- Low pH lowers permeate quality due to higher TDS of feed water and increase in silica and carbonic acid.
- Permeate TDS increases when using hydrochloric acid because added chloride has a lower rejection than sulphate. Hence, acid treatment is usually used for carbonates and phosphates scale prevention.

Anti-scalant threshold treatment

Scale inhibitors or anti-scalants (A/S) are generally organic compounds containing sulphonate, phosphonate, or carboxylic acid functional groups and chelating agents such as carbon, alum and zeolites that sequester and neutralise a particular ion that may be formed. The majority of scale inhibitors can be classified as "threshold inhibitors." In addition, chelating agents such as EDTA (tetra sodium salt of ethylene diamine tetra acetic acid) are used to control hardness (at $pH > 6.0$) and metallic ion deposits. Anti-scalants prevent mineral scaling by getting absorbed on the scale forming salt crystals thereby preventing the attraction of the supersaturated salt to the crystal surfaces. Since anti-scalants inhibit the growth of crystal, it does not grow to a size or a concentration large enough to precipitate out of the suspension. Many scale inhibitors also contain dispersants that keep the precipitates suspended in solution [14,40,41].

Anti-scalants are preferred to IX softening when the feed water hardness is less than 100 ppm because of cost and ease of operation. Although anti-scalants are very effective in preventing carbonate and sulphate scaling of membranes, they do not prevent scaling from occurring; rather they delay the formation of large crystals that form scales. The effectiveness of scale inhibition is approximately 30 min. A RO/NF system that uses anti-scalants must be designed with automatic flush cycle after shut down to prevent scaling by concentrated salts in the feed-reject channel above the membrane surface.

Anti-scalants can be used alone, but are almost always used with acid feeds. When acid is used with an A/S, the LSI value (of the reject stream) of 1.0 is acceptable (see Table 2.6), although some A/S manufacturers claim an LSI of 2.7 is acceptable when using their recommended product [42]. The A/S dosage ranges between 2 and 10 ppm depending on the scale-forming potential of the RO feed water, product water recovery and manufacturer's recommendations. The main advantage of a higher LSI value is that the RO/NF system can be operated at higher recovery resulting in lower operating costs. From a process point of view, higher recovery results in higher salt concentration in the feed-reject channel that in turn results in sparingly soluble salts exceeding their solubility limits faster. Hence, high recovery is only an option when operating a second-pass RO unit or when the feed water is pure.

Although the solubility of silica is ~120 mg/l at neutral pH and 25°C, the solubility increases with temperature and at $pH > 9.0$ (also at $pH < 6.0$). For normal operation, silica solubility can be increased to 300 mg/l in the presence of a dendrimer A/S [42]. Dendrimers are highly branched polymers. Dendrimer-based anti-scalants do not contain phosphates and do not foul membranes even when the A/S concentration exceeds 100 ppm. Also, the membrane manufacturer's recommendation the following saturation limits for other sparingly soluble salts when anti-scalants are used: $BaSO_4 = 6000\%$, $SrSO_4 = 800\%$ and $CaSO_4 = 230\%$.

Sodiumhexametaphosphate (SHMP) is a threshold agent derived from the dehydration of orthophosphoric acid or its sodium salt. It is used to inhibit the formation of calcium carbonate and metallic sulphate scale. It is mostly widely used because it offers good inhibition at a low cost. Depending on the concentration of calcium and sulphate, and depending on the CF (Equation 2.31), the dosage is in the range of 2–5 ppm. SHMP can prevent calcium sulphate precipitation up to 150% of the saturation limit. Organophosphonates are an improvement over SHMP since they are more resistant to hydrolysis, but are more expensive. They offer scale inhibition and dispersion ability similar to SHMP [14,40,41].

Polyacrylic acids (PAA) are good at both scale inhibition and dispersion, and are more effective than SHMP. Polyacrylic acids with high molecular weight distribution show the best dispersion ability at the cost of scale inhibition ability. However, precipitation may occur with cationic polyelectrolytes or multivalent cations such as aluminium or iron, resulting in fouling the membranes. Blend inhibitors are a combination of low (2000–5000 Da) and high molecular weight (6000–25,000 Da) of PAA or a blend of low molecular weight PAA and organophosphonates, giving excellent dispersive and inhibitor performance.

Anti-scalant treatment can, however, contribute to fouling largely due to either under-dosing or over-dosing; the former can result in scaling while the latter can lead to fouling [37,41]. Overdosing can also lead to biofouling and can result in complexes formed with hardness ions (since assimilable organic carbon content is a food source for microorganisms).

2.4 MEMBRANE SYSTEMS DESIGN

The design of an integrated or hybrid membrane water system entails a comprehensive design of the feed water treatment system, the design of the membrane array based on optimum product water recovery and solute rejection, membrane feed water pressure, process control and post-treatment for higher purity product. Membrane system design, therefore, is an iterative procedure encompassing membrane selection (size of membrane element and type of membrane), membrane array (number of stages and passes, and number of elements), design, and product quality calculations until the desired quality is obtained. In the case of RO and NF systems, membrane manufacturers have generated computer programmes for designing their membrane-based systems. In the case of UF and MF systems, however, pilot data are required to design a membrane system.

2.4.1 RO/NF system basics

The RO and NF membrane processes are discussed in detail in Chapter 1. RO membranes are well-suited to rejecting dissolved ions and most organics (some organics such as ethanol and acetone have very low rejections of 45–55%). The rate of water transport through a membrane depends on membrane properties (polymeric, chemical, morphological), water temperature, and the difference in applied pressure across the membrane, less the difference in osmotic pressure between the concentrated and dilute solutions. Osmotic pressure is proportional to the solution concentration and temperature, and depends on the type of ionic species present. For solutions of predominantly sodium chloride at 25°C, a rule of thumb is that the osmotic pressure is 0.7 bar per 1000 mg/l concentration (see Table 6.11 for osmotic pressures of various solutions).

The choice of a membrane is usually determined by the composition of feed water and the final product water quality. Homogenous asymmetric cellulose acetate (CA) membranes (blends of CA and cellulose triacetate) and thin-film composite (TFC) membranes are the most commonly used, as discussed in Chapter 1. Performance specifications of CA and PA membranes are detailed in Table 1.6. CA membranes have a neutral charge, are more hydrophilic, less prone to fouling, and can tolerate low levels of chlorine. Because of these properties, CA membranes are often preferred in wastewater applications where the SDI is high, and in potable water purification where residual chlorine is required. TFC polyamide and polyetherurea (PEU) membranes have higher rejection and flux and higher durability than CA membranes but are have very limited tolerance to chlorine. TFC membranes have a higher rejection than CA membranes due to co-ion repulsion since the membrane has a net negative charge at a pH greater than 5.0. Below a pH of 4.0, the membrane has a net positive charge. Hence, at low pH values (e.g. due to the presence of carbon dioxide/carbonic acid), the rejection decreases. In order to increase the dissolved ion rejection, caustic soda is often injected (unless the feed water is degasified) to raise the pH to between 7.0 and 8.0. Under alkaline conditions, the CO_2 is converted to bicarbonate and carbonate ions by raising the pH to greater than 7.5. The sodium bicarbonate ions are easily rejected by the RO membrane, whereas carbon dioxide is not. Several applications of TFC membranes are listed in Table 1.8.

Membrane manufacturers are continuing to develop newer and more efficient membranes and modules such as (a) high rejection, (b) high flux, (c) loose-wrap, (d) hot water sanitisable (80°C), (e) low energy, (f) low fouling, and (g) hydrophilic. SW modules are compact and inexpensive. The flow regime in SW elements is turbulent with superficial velocities ranging between 10 and 60 cm/s corresponding to Reynolds (Re) numbers of 100–1300. Although these Re numbers indicate laminar flow, turbulence is due to the mesh spacers in the feed channel shown in Figure 2.17.

Standard SW modules are 20 cm diameter × 100 cm long with a membrane surface area of 41 m^2 (see Table 2.10). Larger SW modules (40 × 100 cm and 45 × 150 cm) have been developed for seawater and brackish water desalination. These larger modules are more efficient and result in lower system costs. The surface area of 40 cm diameter × 104 cm long (nominal) modules is 158 m^2. The world's largest SWRO desalination plant (540,000 m^3/day) in Sorek, Israel (commissioned in 2013) is the first large desalination plant using 40 cm diameter SW modules.

Spiral-wound loose wrap or full-fit modules (FFM) are used in many pharmaceutical systems because there are no brine seals to prevent the by-pass of feed water. When a brine seal is utilised, a large pocket of water remains stagnant around the RO membrane. Since the water is not chlorinated in the case of PA membrane elements, stagnant water is

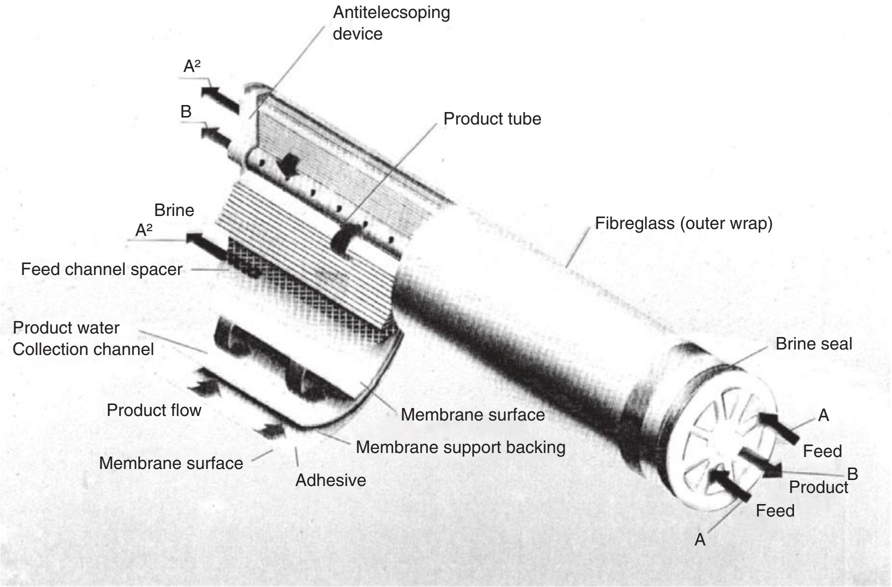


Figure 2.17 Cut-up diagram of a typical spiral-wound RO membrane element. *Source: SAEHAN brochure.*

Table 2.10 Typical specifications of RO and NF membrane spiral wound elements[a]

Item/property	NF[b]	BWRO[c]	BWRO[c]	SWRO[d]
Membrane type	Thin-film composite polyamide	Thin-film composite polyamide	Homogenous[e], cellulose acetate blends	Thin-film composite polyamide
Salt rejection	~99.7% $MgSO_4$, >50% NaCl	99.7%	~98%	99.8% 92% boron
pH operating range	3–9	2–11	4–6	2–11
Feed pressure (max)	40 bar g	40 bar g	15–30 bar g	82 bar g
Pressure drop (max)	0.7 bar	0.7 bar	1.0 bar	0.7 bar
Max. temperature	45°C	45°C	40°C	45°C
Chlorine (oxidants) tolerance	<0.1 ppm	< 0.1 ppm	2–5 ppm[f]	<0.1 ppm
Feed water turbidity (max)	1.0	1.0	1.0	1.0
Feed water SDI (max)	5.0	5.0	5.0	5.0
Membrane surface area	40.8 m^2	40.9 m^2	49 m^2	40.8 m^2
Feed flow rate	17 m^3/h	17 m^3/h	8 m^3/h	17 m^3/h
Product water recovery	15–17%	15–17%	20%	10–12%
Flux – see Section 2.4.3	–	–	–	–

[a] 20 cm diameter × 100 cm long (nominal). *Note:* Membrane surface area of 40 cm diameter × 100 cm long (nominal) elements is ~158 m^2.
[b] Nanofiltration.
[c] Brackish water RO.
[d] Seawater RO.
[e] Phase inversion homogenous asymmetric.
[f] 2 ppm for standard CA blends, up to 5 ppm for CTA hollow fibre membranes (e.g. Toyoba SWRO).

prone to bacterial growth on the outside surface of the membrane. A FFM uses the feed pressure to expand the membrane diameter. This expansion provides the control of feed water by-pass while allowing a small flow of water to pass around the membranes outer surface. This small flow of water eliminates the stagnant pocket of water that the brine seal units retain, and can be rinsed in much shorter time. Hence the FFM offers better control of bacterial growth and is often used for pharmaceutical applications. The by-pass flow may be as high as 20% of the feed flow to the membrane. This means that the cross-flow velocity is considerably lower and the permeate flow rate is produced with less feed water when compared with membranes that utilise brine seals (because some flow is by-passed and not available for filtration). The actual recovery is, therefore, considerably higher when compared with membranes that utilise brine seals.

An RO/NF membrane unit consists of the following components: (a) a high-pressure pump, (b) a membrane element/pressure vessel assembly (array), (c) instrumentation, and (d) a clean-in-place (CIP) unit (see Figure 2.25). A typical RO/NF membrane assembly consists of either spiral-wound (SW) or hollow-fibre (HF) membrane elements housed in fibreglass-reinforced plastic (FRP) or stainless steel pressure vessels. Two to seven SW elements are connected in series in a single-pressure vessel depending on the feed flow and system design as shown in Figure 2.18. Pressure vessels can be 8–10 m long. The desired system capacity and recovery are achieved by connecting pressure vessels in parallel, and by staging the reject stream in an array with a decreasing number of pressure vessels; the tapered configuration design is shown in Figure 2.19. The brine volume gets reduced in each stage, so that the number of modules in successive stages is reduced usually in the ratio of 2:1 to maintain optimum reject-flow velocities. High feed channel

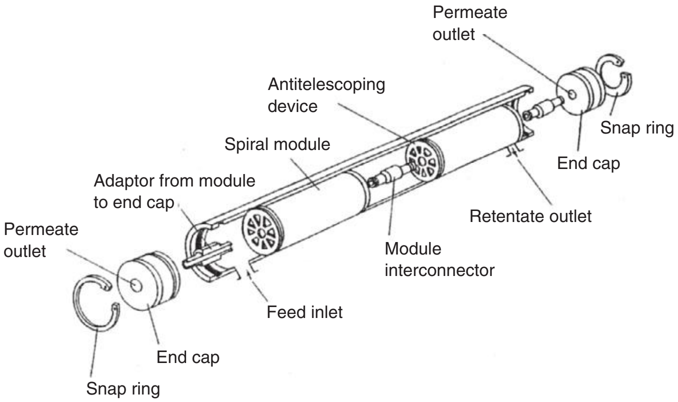


Figure 2.18 Multiple spiral wound elements connected in series in a pressure vessel. Permeate tubes of each element are connected by module inter-connectors. Up to seven elements are connected for RO applications, and two to four elements in the case of UF and MF applications. *Source: Cheryan, Copyright 1998 from Ultrafiltration/Taylor & Francis Group, LLC.*

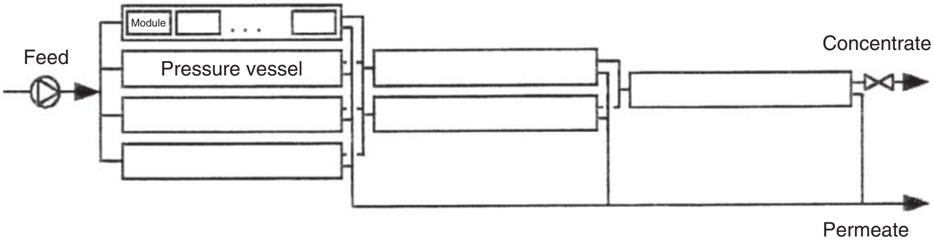


Figure 2.19 Typical RO and NF membrane array. The tapered configuration has four pressure vessels in Stage l, two in Stage 2, and one in stage 3. *Source: Wittman and Thorsen.*

flow velocity is desired in order to reduce concentration polarisation at the membrane surface. The number of elements required is calculated using the formula:

$$N_{\mathrm{E}} = (\text{permeate flow rate})/(\text{permeate flux} \times \text{active membrane area})$$

The amount of product water (permeate) recovered is generally dependent on: (a) the total area of membrane within each vessel; (b) membrane pressure supplied by the high-pressure pump(s); (c) reject-flow rate; and (d) feed water quality. General rules of thumb for RO membrane product water recovery are as follows: (a) 70–75% for normal or brackish feed water, (b) 30–45% for seawater, (c) 80–85% for purified feed water, e.g. first-pass RO permeate as second-pass RO feed and (d) 40–45% for seawater.

RO/NF systems used for brackish water and low TDS feed water are invariably two or three-stage designs as shown in Figure 2.19 (see also Figures 2.22, 2.23, 4.7). Seawater RO systems, on the other hand, are typically single-stage designs (see Figure 3.33) because of low product water recovery.

During RO/NF operation water is forced into the membrane module pressure vessel by a high-pressure pump at pressures in the range of 10–30 bar g for brackish water and from 55 to 80 bar g for seawater. The desalted product (permeate) is removed from the opposite side of the membrane at low pressure. A flow-regulating valve on the reject side is used to create back-pressure and increase recovery, as shown in Figure 2.20. The total pressure drop from the feed inlet to reject outlet is minimal (<2 bar g), which allows the high-pressure reject to be fed to successive RO stages to increase recovery or productivity.

The simplest membrane element assembly consists of one pressure vessel containing one membrane element with a product water recovery (yield) of about 15%. In order to increase %recovery and still maintain an acceptable concentrate flow, a part of the concentrate stream may be recycled to the inlet side of the high-pressure pump. Concentrate recycling design is used with very small RO units and is discussed later in the chapter (e.g. see Figure 2.24). The main advantage is the compact size of the RO unit. The disadvantage is a larger feed pump to handle higher feed flow. Accordingly, the power consumption is relatively higher than that required in a multistage configuration. In addition, due to blending of the feed with the concentrate stream, the average feed salinity is increased. Therefore, both the feed pressure and the permeate salinity are higher.

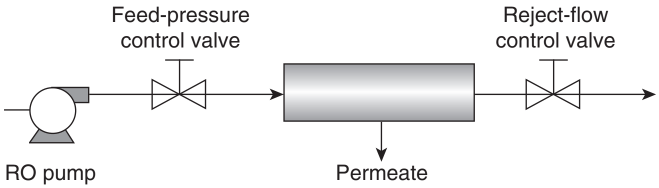


Figure 2.20 Schematic of a basic RO/NF control system diagram. *Source: Singh and Tembrock, Reproduced with permission from Chemical Engineering Progress, Sept. 1999. Copyright 1999 AIChE.*

For some applications, a single-pass RO system may not be capable of producing permeate of a required quality. For example: (a) seawater RO systems, which operate on a very high salinity feed water, at high recovery and/or at high feed water temperature; and (b) brackish RO systems, which require very low permeate conductivity for supplying make-up water to high-pressure boilers. Two-pass RO systems are also used in the production of high-purity water for semiconductor, beverage, medical and pharmaceutical production to optimise solute rejection and productivity. In this design, the primary (first-pass) unit permeate is fed to the secondary (second-pass) unit (e.g. see Figure 2.21). Because of very low dissolved solids ion content of the first-pass RO permeate, the

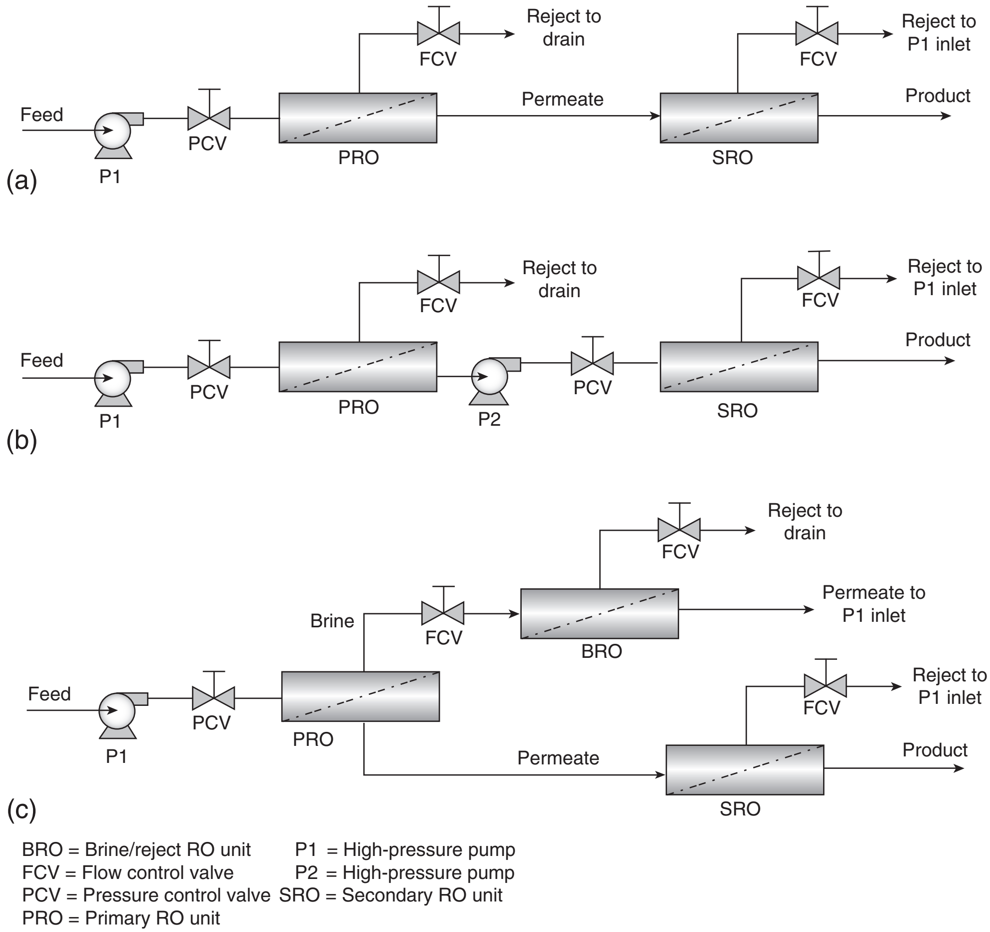


Figure 2.21 High recovery or high product quality two-pass RO systems. (a) Two-pass RO without inter-stage pressure boosting; (b) two-pass RO with inter-stage pressure boosting; and (c) two-pass RO with brine RO reject recovery. *Source: Singh and Tembrock, Reproduced with permission from Chemical Engineering Progress, Sept. 1999. Copyright 1999 AIChE.*

second-pass RO membranes can operate at a higher flux (e.g. 34 lmh) and high recovery (e.g. 85–90%). Further, to increase the overall recovery and conserve water, the reject stream from the second pass is recycled back to the RO pump inlet. The dissolved ion concentration in the concentrate from the second-pass is usually lower than the concentration of the first-pass unit feed water. Therefore, blending the first-pass feed water with the second-pass concentrate reduces slightly the concentration of the feed and increases product water recovery.

2.4.2 Membrane system controls

Of all the major membrane processes, RO/NF separation is the most complex both in terms of operation and controls [43]. RO (and NF) membrane systems operate in a continuous mode with minimum or no recycle. RO desalination plants can be generally quite large (see Table 3.5); for example the largest seawater RO desalination plant in Sorek, Israel has a capacity 150 million m^3/year. Further, for hybrid membrane systems the process control becomes even more complex. RO/NF plants require different levels of process control depending upon the quality of feed water supplied and product water quality requirements.

Systems discussed provide monitoring and controls of major process variables in RO/NF plants to ensure that the design conditions of flux and rejection are achieved with minimal membrane fouling while ensuring fail-safe operation. New control systems are being designed that interlock the pressure drop across a membrane stage with the high-pressure RO pump or the membrane array inlet-pressure control valve to maintain constant permeate flux. Similarly, new systems designs are envisaged where the pressure drop is monitored across each element in a pressure vessel rather than across the entire pressure vessel or stage. Since each pressure vessel has up to seven elements in series, closer monitoring of pressure drop would help in monitoring fouling and/or scaling, and enhance system efficiency. Nowadays an increasing number of RO systems use electric motors with variable speed drives, which enable adjustment of flow and feed pressure of the pump over a wide range with very little loss in efficiency. The variable speed drive thus reduces pressure losses, and the membrane units can be operated at constant flux.

Basic controls

The basic level of control routinely used in the chemical process industries involves sequencing operations such as manipulating valves or starting/stopping pumps, instrument verification, data acquisition, on-line maintenance and fail-safe shut down procedures. The next level of computer control involves process control of parameters such as flow, pressure and temperature. RO/NF systems require both levels [43].

The simplest form of RO/NF system contrail entails the adjustment of only two variables: membrane inlet pressure and reject-flow rate, as shown in Figure 2.20. These functions affect the quantity and quality of RO permeate and indirectly potential for membrane fouling. The reject-flow control valve must be throttled in conjunction with the inlet-pressure control valve to achieve the desired productivity or product water recovery, i.e. yield.

Several more complex valve control sequences are illustrated in Figure 2.21. In a two-pass RO system (Figure 2.21a), the first-pass RO inlet-pressure and reject-flow control valves are adjusted simultaneously with the second-pass RO reject-flow control valve to achieve the desired recovery. In the case of a two-pass RO system (Figure 2.21b), where the feed to the secondary RO unit is re-pressurised, the secondary membrane unit inlet-pressure control valve is also adjusted. In order to reduce the size of the waste stream and increase overall product water recovery, the reject stream from the primary RO unit is sometimes further processed in a brine RO unit (Figure 2.21c). In such setups, the primary RO inlet-pressure and reject-flow control valves, the brine RO reject-flow control valve and the secondary RO reject-flow control valve are all adjusted simultaneously to achieve the desired recovery.

RO system performance (%recovery and %rejection) for a given membrane is a function of the operating conditions. Hence, the control system is designed to run the system at the membrane inlet pressure and recovery specified by the system manufacturer. Membrane performance, however, declines with time due to changes in the material properties of the polymer, so that control valve settings periodically require adjustments – for instance, raising the membrane inlet pressure. In addition, the control system may be used to monitor RO/NF pump inlet and outlet pressures, membrane reject and permeate pressures, membrane array pressure drop (ΔP), feed water temperature, pH, conductivity, chlorine level and permeate conductivity. Continuous monitoring of RO/NF performance, alarms, shutdown regime, data logging and performance trending are essential; for example, high ΔP across a membrane stage or an array is a good indicator of membrane fouling.

When specifying the high-pressure feed pump, membrane manufacturers assume that membrane flux will decline by about 20% in 3 years. The pump is, therefore, designed to provide feed pressure corresponding to the initial membrane performance and to compensate for expected flux decline. In the case of centrifugal pumps, the pump selected is oversized, and during operation the feed pressure is regulated by throttling (turning down the pump discharge valve) or by a variable frequency drive.

Control systems

A programmable logic controller (PLC)-based membrane system utilises remote input/output (I/O) functionality. The PLC communicates with various remote I/O control enclosures in the membrane plant, and performs all sequencing and inter-locking functions. In a fully automated system, independent (non-PLC) controllers such as PID (proportional plus integral plus derivative) or other tuning allow the operator to modulate control valves, e.g. feed water temperature, membrane inlet pressure and reject-flow rate [43]. The PID controllers also give the operator easy access for changing set point values, and supervise alarm conditions without the need for an operator interface screen. Independent PID controllers can allow the operator to run the system without a working PLC; if a single independent PID controller fails, only the particular parameter it was controlling cannot be adjusted.

Process control valves

Membrane feed-pressure control may be performed via two different techniques: proportional valve position or pump motor speed [43]. The valve solution is generally less expensive in initial capital but solid state control of pump motor speed reduces operating expense because electrical power savings can be realised over the life of the equipment. The long-term reliability of the motor speed solution is greater if done properly, but the process control is slightly better with the proportional control valve.

Control of the reject-flow rate can only be achieved with the use of a proportional valve. Since the type of valve can affect the performance of the system, the valve should be capable of reducing the pressure (up to an order of magnitude bar, if necessary) while maintaining a smooth linear response throughout the required range of flows. In seawater RO applications, energy recovery from the high-pressure reject stream (>55 bar g psig) is an important economical requirement [44,45]. High-pressure drop control is, however, complex. Some systems may be designed with a fixed pressure drop, using an orifice plate, upstream of the reject control valve. The orifice plate lowers the amount of pressure that must be dropped across the control valve. Although this reduces the sensitivity of the valve, it enables the control-system output signal to operate over a greater range, thereby, increasing the accuracy of control.

The difficulty with controlling membrane feed-pressure and reject-flow rate simultaneously is that one affects the other. This gets more complicated with a two-pass system. If the membrane feed pressure is reduced, the reject-flow rate also will decrease if all other parameters (feed water temperature, quality and membrane condition) in the system remain constant. The danger, then, is that the whole system may oscillate if the PID controllers are not properly tuned. Tuning one controller for fast operation and the other for relatively slow operation is often the solution. Fast operation generally is best applied to the membrane feed-pressure controller because during start-up this parameter must be adjusted first. Manual control of these valves is, therefore, often preferred.

Incorporating the controller start-up output condition is also necessary to prevent the controller from drifting towards 0% or 100% – i.e. fully closed or fully open, respectively – during idle periods; otherwise, if the RO/NF pump starts when the membrane feed pressure or the reject-flow control valve is closed, a sudden spike in initial pump discharge pressure can result in equipment damage. Conversely, if the membrane feed-pressure valve is fully open during startup, the membrane elements are exposed to excessive pressure, which may cause compaction of the membranes in the leading elements.

Product quality controls

Feed water parameters that affect membrane life adversely such as high pH, free chlorine and high temperature are shown in Figure 2.22. Often, automatic on/off valves are provided to divert the feed or the permeate stream to drain when the stream quality is not in the desirable range. For example, if the feed water conductivity is much higher than the system is designed for, membrane scaling may result. A much higher-than-design permeate conductivity, on the other hand, indicates membrane scaling, membrane element integrity, or membrane damage. Hence, a low rejection alarm is often provided. Similarly, when the permeate flow rate exceeds the design point (or the reject flow is less than the design value), the potential for membrane scaling is substantially increased. A high recovery alarm is also included to alert the operator to reset the reject-flow control valve setting or shut down the unit.

High-pressure drop across a membrane array is a strong indicator of membrane fouling due to constriction in the reject/concentrate flow channel above the membrane, and calls for membrane cleaning. Usually RO/NF plant designs incorporate an automatic 5-min flush cycle preferably with RO permeate before shutdown to protect the membranes from (a) scaling by sparingly soluble salts in the salt concentrated stagnant reject channel, and (b) biological fouling. Often the flush cycle is programmed in the PLC to run at a preset interval such as every 4 h. During flushing the high-pressure RO pump is off. Flushing minimises the likelihood of scaling and fouling but is not a substitute for feed water pre-treatment.

Safety features

RO control systems provide safety features for operating high-pressure RO feed water pumps. Pressures at pump inlet and discharge, membrane inlet, product output and reject

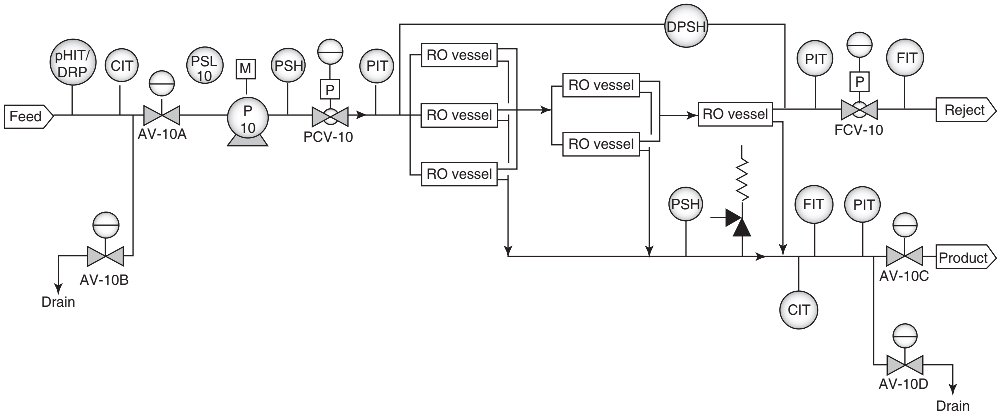


Figure 2.22 Typical first-pass RO unit process flow sheet. *Source: Singh and Tembrock, Reproduced with permission from Chemical Engineering Progress, Sept. 1999. Copyright 1999 AIChE.*

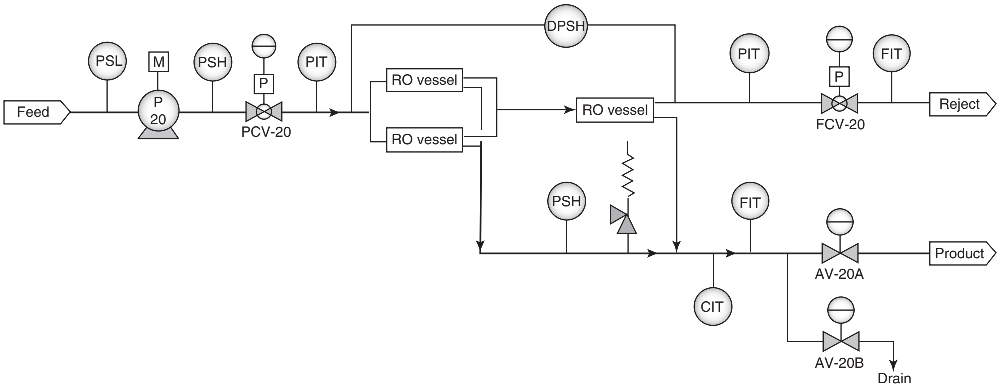


Figure 2.23 Typical second-pass RO unit process flow sheet. *Source: Singh and Tembrock, Reproduced with permission from Chemical Engineering Progress, Sept. 1999. Copyright 1999 AIChE.*

output are, therefore, monitored by pressure switches and transmitters as shown in Figures 2.22 and 2.23. To ensure long-term safe operation of the equipment, pressure switches shut down the pump during low inlet pressure and high discharge pressure conditions. The high-pressure RO pump must be run in auto mode to ensure it shuts down automatically during an emergency. A relief valve is provided in the permeate line to protect membrane elements from damage due to any back-pressure downstream. Further, in a fully automated RO system, the membrane inlet pressure and the reject-flow control valves are of the air-to-open type. Air-to-close valves should not be used because it would result in excessive membrane pressure during start-up.

The following general process conditions are taken into consideration when designing a control system to ensure safe and reliable operation [14]:

- Product water back-pressure greater than the system pressure at any time will damage the RO membranes.
- Operate the RO unit at the lowest system pressure that produces the design flow rate and salt rejection.
- The initial minimum salt rejection is based on chloride ions and applies to each individual membrane element. The total %rejection may be lower depending on the array. Membrane deterioration may result in salt passage to double within 3 years.

2.4.3 RO/NF array design

The following basic membrane separation phenomena should be kept in mind when designing a membrane system:

- The permeate flow rate (convective) is proportional to the net driving pressure (NDP) differential across the membrane.
- The salt flow rate (diffusive) is proportional to the concentration difference across the membrane, and is independent of applied pressure.

- Permeate TDS depends on the relative mass transfer rates of water and dissolved solutes through the membranes.
- The chemical and physical nature of the membrane determines the preferential transport of water over dissolved solutes.
- The higher the permeate flux, the greater the likelihood of higher concentration polarisation (CP). As CP increases, the osmotic pressure of the solution in the feed-reject channel increases, salt passage increases, and the risk of scaling and/or fouling increases.

Membrane manufacturers provide design guidelines based on the parameters given below. These guidelines are usually modified based on the type of feed water and pre-treatment [33,40].

- Maximum feed flow rate to any element in the pressure vessel
- Maximum reject-flow rate from any element
- Maximum product water recovery for an element
- Maximum flow rate (or flux) for any element
- Maximum average flux for a system
- Maximum applied pressure

The optimal design of the RO system incorporates certain rules of thumb based on the membrane for the particular application:

- Recovery per element is <19% for softened water or well water with SDI < 3
- Recovery per element is <16% for unsoftened water or surface water with SDI = 3–5
- Net pressure drop across the array is <7 bar
- Average flux for each element depending on the type of feed water[1]
- Percent variation in permeate flow rate is <10% between the first and last elements in the same pressure vessel
- Feed water flow rate to the first element of each stage is the same, <10%

In order to avoid excessive concentration polarisation at the membrane surface, permeate recovery per membrane element should not exceed 18%. In the case of brackish water RO systems, the average recovery per 100 cm (40-in.) long membrane element is usually about 9%. The overall recovery for a staged system with pressure vessels containing six elements is usually as follows [46]:

- One-stage array (1) = 52–56%
- Two-stage array (2:1) = 75–80%
- Three-stage array (4:2:1) = 85–90%

The recovery in each element is controlled by the concentration of rejected species, especially, sparingly soluble salts of calcium and magnesium and silica in the brine stream.

---

[1] 14–20 l/m^2 /h municipal wastewater (sewage); 17–24 l/m^2 /h for treated river water; 20–27 l/m^2 /h for lake water; 27–34 l/m^2 /h for deep well water (low turbidity); and >34 l/m^2 /h for RO permeate water when there is no fouling and/or scaling potential [46,47].

When the product recovery is 50%, the salt concentration in the reject stream is doubled, whereas the salt concentration increases fourfold when the recovery is 75% due to the concentration factor. Hence, the RO system is operated below the design recovery point. In general, the product water recovery is maintained well below 15%, and the systems are usually designed for a recovery of 8–10% per element. The scaling and fouling potential is usually the highest in the last elements of the final stage as stated in Table 2.9.

The above conditions are taken into consideration when modelling a RO/NF membrane system. The engineers use computer-generated performance projection software provided by membrane manufacturers to design an optimal membrane array design that maximises the operating conditions and minimises fouling and scaling. A typical RO/NF programme calculates permeate quality (conductivity, pH), feed-pressure requirements, and the final concentrate stream solubility numbers such as LSI and SDSI depending on (a) permeate flow rate, (b) %recovery, (c) feed water composition, (d) feed water temperature, (e) type and number of membrane elements, (f) the rate of flux decline, and (g) the rate of salt passage increase.

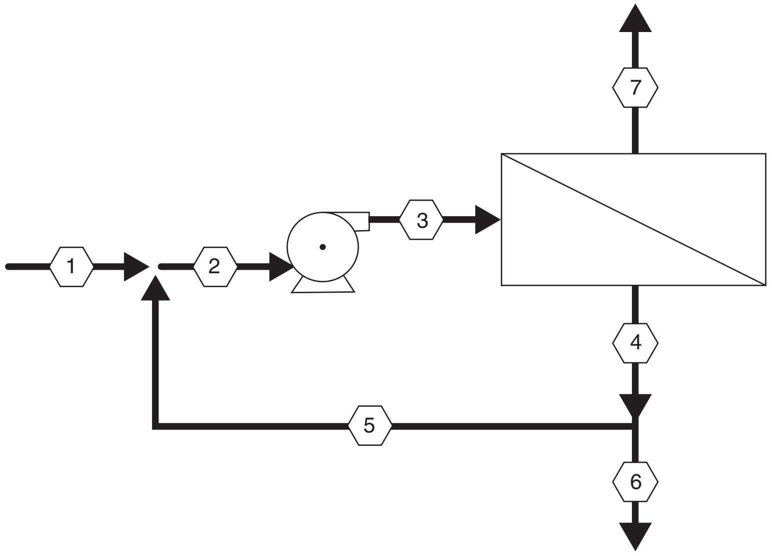
The programme algorithm is an iterative calculation in which the computer first estimates a feed pressure to satisfy the desired recovery and then calculates the performance of the first element of the system [46,47]. The concentrate from the first element becomes the feed to the second element, and a second calculation of membrane element performance is made, and so on from element to element through the complete array of the proposed design. The programme then sums the permeate flow from all elements and compares this value to the target value. The programme adjusts the feed pressure based on this comparison, causing the solution to converge to the required feed pressure to achieve the required permeate recovery given the user-defined system parameters and until the programme has converged on a single unique solution. Calculations can be repeated with different design parameters or membrane element array configurations. If the programme does not converge, a warning is issued requesting a revised number entry. The programme also calculates the concentration polarisation coefficient called the β factor:

$$\beta = \text{concentration at the membrane surface/concentration in the bulk fluid}$$

β is a function of the ratio of permeate flow from an element to the feed-brine average flow for that element. The optimum value is 1.13 for the last element of the last stage of a membrane array. To maintain this value of β when using 100 cm (40 in.) long SW elements, the maximum recovery is usually limited to 15% for one element, 30% for two elements in series, and so on to 50% for six elements in series in a pressure vessel.

Computer-generated design of a single-pass, three-stage RO membrane array (4:3:3) with concentrate recycling is shown in Figure 2.24 and given in Table 2.11. The stream numbers in the figure are 1 is raw water, 2 is blended water, 3 is membrane array feed, 4 is reject, 5 is reject/concentrate recycle, 6 is reject to drain, and 7 is permeate. The RO unit is designed to produce 27 gpm (6.13 m^3/h) permeate corresponding to an overall recovery of ~75% (27 gpm permeate/36 gpm raw water feed). The TFC polyamide RO membranes reduce the TDS content from 421 mg/l in blended feed water to 5 mg/l in product water at an average rejection of 98.8%. A portion of reject flows to the drain at 9 gpm (2 m^3/h), and the remaining recycles to the RO pump inlet at 5.5 gpm (1.25 m^3/h). The design feed pressure is 145 psig (10 bar g). The β factor is within range, and the LSI is <1, which is within range with anti-scalant dosage. The RO membranes are spiral-wound modules, 4 in. diameter × 40 in. long.

A typical RO skid is shown in Figure 2.25. It is a single-pass, two-stage (4:2 array) unit with pressure vessels containing six spiral wound membrane elements (20 cm × 100 cm) in series in each vessel. There is room on the backside of the skid to double the number of vessels to make it into an 8:4 array with permeate flow rates approaching 70 m^3/h at 75%. The RO high-pressure pump is multi-stage, horizontal, submersible type. The skid



		1	2	3	4	5	6	7
Flow	(gpm)	36.0	41.5	41.5	14.5	5.5	9.0	27.0
Pressure	(psi)	0.0	0.0	115.6	72.2	0.0	0.0	0.0
TDS	(ppm)	302.6	420.9	420.9	1195.9	1195.9	1195.9	4.7

Figure 2.24 Block-flow diagram of the single-pass RO membrane design given in Table 2.11 with reject recycling. Stream 1 is feed, 2 is blended feed, 3 is membrane array pressurised feed, 4 is reject, 5 is reject/concentrate recycle, 6 is reject-to-drain, and 7 is permeate.

Table 2.11 RO membrane system performance projection (Hydranautics)

Project name	Single-pass RO design	Permeate flow	27.00 gpm
HP pump flow	41.5 gpm	Raw water flow	36.0 gpm
Recommended pump pressure	144.6 psi	Total system recovery	75.0%
Feed pressure	115.6 psi	Permeate recovery ratio	65.1%
Feed water temperature	25.0°C (77 °F)	Concentrate recirculation	5.5 gpm
Feed water pH	7.14 (0.00)	Element age	0.0 years
Acid dosage, ppm (100%)	0.0 H_2SO_4	Flux decline % per year	7.0
Acidified feed CO_2	11.1	Salt passage increase, % per year	10.0
Average flux rate	15.2 gfd	Feed type	Well water

		Flow/vessel				**Conc and throt. pressure**				
Stage	**Perm. flow (gpm)**	**Feed (gpm)**	**Conc (gpm)**	**Flux (fgd)**	**Beta**	**(psi)**	**(psi)**	**Element type**	**Elem. no.**	**Array**
1–1	12.8	10.4	7.2	18.1	1.13	100.5	0.0	ESPA2-4040	12	4 × 3
1–2	7.8	9.6	6.9	14.8	1.11	83.8	0.0	ESPA2-4040	9	3 × 3
1–2	6.3	6.9	4.8	11.9	1.12	72.2	0.0	ESPA2-4040	9	3 × 3

	Raw water		**Feed water**		**Permeate**		**Concentrate**	
Ion	**mg/l**	**$CaCO_3$**	**mg/l**	**$CaCO_3$**	**mg/l**	**$CaCO_3$**	**mg/l**	**$CaCO_3$**
Ca	32.6	81.3	45.5	113.4	0.16	0.4	129.9	323.8
Mg	7.4	30.5	10.3	42.5	0.04	0.1	29.5	121.3
Na	47.8	103.9	66.3	144.2	1.11	2.4	187.8	408.3
K	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0
NH_4	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0
Ba	0.000	0.0	0.000	0.0	0.000	0.0	0.000	0.0
Sr	0.000	0.0	0.000	0.0	0.000	0.0	0.000	0.0
CO_3	0.1	0.2	0.1	0.2	0.00	0.0	0.4	0.7
HCO_3	69.3	56.8	96.5	79.1	0.80	0.7	274.7	225.1
SO_4	44.7	46.6	62.4	65.0	0.07	0.1	178.5	185.9
Cl	50.5	71.2	70.4	99.3	0.33	0.5	200.9	283.4
F	1.8	4.7	2.5	6.6	0.02	0.1	7.1	18.8
NO_3	44.7	36.0	61.6	49.7	2.11	1.7	172.4	139.1
SiO_2	3.7		5.2		0.03		14.7	
TDS	302.6		420.9		4.7		1195.9	
pH	7.0		7.1		5.3		7.6	

Table 2.11 RO membrane system performance projection (Hydranautics)—cont'd

	Raw water	Feed water	Concentrate
$CaSO_4/K_{sp} \times 100$	1%	1%	6%
$SrSO_4/K_{sp} \times 100$	0%	0%	0%
$BaSO_4/K_{sp} \times 100$	0%	0%	0%
SiO_2 saturation	3%	4%	11%
Langelier Saturation Index	−1.21	−0.79	0.58
Stiff and Davis Saturation Index	−1.16	−0.74	0.60
Ionic strength	0.01	0.01	0.02
Osmotic pressure	2.5 psi	3.4 psi	9.8 psi

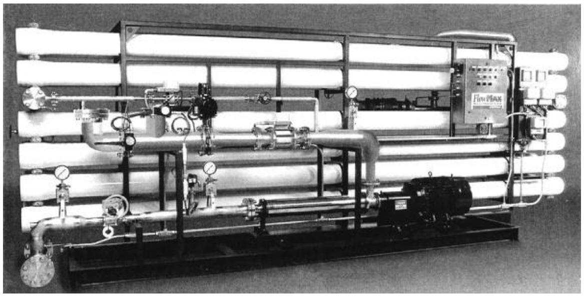


Figure 2.25 A typical RO skid showing a 4:2 two-stage membrane array, high-pressure pump, instruments and control panels. The high-pressure RO pump is a horizontal, multi-staged submersible type. Each pressure vessel contains six spiral-wound modules, 20 cm dia. × 100 cm long. *Source: USFilter.*

includes a control panel and instruments such as conductivity and flow monitors shown on the right-hand side. The end view of a large RO/NF membrane system is shown in Figure 2.26.

The effect of colloidal fouling on membrane processes was discussed earlier in this chapter; it is a function of the permeate flux and the solids content of the feed solution. Since colloidal fouling has a strong negative effect on membrane performance, membrane systems are designed by limiting the permeate flux of each element based on the recommendations of the membrane manufacturers. One such plot for a RO membrane with various natural water feeds is shown in Figure 2.27. The data show that as the quality of feed water improves, the recommended permeate flow rate also increases. For example, as the membrane flux is linear with pressure in the case of nearly pure water or RO permeate. The figure shows that the flux reaches a plateau at higher pressures for solutions other than pure water due to concentration polarisation (CP) as discussed in Chapter 1. The mid-point of the non-linear curve is the region of critical flux and the optimal operating condition to minimise CP as discussed earlier.

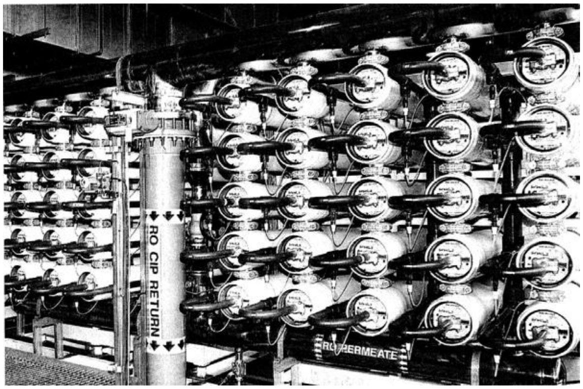


Figure 2.26 End view of a RO/NF membrane plant. *Source: Ultrapure Water.*

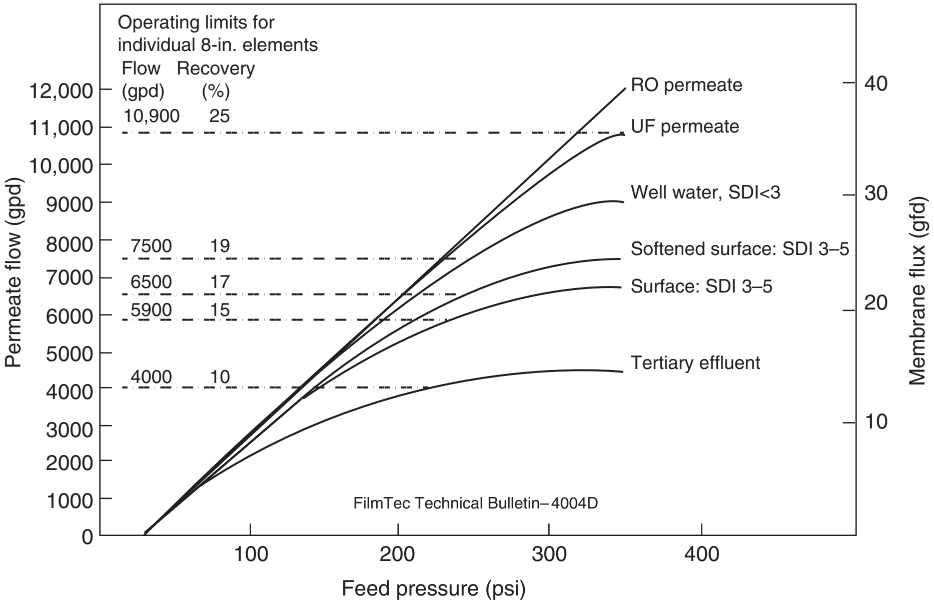


Figure 2.27 Membrane flux characteristics of a spiral wound RO module for various feed waters. *Source: Film-Tec membrane catalogue.* For non-pure water solutions the flux reaches a constant, steady state value at higher pressures. For optimal performance, the system should be run below the "critical flux" region, which is the mid-point of the curved part of the curve.

2.4.4 Cross-flow (constant pressure) UF/MF design

Cross-flow systems typically operate at constant pressure and not at constant flux. The design and mode of operation of UF and MF systems are defined by the process needs and application. There are three main process configurations: (a) single-pass, (b) batch filtration, and (c) feed-and-bleed [34,48]. By contrast, all RO and NF systems are of single-pass design. Batch and feed-and-bleed designs involve extensive recycling to remove ≥ 95% of the solution as permeate. In biological applications, heat exchangers are required in the recycle loop for cooling to protect biologicals and proteins from irreversible damage.

Single-pass system

The single-pass process schematic shown in Figure 2.28a is the simplest process configuration. It is a continuous process in which modules are arranged in series to achieve complete separation in a single pass. Complete separation in one pass is difficult and

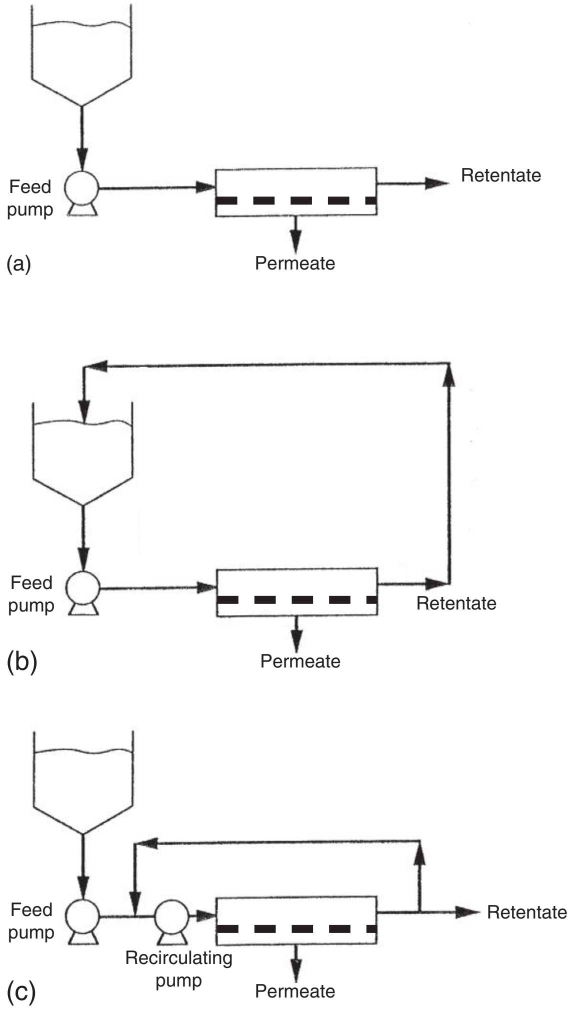


Figure 2.28 Typical process configurations of UF/MF cross-flow systems: (a) single pass, (b) batch process, and (c) feed-and-bleed.

requires substantial membrane area to achieve the desired permeate recovery. This in turn results in higher energy consumption and pumping costs to maintain high velocities (5–10 times higher than in RO systems) to minimise concentration polarisation and/or fouling as the feed becomes more viscous and to overcome higher pressure drops to pump the viscous concentrate through the feed channels.

Batch filtration

Batch systems are used in small-scale applications for processing high value solutions common in the biotechnical, pharmaceutical and laboratories. As shown in Figure 2.28b, the retentate (concentrate) recycles to the feed tank so that the concentration of the retained particles and solutes in the feed tank increases as the permeate is removed. This results in a decline in permeate flux with time; the initial concentration is relatively low and flux relatively high. The permeate recovery per pass is much smaller than in a single-pass system as is the membrane area, but the residence time is very long, contributing to high pumping costs in large systems; hence it is best suited for small volumes. It is also used in small-scale and pilot-scale applications when the permeate is the product; for example, fruit juice and for effluent treatment where the concentrate is disposed off. Prolonged constant recirculation of the concentrate often results in denaturation of proteins and cells. Hence, it is not suitable for applications when the concentrate is a biological product because it can get damaged due to extended exposure to heat and shear as well as bacterial growth.

Feed-and-bleed configuration

The feed-and-bleed (F&B) design is used in most large-scale commercial applications. As shown in Figure 2.28c, a part of the concentrate is recycled. The flow rate in the recirculation loop is 5–10 times the feed solution rate. This means the concentration of retained solutes in the recycle loop is close to that in the bleed solution, and is significantly higher than in the feed solution. In other words, the entire system operates at the final retentate concentration corresponding to the lowest permeate flux. Since the flux decreases with increasing concentration, the membrane area required is significantly higher than in a batch or a single-pass system; for example, the area required to obtain a concentration factor of 10 in a F&B system is three times higher than a batch system and 60% higher than a single-pass system [34].

Multiple array design

In order to overcome the inefficiency of the single-stage design, F&B systems used in industrial applications are often configured as multi-stage units, as shown in Figure 2.29. In this design, the concentrate from the first stage flows to the second stage as feed and so on. With multiple stages, the difference in concentration between the solution circulating in a stage and the feed solution entering the stage is reduced. Because the membrane

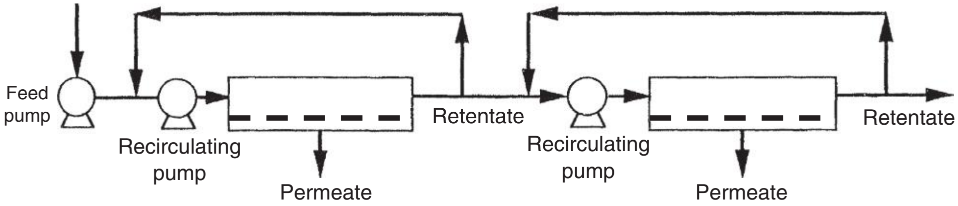


Figure 2.29 Schematic representation of a multi-stage, feed-and-bleed UF/MF cross-flow system.

elements in the first-stage operate at a lower concentration than in the next stage, the membrane flux in the first-stage is higher than in the next stage, and so on.

Most commercial processes use three to five stages, as shown in Figure 2.30. As the number of stages is increased, the average concentration of the solution circulating through the membrane elements decreases. Thus, the total membrane area in a multi-staged system is significantly lower than in a single-stage system. The most efficient design is one when all stages have about the same membrane area [34,48]. Flux vs. concentration curves for the system illustrated in Figure 2.30 are shown in Figure 2.31.

UF/MF performance

The processing time required for a given UF/MF operation is controlled by the membrane area, feed volume to be processed and solute concentration. Of these, solute concentration is the most important factor as it controls flux and the membrane gel concentration, which is determined by the well-known flux-concentration mass transfer limited gel-polarisation model introduced in Chapter 1 as:

$$J = k\ \ln\frac{C_g}{C_b} \tag{2.34}$$

The semi-log relationship of flux vs. feed concentration for a batch filtration test run is shown in Figure 2.32 [49], where C_g is the "gel layer" concentration and C_b is the bulk feed concentration (in the absence of a gel layer, $C_g = C_w$). The C_g value, ~14%, is considerably lower than that for macromolecules and colloids, but is consistent with the data for other surfactant systems. A low C_g value restricts the maximum practical level of final concentration in similar UF applications.

The mass transfer coefficient, k, is the slope of the curve. The steeper the slope (the higher the Sherwood number, $\mathrm{Sh} = kL/D$, where k is the mass transfer coefficient, L is a characteristic dimension and D is molecular diffusivity), the faster the rate the solutes migrate to the membrane surface. The UF membrane used was a regenerated CA with a MWCO = 10,000 Da.

The experimental data were used to generate a preliminary design of a UF plant [49]. The design parameters are given in Table 2.12. The design is based on a PVDF tubular membrane (MWCO = 18,000 Da). A tubular membrane plant consumes 50% more

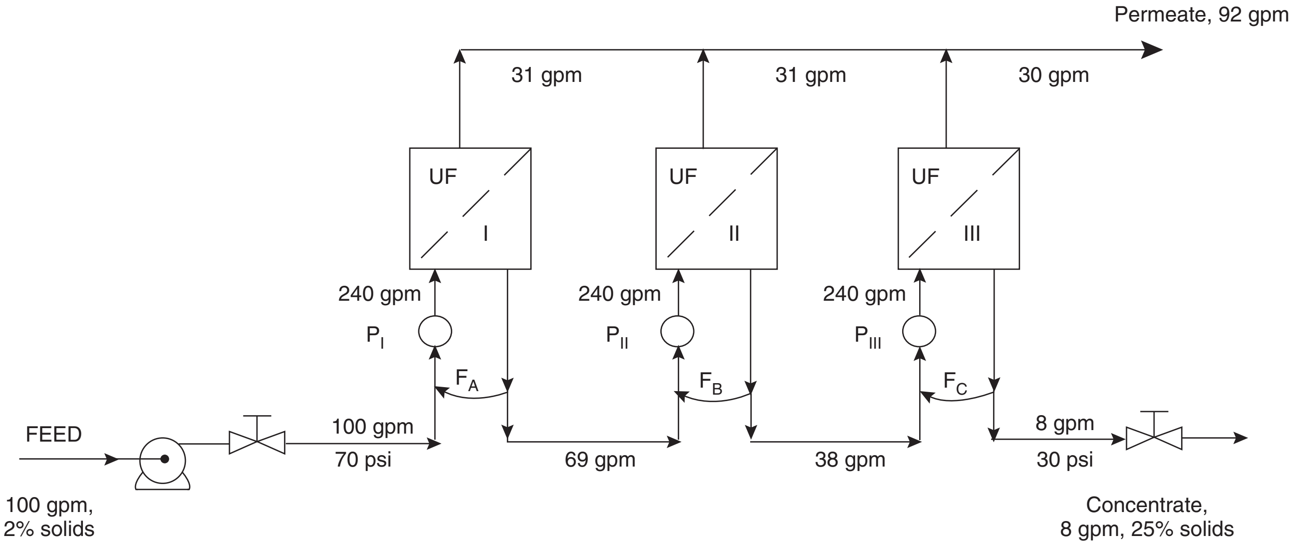


Figure 2.30 Design and operation schematic of a multi-stage, feed-and-bleed UF cross-flow system. Each membrane stage contains four UF modules in series. F_A, F_B and F_C represent recycle streams operating at 140, 171 and 202 gpm. P_I, P_{II} and P_{III} are recirculation pumps.

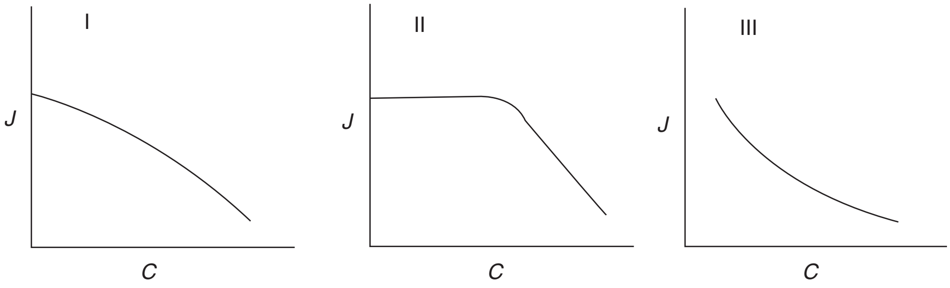


Figure 2.31 Typical flux (*J*) vs. feed concentration (*C*) curves for the UF system in Figure 2.30.

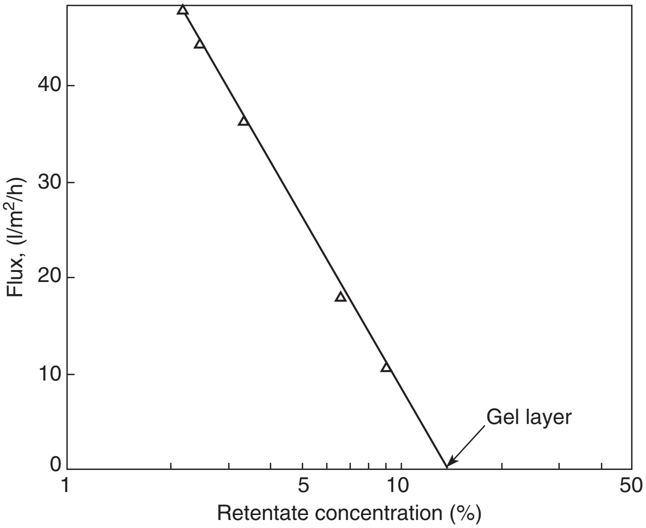


Figure 2.32 Batch UF membrane flux vs. concentration curve for a surfactant feed water. Cross-flow cell at 2.76 bar g; 1100 ml/min; 20°C; Amicon regenerated cellulose YM-10 membrane with MWCO of 10,000 Da. *Source:* [49].

power than either a HF or a SW plant. The final concentrate volume is, however, 50% smaller. In addition, tubular membranes have a longer life than HF membranes (5 years vs. 3 years) and are cheaper than HF modules.

The curve shown in Figure 2.32 is a standard flux vs. concentration plot and holds true for almost all UF/MF cases. A slight variation of the plot for batch UF of a protein solution is shown in Figure 2.33 [50]. In this plot, gel polarisation seems to be a two-step process involving build-up and clogging at low concentrations followed by compaction of the sub-layer. The test run used three membranes: DPO6, an isotropic microfilter with a pore size of 6000 Å; PM-10, a polysulphone UF membrane with a MWCO = 10,000 Da; and PM-30, a polysulphone UF membrane with a MWCO = 30,000 Da. The pure water

Table 2.12 Tubular UF plant design parameters

Item description	**Design parameter**
System flow rate (m^3/day)	327
Permeate flow (m^3/h)	13.6
Reject recycle flow(m^3/h)	455
Product water flux (l/m^2/h)	51
Product water recovery (%)	96.5
Final concentrate volume (m^3)	11.4
Feed pressure (bar g)	3.45
Penreco oil/lgepal CO-660 conc in feed (%)	2.0/0.2
Oil/surfact injection rate (m^2/h) at 1.4 bar g	0.4
Final concentration in reject (%)	30.0
Membrane (Da)	PVDF, MWCO = 18,000
Membrane tube size:	
Diameter (cm)	2.54
Length (m)	3
Number of tubes	1200
Tubes/bank	12
Number of tube banks	50
Number of parallel arrays	2
Membrane life (y)	5
Feed equalisation tank (m^3), FRP[a]	3.8
Feed/recycle tank (m^3), FRP[a]	38
Feed pump (m^3/h)	455
Membrane cleaning tank (m^3), LDPE[b]	1.9

[a] Fibre glass-reinforced plastic.

[b] Low-density polyethylene.

Source: [49].

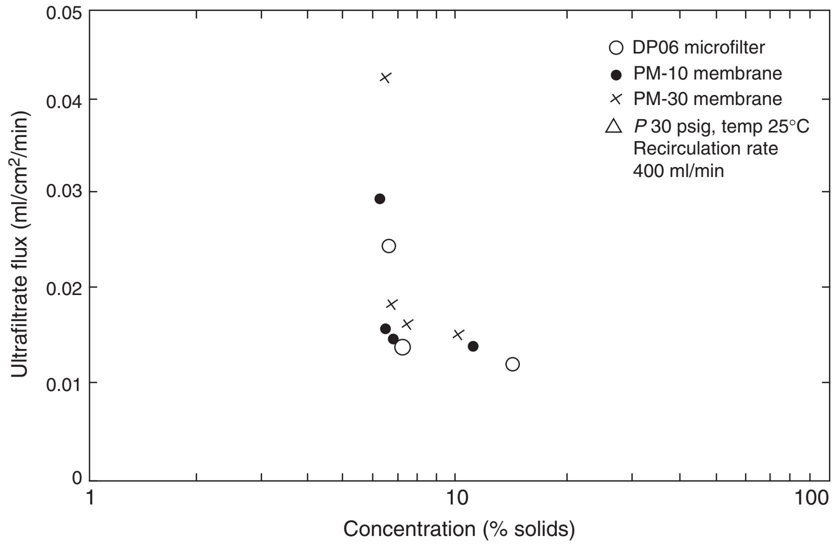


Figure 2.33 Batch cross-flow membrane filtration flux vs. concentration curve for a protein feed solution for various UF and MF membranes. Amicon polysulphone PM-10 and PM-30 membranes with MWCO of 10,000 and 30,000 Da. The "gel layer" concentration is between 30 and 40%.

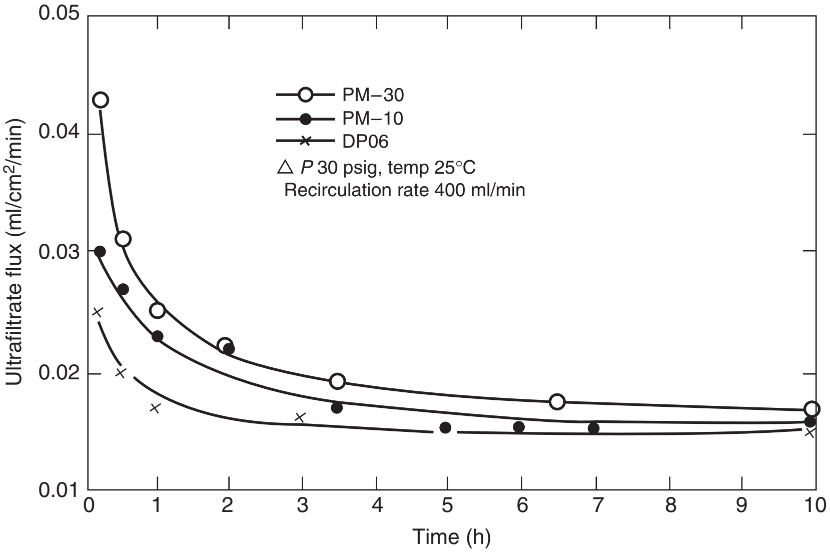


Figure 2.34 Cross-flow membrane filtration flux vs. time curve for the system in Figure 2.33.

flux for these membranes was 0.66, 0.25 and 0.58 ml/cm^2 min. The isotropic microfilter fouled easily due to internal pore plugging, and had the lowest flux with the protein solution feed even though it had the highest water flux, as shown in Figure 2.34. This figure also shows that flux declines rapidly with time due to the formation of a gel layer and fouling by microsolutes, in this case protein macromolecules (see Equation 1.14). It is typical of UF/MF membrane systems, and follows a simple empirical relationship given by Equation (1.7) in Chapter 1.

2.4.5 Constant flux (variable pressure) UF/MF design

Membrane filtration systems for water treatment are a semicontinuous and dead-end type. The most common design is submerged membrane modules operating in a constant flux mode. The flux is maintained constant by a variable speed pump that sucks the permeate under vacuum. An increase in suction pressure (TMP) is applied as the membrane fouls to maintain the design water flux. The permeate solution is removed from the top with a pump, which is usually set to maintain a flux of 10–30 lmh. Membrane fouling is controlled by a combination of backflushing and air sparging, as discussed in Section 2.2.5. Submerged membrane design saves the capital cost of encapsulation (no pressure vessels) but restricts TMP due to the practical limitation of drawing a vacuum [51].

2.4.6 ED design

ED systems are classified as continuous (one-pass flow), batch and feed-and-bleed processes. The continuous process is used in large-scale plants [52]. Batch processes are applicable for small and middle-scale plants. ED is used for desalinating brackish water with feed salinity less than 5000 mg/l for treating municipal water and for treating wastewater. Depending on the water temperature, solids content, flow rate and applied voltage, one ED membrane stack produces about 30–60% desalinated water. In large systems, using several ED stacks in series for separation is more efficient, i.e. to achieve a practical level of 75–95% or higher salt removal. For example, two ED stages for 75% salt removal, four stages for 94% salt removal and six stages for 98% removal. The water recovery with EDR (ED reversal) is up to 95%. Flow schematics of ED systems are shown in Figure 2.35.

A schematic drawing of an ED stack is shown in Figure 2.36. A stack generally contains 100–200 membrane cell pairs each with a membrane area of 1–2 m^2. Plastic mesh spacers form channels through which the feed and concentrate solutions flow. The two main spacer designs are flat sheet and tortuous path flow. Multiple stacks are used because the current density of the first stack is higher than that of the last stack which operates on a more dilute feed solution. Because concentration polarisation becomes limiting as the solution gets diluted, the solution velocity in the stacks is increased to control polarisation. The velocity, in turn, is controlled by the number of cell pairs through which

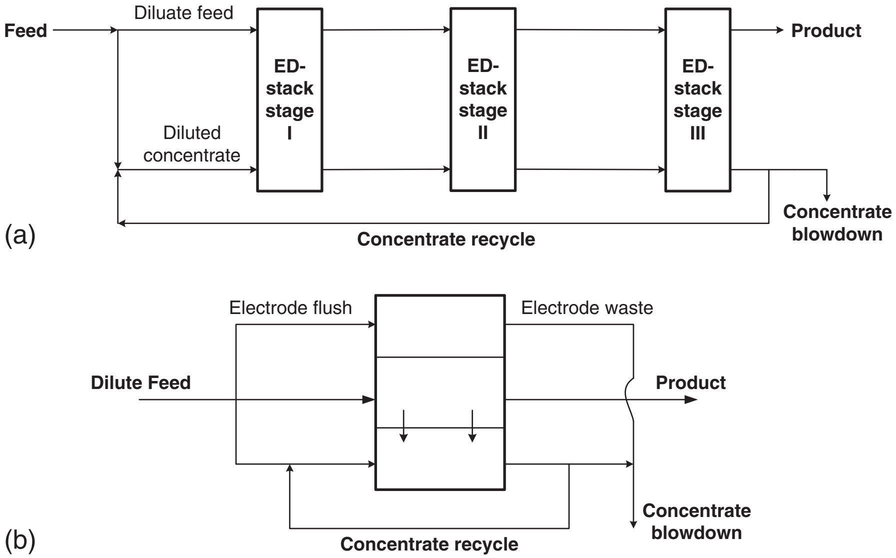


Figure 2.35 (a) Flow schematic of a typical multi-stage ED unit. Typical recovery is 90%. (b) Flow distribution in an ED stack. *Source: Adapted from Ref. [52].*

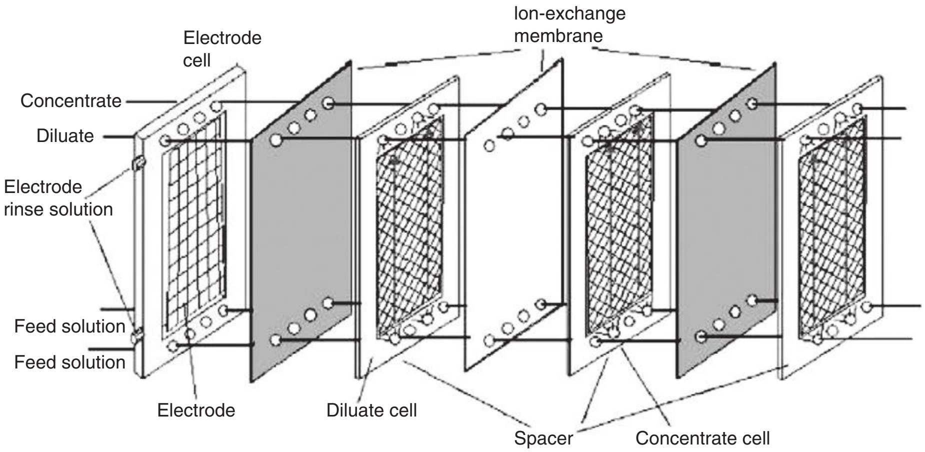


Figure 2.36 Schematic drawing of a sheet flow design ED stack. *Source: [52].*

the solution passes in each stack. The number of cell pairs used in series decreases from the first to the last stack.

ED systems consume large amounts of DC power, and a rectifier is used to convert AC to DC. A typical voltage drop across a single-cell pair is 1–2 V, and the current density is 40 mA/cm^2. For a 200-cell pair stack containing 1 m^2 of membrane/cell, the total voltage is 200–400 V and the current is about 400 A/stack. A large fraction of total power is consumed by the water pumps required to circulate feed and concentrate solutions through the stacks. Power consumption increases as the average salt concentration of the feed decreases, especially when the feed salt concentration decreases to <500 ppm. The pressure drop per stack is 1–2 bar for sheet flow cells and 4–6 bar for tortuous path cells [48]. Energy consumption of ED plants is discussed in Chapter 5.

2.4.7 Performance monitoring

Most membrane system problems occur due to a failure to record and analyse data after it is recorded. Data trending helps in diagnosing the system. Without data trending it is difficult to analyse when the membrane unit should be shut down for cleaning the membranes (e.g. see Figure 2.37). The performance data reflected in Table 2.5 provide markers for cleaning the membranes as discussed in the next section. The following relationships are used when evaluating data and monitoring membrane system performance. Additional correlations for RO/NF and UF/MF systems are given in Section 5.1

1. *% Rejection, Rej (or %Retention):*

$$\mathrm{Rej} = \frac{[(\text{feed} + \text{reject})/2]\ \text{solute concentration} - \text{permeate solute concentration}}{[(\text{feed} + \text{reject})/2]\ \text{solute concentration}} \times 100$$

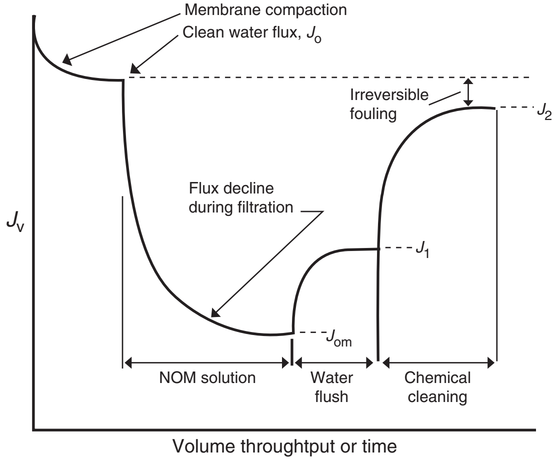


Figure 2.37 Typical membrane flux decline with time due to fouling, and post-cleaning recovery for a membrane system processing high fouling streams. *Source: Schafer et al.*

2. *% Recovery, Rec:*

$$\text{Rec} = \frac{\text{permeate flow rate}}{\text{feed flow rate}} \times 100$$

Rejection and recovery are the two basic indicators of membrane performance.

3. *Concentration factor, C_f:*

$$C_f = 1/(1 - \text{Rec})$$

It is a useful parameter but not often used.

4. *Temperature correction factor, TCF:*

$$\text{TCF} = 1.024^{(\text{T}_\text{m} - \text{T}_\text{s})}$$

where T_m and T_s are solution temperatures at operating and standard (e.g. 25° C) conditions.

5. *Normalised productivity, Q_p:*

Field permeate flow rate (productivity) should be normalised for temperature and pressure, and re-plotted to provide an accurate basis for comparing data over time.

$$\text{Q}_\text{p} = \text{Q}_\text{t} \times (\text{NDP}_\text{i}/\text{NDP}_\text{t}) \times (\text{TCF}_\text{i}/\text{TCF}_\text{t})$$

where Q_p is normalised flow rate at time t, Q_t is actual flow rate at time t; NDP_i is net driving pressure (see Equation 5.5) at initial or referenced condition, NDP_t is net driving pressure at time t; TCF_i and TCF_t are temperature correction factors at initial condition and at time t, respectively.

2.5 MEMBRANE CLEANING AND SANITISATION

Membrane cleaning has not historically been the focus of major study vis-à-vis fouling even though it is a key element in long-term membrane life and operation. Membrane cleaning is required to restore membrane performance. Prompt and regular cleaning is necessary to prevent fouling from getting worse with long-term adverse effects. A typical flux vs. time curve for the UF membrane system shown in Figure 2.37 illustrates the effects of fouling and cleaning on flux. Flux decline slope values are used to judge the rate of colloidal fouling and to determine when cleaning is required [32]. In the case of RO, cleaning should be initiated when any of the following conditions are true:

- Permeate flow has dropped to 10–15% below the rated flow at normal pressure
- Temperature-corrected feed pressure has increased 10–15% to maintain the rated permeate flow
- Permeate quality has decreased 10–15%; salt passage has increased 10–15%
- Applied pressure has increased about 10–15%
- The differential pressure across an RO unit has increased noticeably (>15%)

2.5.1 Membrane cleaning

Cleaning is the removal of foulants and scalants from the membrane element to restore membrane flux and rejection as far as possible. The main chemical and physical cleaning methods used are [32–34]:

1. Chemical detergents and cleaners solubilise or disperse the foulants. Chemical cleaning efficiency increases with temperature since the rate of chemical reaction doubles with every 10°C increase in temperature.
2. Hydraulic energy in the form of high flow velocity in the feed channel. Ideally, cleaning should be done at turbulent conditions, i.e. $Re > 2100$, which is only possible with tubular membranes. Sometimes foam balls are used to scrape dirt from the surface of tubular membranes, as shown in Figure 2.38.
3. Backflushing is used to remove colloidal and particulate foulants from hollow fibre and tubular UF/MF membranes. Fouling is minimised and the frequency of chemical cleaning is reduced substantially. The operation is described in Chapter 4.
4. Other physical methods include air sparging, vibrations, sonication, and CO_2 back-permeation.

The frequency of cleaning can affect membrane longevity. Hence, the following general precautions during cleaning should be noted:

- Clean at the recommended temperature to optimise cleaning efficiency and membrane life.
- Use the minimal amount of chemical contact time to prolong membrane life.
- A “gentle” pH range is 4–10, while the harshest is 1–12. Extremes of pH have an adverse effect on the life of RO and NF membranes. During recirculation, the

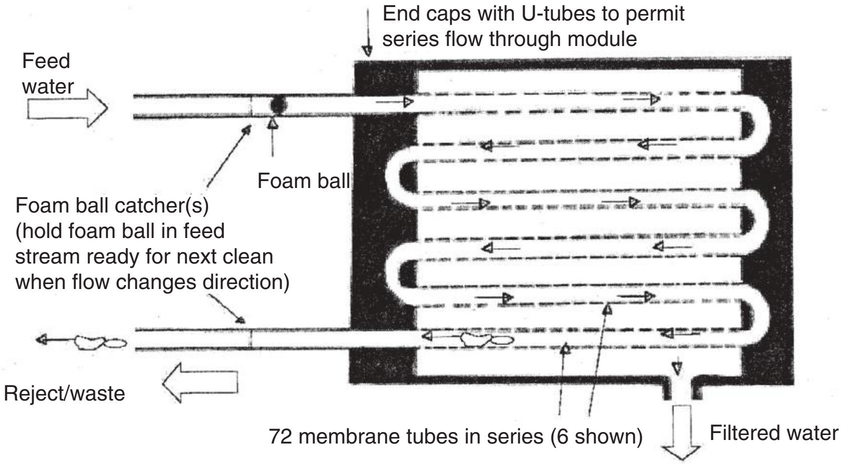


Figure 2.38 The operating principle of cleaning of tubular membranes with foam balls. *Source: Wittman and Thorsen.*

temperature must be less than 50°C at pH 2–10, <35°C at pH 1–11, and 30°C at pH 1–2 for PA membranes. Always monitor the cleaning solution pH.

- Improper selection of a cleaning chemical, or the sequence of chemical introduction, can result in worsening fouling.
- The TMP drop should be minimal; high pressure drops aggravate fouling during cleaning. High pressure drop can be used after the membrane has been cleaned to remove matter from pores in the case of UF and MF membranes.

Cleaning chemicals

Chemical cleaning is based on chemical reactions – hydrolysis, saponification, solubilisation, dispersion, chelation, and/or peptisation – to break down bonds and cohesion forces between the membrane surface and the foulants [32]. Commonly used chemical cleaners for membrane systems are given in Table 2.13. Acids being low pH cleaners are used first to remove precipitated salts or mineral scale. Phosphoric acid is the least aggressive (not recommended for ceramic membranes). It also has its own detergent action because of the phosphate groups. Nitric acid is very corrosive but effective. Citric acid is very effective for iron foulants. It combines acidity with detergency and chelating ability. Sulphuric acid and hydrochloric acids are not recommended when there are stainless steel components. Alkalis being high pH cleaners are used for removing organics and proteins; they act by solubilising them. Polyphosphates are added to help solubilise carbonates and emulsify fats [32,53]. Caustic solutions act by breaking the bonds between the membrane surface and the foulant.

Table 2.13 Chemicals for cleaning membrane elements

Foulant	Example	Chemical cleaner
Salts	Mineral	0.1–0.5 M acid (acetic, citric, nitric)
Scale	$CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, SiO_2	Citric acid, 0.2% (wt.) HCl, 0.5% (wt.) phosphoric acid, or EDTA-based solution; clean silicate-based foulants with ammonium bifluoride-based solutions
Colloidal clays/silt	SiO_2, $Fe(OH)_3$, $Al(OH)_3$, $FeSiO_3$	EDTA or BIZ type detergents at high pH; clean silicate-based foulants with ammonium bifluoride-based solutions
Biological	Iron reducing bacteria, sulphur reducing bacteria, mycobacteria, pseudomonas	EDTA or BIZ type detergents at high pH; shock disinfection with hydrogen peroxide, peracetic acid
Organic	Fats, oil, grease	Detergents/surfactants, isopropanol, 2–50% ethanol
Bio-organics	Fats, oils, proteins, biopolymers	0.1% sodium dodecyl sulphate, 0.1% TritonX-100

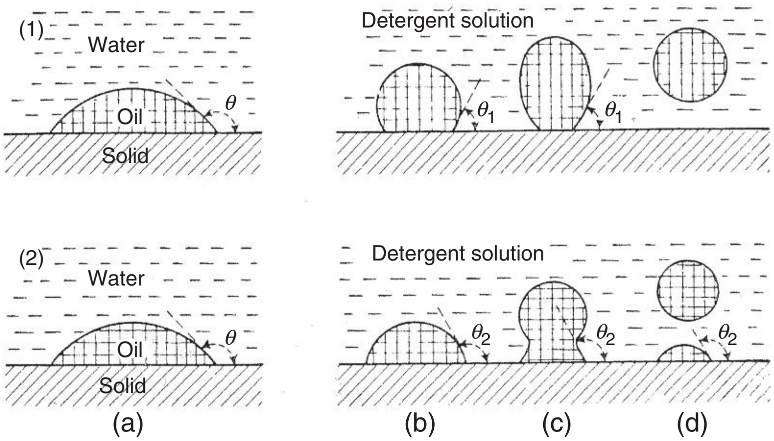
Chlorine in the form of household bleach (4 ml of 55 bleach in 1 litre of 0.5 N caustic soda results in 200 ppm of chlorine) is an effective cleaner (not to be used for PA membranes) especially when the pores are fouled in the case of UF and MF membranes. The recommended dosage is 50 ppm for CA membranes, 20–400 ppm for polyether sulphone membranes and 1000–2000 ppm for inorganic membranes. In the case of UF and MF polymeric membranes, chlorine action results in opening the pores that allows the foulant to be flushed out at high pressure.

Sometimes a number of different cleaning chemicals are used in a specific sequence for optimum cleaning; for example a high pH cleaner to remove foulants such as oils or biological matter followed by a low pH cleaner. Some cleaning solutions have detergents (surface active agents) added to aid in the removal of heavy biological and organic debris, while others contain a chelating agent like EDTA added to aid in the removal of colloidal material, organic and biological material, and sulphate scale. Enzymes are effective for removing proteins and other severe foulants that form strong bonds with the membrane surface due to charge interactions. Organic solvents such as ethanol solutions are sometimes used to remove hydrophobic foulants including fats, oils and grease. Cleaners require 30–90 min for effective action; enzyme cleaners require 60–90 min, whereas optimum time for chlorine-containing cleaners (not applicable to PA membranes) is 60 min [34,53]. Prolonged cleaning beyond the design time, however, can foul the membranes again.

The cleaning action of chemicals is illustrated by a few examples. Detergents are used when the foulant is oil or grease. The addition of a detergent lowers the contact angle,

θ at the solid-oil-water boundary, as shown in Figure 2.39 [54]. If $\theta = 0$, the oil will detach from the membrane surface spontaneously, and will be washed away with water during cleaning. If the contact angle is in the range, $90° < \theta < 180°$, only part of the oil can be detached by water under hydraulic pressure, while some remains attached. Hence, a different mechanism such as solubilisation is needed to remove the residual oil; for example increasing the temperature to 45°C increases the detergent efficiency markedly. Similarly, the process of removing foulants from the membrane surface by the action of a detergent and mechanical action are depicted in Figure 2.40.

The effectiveness of cleaning a UF membrane fouled by organics – proteins, lipids and carbohydrates – when processing aqueous soy flour extract is shown in Figure 2.41 (as shown in Figure 2.37, the flux declined sharply due to fouling). The data show the effects of step-wise cleaning protocols: (a) rinsing; (b) 0.5% (wt.) sodium hydroxide cleaning; (c) 0.75% (wt.) protease detergent cleaning; and (d) sanitising with sodium hypochlorite (150 mg/l) [32]. There is a dramatic increase in flux recovery after treatment with the enzyme-based detergent, most likely because the enzymes are action specific (catalysts), and the enzyme used was directed to the specific foulant. Enzymes are often used when the cleaning conditions are around neutral pH, when there is a likelihood of biofouling. The effectiveness of sodium hypochlorite was most likely due to its ability to cause swelling of the membrane [55,56].

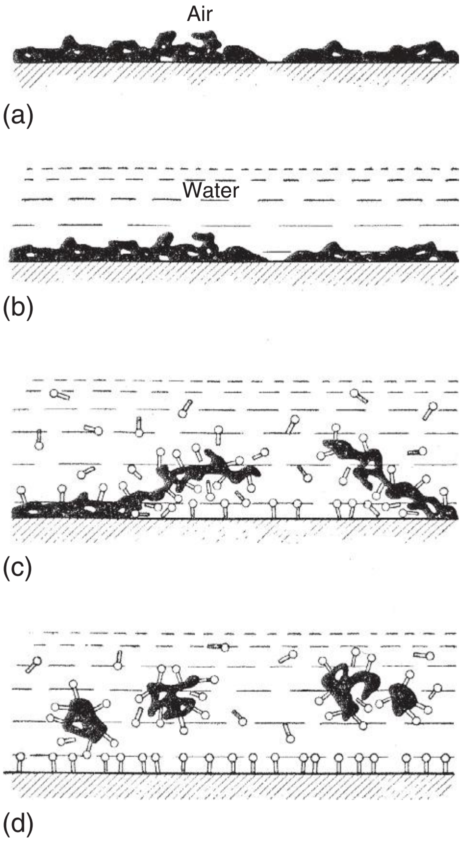


Detachment of oily dirt from a solid surface. The sequences (left to right) show: (a) the substrate/dirt system in contact with pure water, (b, c) lowering of contact angle caused by detergent ((1) $\theta < 90°$, (2) $\theta > 90°$), and (d) mechanical (hydraulic) detachment of oil droplets.

Figure 2.39 Detergent cleaning action for removing oily dirt from a solid surface. *Source: Shaw.*

In situ RO/NF element cleaning procedure

The membrane elements are cleaned in the pressure vessels by re-circulating the cleaning solution across the high pressure side of the membrane at low pressure and relatively high flow rates. A typical clean-in-place (CIP) unit schematic is shown in Figure 2.42. The



Removal of dirt from a solid surface by detergent and mechanical action. (a) Surface covered with greasy dirt. (b) Water by itself fails to dislodge the dirt mainly because of its high surface tension and inefficient wetting action. (c) Detergent is added to the water. The hydrophobic parts of the detergent molecules line up both on the dirt and on the solid surface, thus reducing the adhesion of the dirt to the solid. The dirt may now be dislodged by mechanical action. (d) Dirt is held suspended in the solution because the detergent molecules form an adsorbed layer on the cleaned surface and around the dirt particles.

Figure 2.40 Removal of dirt from a solid surface by detergent and mechanical action. *Source: Shaw.*

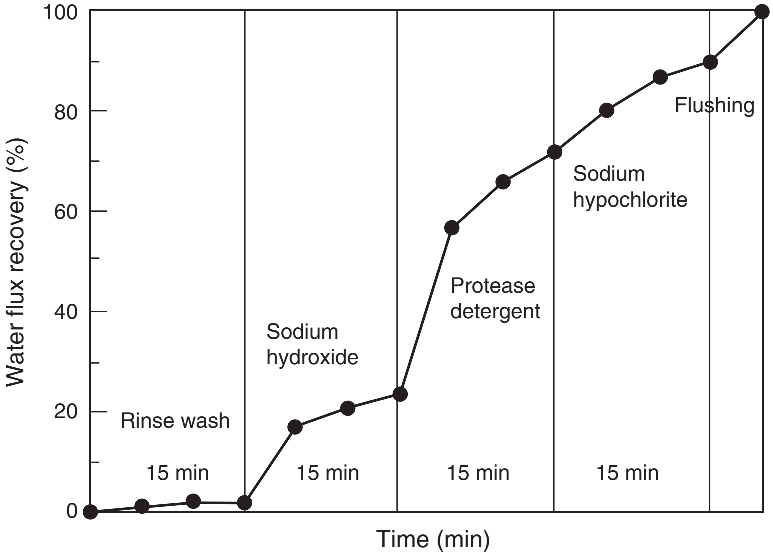


Figure 2.41 Membrane flux recovery with successive cleaning steps. *Source: Schafer et al.*

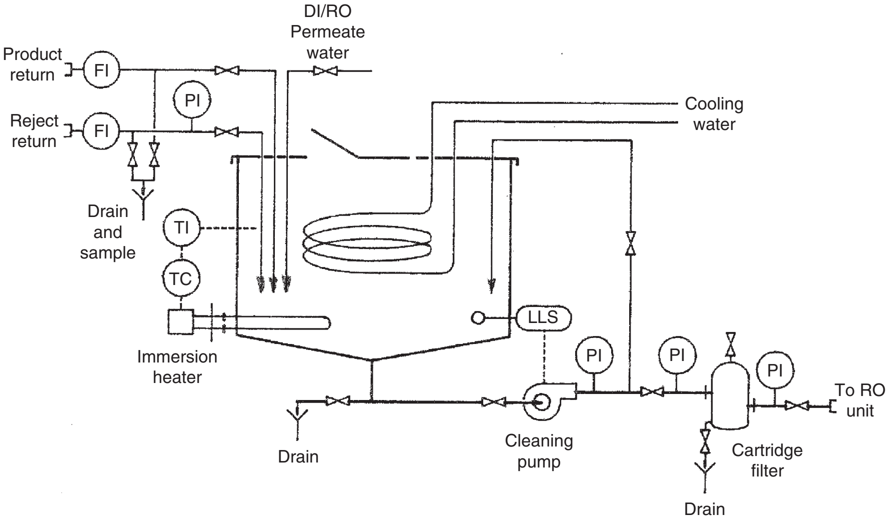


Figure 2.42 Schematic diagram of a typical membrane clean-in-place (CIP) system. The cartridge filter is rated for 5.0 μm. The heating/cooling system is optional.

time required to clean a stage or a pair of stages is 2–3 h for small systems and 4–8 h for large systems. A general procedure for cleaning RO/NF membrane elements is described below:

1. Start with a low pressure flush (<4 bar g) by pumping clean water from the cleaning tank (or equivalent source) through the pressure vessels to drain for several minutes. Flush water should be RO/NF permeate or DI water, and free of hardness, transition metals, and also chlorine-free when using PA membranes.
2. Mix a fresh batch of the selected cleaning solution in the cleaning tank. The dilution water should be clean water – RO/NF permeate or DI water.
3. Circulate the cleaning solution through the pressure vessels for 30–60 min at 8–10 m^3/h per pressure vessel in the case of 20-cm diameter SW elements. High flow rate flushes away the foulants. The maximum pressure drop should be 1 bar per element or 3 bar per pressure vessel. The solution temperature must be >15°C.
4. Initially, send the displaced water to drain so as not to dilute the cleaning chemical. Divert up to 20% of the most highly fouled solution to drain before returning the cleaning solution back to the CIP tank. Initially for the first 5 min, throttle the flow rate to two-thirds of the maximum design flow rate slowly, and then increase the flow rate to the maximum design flow rate. If required, readjust the pH to the target when it changes more than 0.5 pH units.
5. An optional soak and recirculation sequence can be used, if required. The soak time can be from 1 to 8 h depending on the type of foulant and the membrane. Ensure proper temperature and pH are maintained. Also note that this procedure increases the chemical exposure time of the membrane.
6. Upon completion of the chemical cleaning steps, a low pressure cleaning rinse with clean RO/NF permeate or DI water at 20°C/min is required to remove all traces of chemicals from the CIP skid and the membrane unit including piping. Drain and flush the CIP tank. Refill the CIP tank with clean water for the rinse step. Rinse the pressure vessels by pumping all the rinse water from the CIP tank through the pressure vessels to drain. A second cleaning can be started at this point, if required.
7. Once the membrane system has been rinsed of cleaning chemicals thoroughly, a final low pressure clean-up flush can be performed using pre-treated feed water. The permeate divert to drain line remains open. Feed pressure should be less than 4 bar g. This final flush continues until the flush water flows clean and is free of any foam or residues of cleaning agents. This usually takes 15–60 min. Sample the flush water going to the drain for detergent removal and lack of foaming by using a clear flask and shaking it. Measure the conductivity to test for removal of cleaning chemicals; the flushed water should be within 10–20% of the feed water conductivity. A pH meter can also be used to compare the pH of flushed water and feed water.
8. Once all the stages of an array are cleaned, and the chemicals flushed out, the membrane system should be placed in a service rinse cycle. The permeate should be diverted

to drain until it meets the process water quality requirements (e.g. conductivity, pH). It can take several hours and even a few days for the permeate quality to stabilise, especially after high pH cleaning.

Membrane filters cleaning procedure

Membrane filters use intermittent backwash sometimes combined with air scour either during the filtration cycle and/or during the backwash cycle to remove loosely attached foulants. Those foulants that are not removed by backwash often require the addition of chemicals. In-line chemical cleaning is referred to as chemical wash or chemically enhanced backwash. This type of cleaning relies on short-soak periods and is not very effective. Hence, off-line cleaning is used when the unit taken is shut down as in the case of RO/NF systems. During off-line cleaning, the membranes are soaked for an extended period of time and the chemical solution is recirculated. Sometimes the chemical solution is heated to 25–35°C to improve its effectiveness [51]. Cleaning procedures are described in Chapter 4.

Off-line cleaning frequency varies between once a week to once a month or more. The following chemicals are used both for in-line and off-line cleaning washes:

- Soaking in alkali (e.g. NaOH) or sodium hypochlorite solution for organics fouling
- Soaking in acid (e.g. HCl, H_2SO_4, or citric acid) for inorganic fouling
- Biocide soak (e.g. H_2O_2, or sodium metabisulphite) for bio-fouling

2.5.2 Membrane sanitisation

Sanitisation means disinfection for reducing microbial contamination down to an acceptable level, whereas sterilisation implies the inactivation of all microorganisms. Cleaning always precedes sanitisation. When a membrane system (membrane elements, pressure vessels and piping) has been infected by bacteria or mould, the system requires chemical sanitisation. Hot water sanitisation is used in pharmaceutical membrane systems.

Chemical sanitisation

The CIP system is used for chemical sanitising also. Disinfection was discussed in Section 2.2. The most common chemical disinfectants are chlorine, hydrogen peroxide and peracetic acid.

- Chlorine is mostly used in the form of hypochlorites as discussed in Section 2.2.
- Hydrogen peroxide is not compatible with PA membranes. It is relatively non-corrosive and slow acting, and decomposes into oxygen and water.
- Per(oxy) acetic acid is a mixture of hydrogen peroxide and acetic acid. It is effective against bacteria, viruses, mould and spores. It releases oxygen that affects microorganisms. Oxygen release is an added benefit as it sanitises the membrane pores. It is fast acting at low temperatures, is non-corrosive to stainless steel, and leaves no harmful

residues. It should not be used with PA membranes unless recommended by the membrane manufacturer.
- Sodium metabisulphite is effective against bacteria, yeasts and moulds. It is non-corrosive and leaves no harmful residues. Since it is a reducing agent, it is also used for storing PA membranes in a 1% (wt.) solution.

The following safety precautions should be followed during chemical sanitisation:

- Continuous exposure to per(oxy) acetic acid at high levels may eventually damage the membranes. Hence, it should be used only periodically. The biocide efficacy of peracetic acid is much higher than that of hydrogen peroxide, but as most peracetic acid solutions also contain hydrogen peroxide, care must be exercised not to exceed the 0.2% concentration total for both compounds.
- When hydrogen peroxide is to be used, the pH of the solution must be <4.0, and preferably equal to 3.0. This will ensure optimal biocide result and longer membrane life. If the pH is high, chemical attack on the membrane will be much faster. When a mixture with peracetic acid is used, pH adjustment is usually not required.
- If an alkaline cleaning has preceded sanitisation, alkalinity must be carefully rinsed out of the membrane vessels, and the pH checked before hydrogen peroxide or hydrogen peroxide/peracetic acid solution is applied. The rinse must include the permeate side. If the alkalinity is not rinsed out, the membranes may get oxidised.
- The sanitising solution temperature must not exceed 25°C. Several hours of sanitising at higher temperatures results in a dramatic increase in the salt passage.
- Iron or other transitional metals must not be present because they will catalyse membrane degradation in the presence of hydrogen peroxide due to oxidative degradation, resulting in an increase in salt passage.

Hot water sanitisation (HWS)

HWS is commonly used to kill microorganisms. RO membranes reject bacteria and other microbes. However, due to defects in the membrane surface, the rejection is not 100% or absolute so that microorganisms can pass through the membrane into the permeate side of the membrane where they can multiply. Hence, sanitisation of a membrane system is essential for the production of US Pharmacopeia (USP) water and water for injection to meet the very low bacterial limits [57–59]. HWS of RO membrane (and EDI) systems is a relatively recent development made possible by the development of TFC membranes and membrane equipment capable of handling hot water at 85°C for a short time; membrane elements are manufactured with special adhesives, permeate tubes and connectors to withstand elevated temperatures. These membranes also make it possible to sanitise and protect the RO membranes from bio-fouling especially when the use of biocides is not acceptable. Typical membrane manufacturers' specifications of hot water sanitisable TFC membranes are given in Table 2.14.

Table 2.14 Hot water sanitisable operating conditions for a TFC-SW-RO membrane element[a]

Item	Specification
Physical size	20 cm dia. × 100 cm long
Type of membrane	Thin film composite
Membrane element configuration	Full-fit
Membrane surface area	36 m^2
Rejection at standard conditions[b]	96–98%
Membrane flow rate (m^3/day)	22–29
Recovery per element	15%
Feed temperature (service)	$\leq$45 °C
Feed pressure (service)	$\leq$40 bar g
Feed SDI rating	$\leq$5
Feed turbidity	$\leq$1 NTU
Feed free chlorine	<0.1 mg/l
Feed pH (continuous)	2–11
Feed pH (cleaning – 30 min)	1–12
Sanitisation temp. (max.)	$\leq$80 °C
Sanitisation feed pressure (max.)	3 bar g
Sanitisation duration	60 min
Sanitisation cycles	$\leq$150
Sanitisation feed flow rate (max.)	10 m^3/h
Sanitisation permeate flow rate	0.2 m^3/h per element
TMP (max.)	1.7 bar

[a] These are based on membrane manufacturer's specified conditions.

[b] Standard conditions are 2000 mg/l NaCl, 16 bar g, 25°C, pH 8, and 15% recovery; *in situ* treatment.

Source: USFilter/Ionpure.

The HWS equipment includes a CIP skid with a heat exchanger to heat and circulate hot water through the membrane system loop. Sometimes a heat exchanger is added to aid in cooling during the cool-down period. The HWS procedure recommended by membrane manufacturers involves separate steps:

1. Clean the membranes with a low-pH cleaner to remove mineral scale and foulants.
2. Heat the water to 80°C at 3–5°C per minute at low flow rate (<10 m^3/h) and pressure (<3 bar g).
3. Circulate the water in the CIP-RO skid loop at 80°C for up to 1 h. Maintain the cross-flow velocity so that the pressure drop is less than 0.15 bar per membrane element.
4. At the end of the re-circulating period, start cooling the membrane system down to 25°C at 3–5°C per min.

HWS is a superior process to chemical sanitisation, and does not require prolonged rinsing as in the case of biocide sanitisation. However, two points need to be noted. First, HWS is performed more frequently than chemical sanitisation. Second, high temperature reorients the polymer chains permanently [60]. At high temperatures, the membrane structure becomes tighter with increased rejection and decreased flux due to changes in the membrane morphology as a result of changes in the glass transition temperature [60] because deformed polymers shrink when heated [61,62]. The first shrinkage results in almost a 50% reduction in flux according to the membrane manufacturers, but after the initial shrinkage subsequent HWS cycles are unaffected. To compensate for the anticipated loss, HWS systems are designed with more surface area then ambient temperature membrane elements [57].

2.6 CONCLUDING REMARKS

According to the U.S. National Council Research Report [63], the principal water problem in the early twenty-first century will be inadequate and uncertain supplies. With growing demands outstripping supply in many regions of the world, the situation is likely to get exasperated by the year 2020. According to the UN, it is estimated that the amount of water available per person will shrink by a third during the next two decades. By the year 2050, between 2 and 7 billion people will face water shortages [2].

Scarcity of water resources is also often the limiting factor for economic and social development. Water is needed not just for drinking, household purposes, and for agriculture, but also for manufacturing goods, food processing and power generation. Current and looming water scarcity and the effects of environmental pollution, groundwater degradation and global warming on water availability can have severe and adverse effects on the world economy, especially developing countries [4,64].

Less than 3% of the world's water has a salinity content that can be considered safe for human consumption. According to the WHO, the TDS should be less than 1000 mg/l in drinking water based on taste considerations. By comparison, seawater has an average TDS of 35,000 mg/l and brackish water TDS varies between 1000 and 10,000 mg/l. It is estimated that less than 0.5% of the world's water supply is easily accessible and has acceptable water quality.

Water pollution from industrial, agricultural and other human activity is polluting natural water sources. Since water availability includes both water quality and quantity, reduction in water quality due to water pollution will further diminish the available water supply. World's water needs, however, can be met by better water management, e.g. by reducing losses using micro-irrigation techniques most of the 66% water lost during irrigation can be recovered, by using advanced water treatment technologies for treating polluted water and reclaiming water for reuse, by desalination seawater and brackish water and by water conservation [65].

Integrated membrane technologies for water treatment have a great potential for meeting the challenges of anticipated water shortages around the globe by treating raw water to produce high-quality potable water for applications as diverse as drinking water, industrial water and reclaimed water for crop irrigation. Appropriate membrane technologies for targeted applications can be summarised as follows: high salinity water (RO), industrial product water (NF/RO/ED/EDI), municipal water (MF/UF/RO), recycled water (UF/MF/RO), reclaimed water (UF/MF/RO), industrial wastewater (UF/RO) and biological wastewater (MBR/NF). Desalination by RO is well established for desalinating seawater and brackish water. Submerged membrane filtration systems along with MBR are being increasingly used for reclaiming wastewater, for municipal water treatment and for seawater RO pre-treatment. Some of these applications are discussed in detail in Chapter 3. Cost reduction and performance enhancement of membrane technologies are being addressed to meet potable water treatment challenges.

REFERENCES

[1] Water, a survey, The Economist, 19–25 July (2003) 42.
[2] The 2nd UN World Water Development Report: Water, a shared responsibility, 2006.
[3] CHEMRAWN XV Conference, Paris. Chem. Eng. News 82 (29) (2004) 25–30.
[4] H. Kulkarni, M. Shah, Punjab water syndrome, Econ. Pol. Wkly VLVIII 52 (2013) 64–73.
[5] A.J. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004.
[6] M.D. Kennedy, J. Kamanyi, S.G.S. Rodriguez, N.H. Lee, J.C. Schippers, G. Amy, Water treatment by microfiltration and ultrafiltration, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 131–170.
[7] P. Cote, M. Liu, S. Siverns, Water reclamation and desalination, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 171–187.
[8] D.A. Furukawa, Global Perspective of Low Pressure Membranes, National Water Research Institute, Fountain Valley, CA, March, 2008.
[9] A.G. Fane, Submerged membranes, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 239–270.
[10] S.D. Strauss, Water treatment, Power, June (1993) 1–52.
[11] D. Bhattacharyya, Membranes in environmental applications, Environ. Prog. 20 (1) (2001) A12.
[12] J.W. Clark, W. Viessman, M.J. Hammer, Water Supply and Control, Harper & Row Publishers, New York, NY, 1977.
[13] W.W. Eckenfelder, Industrial Water Pollution Control, McGraw-Hill, New York, NY, 1989.
[14] S.V. Cabibbo, D.B. Guy, A.C. Ammerlaan, A. Ko, R. Singh, Reverse Osmosis Technical Manual, NTIS Publication, Springfield, Virginia, 1979.
[15] C.E. Harland, Ion Exchange, Royal Society of Chemistry, Herts, UK, 1994.
[16] D.L. Owens, Practical Principles of Ion Exchange Water Treatment, Tall Oaks Pub, Littleton, CO, 1995.
[17] G. Pearce, Membrane filtration technology, Filtration + Separation 45 (8) (2007) 48–53.
[18] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, Environ. Sci. Technol. 36 (16) (2002) 3571–3576.
[19] H. Huang, K. Schwab, J.G. Jacangelo, Pretreatment for low pressure membranes in water treatment: a review, Environ. Sci. Technol. 43 (9) (2009) 3011–3019.
[20] S. Judd, The MBR Book, Elsevier, Oxford, UK, 2006.
[21] W. Yang, N. Cicek, J. Ilg, State-of-the-art of membrane bioreactors: worldwide research and commercial applications in North America, J. Memb. Sci. 270 (2006) 201–211.
[22] P.K. Holt, G.W. Barton, C.A. Mitchell, The future for electrocoagulation as a localized water treatment technology, Chemosphere 59 (2005) 355–367.
[23] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.

[24] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Mgmt. 90 (2009) 1863–1879.

[25] A. Dey, Ultrapure water by membranes, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 371–405.

[26] G.C. Ganzi, A.D. Jha, F. DiMascio, J.H. Wood, Electrodeionization theory: theory and practice of continuous electrodeionization, Ultrapure Water 14 (6) (1997) 64–69.

[27] J. Wood, J. Gifford, J. Arba, M. Shaw, Production of ultrapure water by continuous electrodeionization, Desalination 250 (2010) 973–976.

[28] I.G. Wenten, Khoiruddin, F. Arfianto, Zudiharto, Bench scale electrodeionization for high pressure boiler feed water, Desalination 314 (2013) 109–114.

[29] A. Grabowski, G. Zhang, H. Strathmann, G. Eigenberger, Production of high purity water by continuous electrodeionization with bipolar membranes: influence of concentrate and protection compartment, Sep. Purif. Technol. 60 (2008) 86–95.

[30] F. Ruggieri, J.L. Fernandez-Turiel, D. Gimeno, F. Valero, J.C. Garcia, M.E. Medina, Limestone selection criteria for EDR water remineralisation, Desalination 227 (2008) 314–326.

[31] D.L. Comstock, Reduction of colloidal fouling in membrane systems, Ind. Water Treat. 2 (4) (1991) 39–42.

[32] A.I. Schafer, N. Andritsos, A.J. Karabelas, E.M.V. Hoek, R. Schneider, M. Nystrom, Fouling in nanofiltration, in: A.J. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 169–240.

[33] E. Wittman, T. Thorsen, Water treatment, in: A.J. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 263–286.

[34] M. Cheryan, Ultrafiltration and Microfiltration Handbook, CRC Press, Boca Raton, FL, 1998.

[35] M. Mulder, Basic Principles of Membrane Technology, second ed., Kluwer, Dodrecht, The Netherlands, 1996.

[36] G. Johnson, B. Culkin, M. Monroe, Vibratory shear guards against mineral scale membrane fouling, Filt. Sep. (2003) 24–29, January/February.

[37] L.F. Comb, Silica chemistry and reverse osmosis, Ultrapure Water 13 (1) (1996) 41–43.

[38] H.-C. Flemming, Mechanistic aspects of reverse osmosis membrane biofouling and prevention, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 163–209.

[39] H.F. Ridgway, Microbial adhesion and biofouling of reverse osmosis membranes, in: B.S. Parekh (Ed.), Reverse Osmosis Technology, Marcel-Dekker, New York, NY, 1988, pp. 429–481.

[40] R. Bradley, Design considerations for reverse osmosis systems, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 104–138.

[41] L.F. Greenlee, D.W. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[42] Professional Water Technologies, Vista, California. www.ptwchemicals.com.

[43] R. Singh, J. Tembrock, Effectively control reverse osmosis systems, Chem. Eng. Prog. 95 (9) (1999) 57–64.

[44] D.B. Guy, R. Singh, Some alternate methods of energy recovery from reverse osmosis plants, WSIA J. 9 (2) (1982) 37–51.

[45] R.L. Truby, Seawater desalination by ultralow-energy reverse osmosis, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 87–100.

[46] ROPRO, Fluid Systems, San Diego, CA. www.kochmembrane.com.

[47] RO Membrane Design, Hydranautics, Oceanside, CA. www.hydranautics.com.

[48] R.W. Baker, Membrane Technology and Applications, Wiley, Chichester, UK, 2012.

[49] R. Singh, Removal of volatile organic compounds by ultrafiltration, Desalination 104 (1996) 203–214.

[50] R. Singh, Surface properties in membrane filtration, Chem. Eng. Prog. 85 (6) (1985) 59–64.

[51] G. Pearce, Fouling behaviour for different module formats in membrane filtration applications for surface water treatment, Desal. Water Treat. 8 (1–3) (2009) 36–38.

[52] L.H. Shaffer, M.S. Mintz, Electrodialysis, in: K.S. Speigler, A.D.K. Laird (Eds.), Principles of Desalination, Part A, second ed., Academic Press, New York, NY, 1980, pp. 257–357.

[53] L.J. Zeman, A.L. Zydney, Microfiltration and Ultrafiltration, Marcel-Dekker, New York, NY, 1996.

[54] D.J. Shaw, Introduction to Colloidal and Surface Chemistry, Butterworths, London, UK, 1986.
[55] S.K.S. Razavi, J.L. Harris, J.L., F. Sherkat, Fouling and cleaning membranes in the ultrafiltration of the aqueous extract of soy flour, J. Memb. Sci. 114 (1) (1996) 93–104.
[56] R. Singh, Characteristics of a chlorine resistant reverse osmosis membrane, Desalination 95 (1994) 27–37.
[57] A. Collentro, M. Costello, G. Zoccolante, Hot water sanitization of reverse osmosis systems for pharmaceutical water production, Ultrapure Water 17 (10) (2000) 1–6.
[58] B. Wise, Hot-water sanitization membranes tackle microbes in RO permeate water, Chem. Process. August 15 (2002) 1-2.
[59] W.V. Collentro, Hot water sanitization of RO and double-pass RO/EDI systems. Executive Forum, Ultrapure Water Journal's Expo 2003, Philadelphia, April, 2003.
[60] A. Pihlajamäki, E. Kaipainen, M. Nyström, M. Mänttäri, Effect of temperature and membrane pretreatment by pressure on the filtration properties of nanofiltration membranes, Desalination 145 (2002) 81–86.
[61] L. Mandelkern, An Introduction to Macromolecules, Springer-Verlag, New York, NY, 1972.
[62] R. Singh, A rubber heat engine for ground water irrigation in India, Agric. Ecosyst. Environ. 25 (1989) 271–278.
[63] National Research Council, Review of the Desalination and Water Purification Technology Roadmap, National Academic Press, Washington, D.C., USA, 2004.
[64] Charting our water future, 2030WaterResourcesGroup@mckinsey.com, 2009.
[65] M. Elimelech, The global challenge for adequate and safe water, J. Water Supply Res. Tech. – AQUA 55 (1) (2006) 3–10.

CHAPTER 3

Hybrid Membrane Systems – Applications and Case Studies

> *"It's tough to make predictions, especially about the future."*
>
> — ***Yogi Berra***

Ultrafiltration (UF) and microfiltration (MF) membrane processes were traditionally used as stand-alone separation processes with nominal pre-treatment; for example, ultrafiltration (UF) processing of industrial wastewater or dairy products. In the case of desalination and water purification by reverse osmosis (RO), however, it was always a hybrid process integrated with other unit operations, as discussed in Chapter 2. The term hybrid or integrated membrane process refers to the integration of one or more membrane processes with or without conventional unit operations to increase performance depending on the type of feed and product quality required [1–3]. The main goal of these systems is to increase purity; for example, in the case of water and gas purification, and productivity and yield of the product, for example, in the case of fermentation processing. Similarly, pervaporation (PV)-based hybrid processes can be more economical than traditional separation processes for the removal of volatile organic compounds from industrial, municipal water, or groundwater contaminated with carcinogenic halogenated hydrocarbons instead of catalytic combustion [4,5]. Hybrid membrane systems also reduce operating costs and environmental pollution and make the overall process more efficient. For a perspective on membrane systems design and operation, the reader should review Chapters 4 and 5, and the relevant portions in Chapter 2.

Hybrid membrane systems for several applications are illustrated in this chapter followed by detailed discussions in case studies specific to water treatment. All examples highlight the centrality of membrane technology; implicit in their performance is the physicochemical properties of each membrane and process in the integrated membrane design. Mechanisms that control separation by various membrane processes were discussed in Chapter 1. Briefly, depending on the physical and chemical characteristics of the membrane and the solute, separation is achieved by one or more mechanisms: (a) physical selectivity based on charge repulsion, size exclusion, or steric hindrance and/or (b) chemical selectivity, i.e., solvation energy, hydrophobic interaction, or hydrogen bonding. Hence, an integrated membrane system becomes an effective and efficient tool utilising membranes and membrane processes appropriate for separating solutes or purifying a particular feed stream.

3.1 NOVEL APPLICATIONS

The hybrid systems described below include membrane technologies for processing a wide spectrum of feed streams in various applications. A small sampling of current and potential applications is discussed. The list of examples selected is intentionally limited; the intention is to illustrate the extent of process alternatives possible with various hybrid membrane processes.

3.1.1 Industrial wastewater treatment

Integrated membrane systems include MF or UF as pre-treatment for NF or RO processing. A laundry wastewater treatment shown in Figure 3.1 is a cross-flow MF-NF system [6]. Industrial laundry wastewater has a high concentration of detergents and surfactants, and is high in BOD and COD. In order to recycle water in the wash cycle or to meet wastewater pollutant requirements, the contaminants must be removed. The integrated membrane process schematic shown in the figure is used to remove oil, grease, detergents, surfactants and other impurities such as heavy metals (e.g. 99.9% removal of lead, chromium and others) from wastewater. MF removes suspended solids including lint, oil, grease and dirt. The permeate flows to a three-stage NF system for removing total dissolved solids (TDS), detergents and surfactants. The face velocity in the cross-flow MF membrane channels is kept high to reduce concentration polarisation by a high recycle flow rate. The NF permeate is reused in the hot water wash cycle.

Another application of an integrated membrane system for treating wastewater is for treating meat and poultry plant effluent for reuse as shown in Figure 3.2. The effluent TDS typically is 2.0–2.5%. The treated effluent should be low in sulphate concentration with a salt concentration in the 1.0–1.5% range. RO is not suitable because some calcium

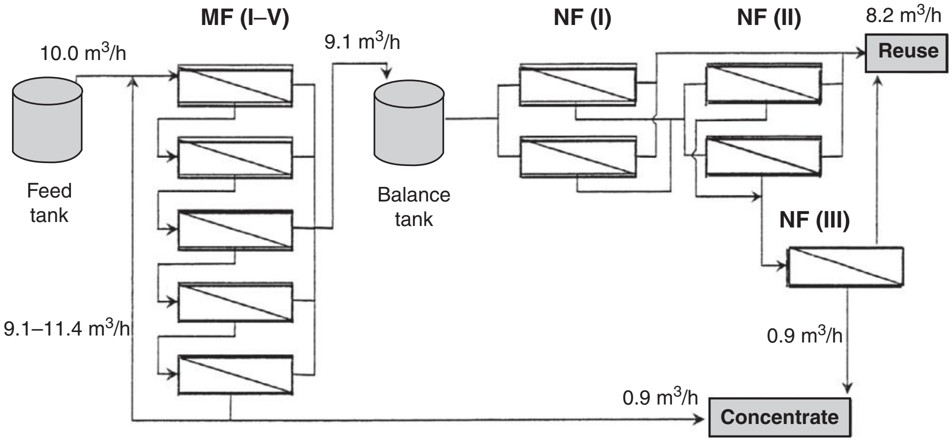


Figure 3.1 A dual-membrane system for laundry wastewater treatment. *Source:* [6].

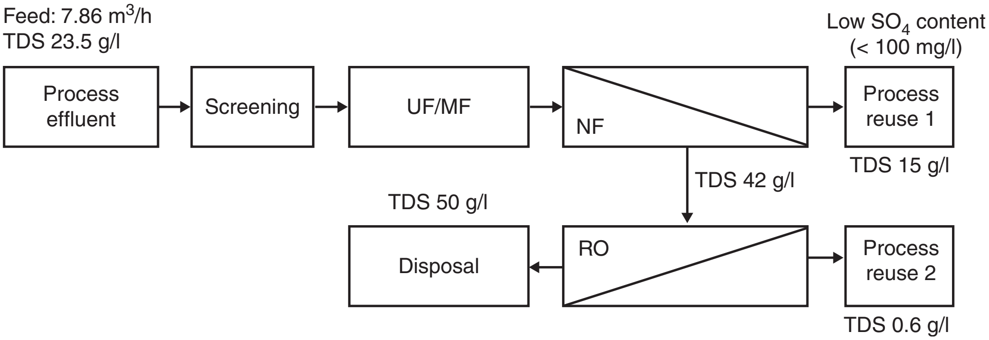


Figure 3.2 Flowsheet of a multi-membrane system for treating meat and poultry wastewater. *Source: [6].*

hardness needs to be present. Both MF and UF are effective in removing bacteria, cysts and other microbiological compounds, whereas UF also removes some viruses [6].

Hybrid membrane systems using RO or NF for pre-concentration followed by mechanical vapour recompression (MVR) are more efficient than the conventional physicochemical and/or biological treatment systems for treating dilute industrial wastewater streams [7]. In the hybrid process, the pre-treated very dilute feed stream (to prevent membrane fouling) is concentrated by RO/NF. The concentrate is fed to a MVR evaporator to further remove the remaining water, whereas the RO/NF permeate (which is of high quality) is recycled back to the process. The MVR concentrate is transferred to the wastewater treatment system. An example of this application is the treatment of wastewater from de-inking processes in the pulp-and-paper industry as shown in Figure 3.3. MVR is also used for zero liquid discharge, treating mining wastewaters in the mining industry and produced water.

3.1.2 Produced water treatment

Produced water is mainly saline water trapped in underground rock formations. Flowback water is the fracture fluids that return to the surface after completion of a well. When oil or gas is extracted and brought to the surface, the fluid stream also contains produced water. In fact, produced water is the largest volume of waste generated in oil and gas explorations; on average, nearly nine barrels of produced water is co-produced with each barrel of oil extracted in the US (1 barrel = 159 litres). After a well has been fracture-treated, it is cleaned up, which involves removing the "frac" water that was used for fracturing. During this "flowback" some natural gas accompanies the water exiting the well. Typically, 4–5 million gallons of water is required to fracture a well [8]. Flowback and produced water is either disposed off by deep-well injection at permitted wells or sent to surface water bodies after extensive treatment to remove all the contaminants. Depending on the well site, the produced water salinity (TDS) ranges from 8000 to

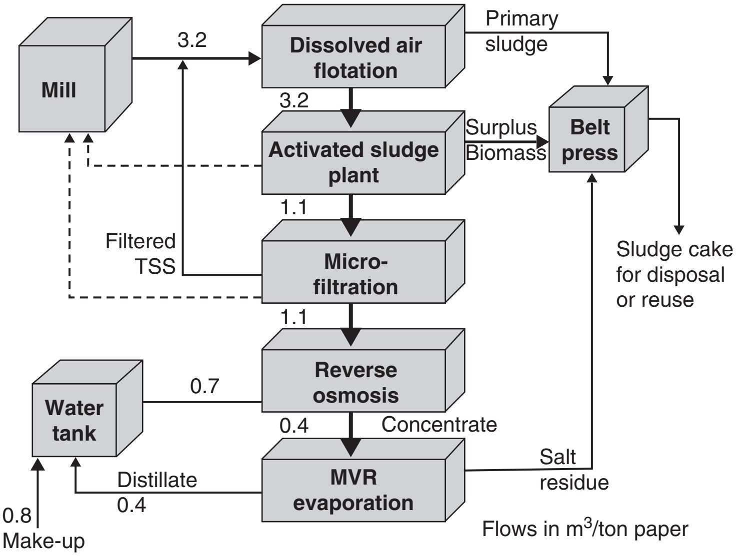


Figure 3.3 A hybrid membrane system for treating wastewater at a pulp-and-paper plant. *Source: [7].*

200,000 mg/l, and also contains hydrocarbons, high levels of suspended solids, iron, and silica. Common contaminants are given in Chapter 6 (Section 6.15). Pollutants can be reduced to undetectable levels by using a combination of different technologies such as electro-coagulation; aerobic biological treatment; chemical oxidation by ozone and hydrogen peroxide; air stripping; carbon adsorption; UV irradiation; RO/NF membrane separation and thermal evaporation [9].

An integrated membrane plant used for treating produced water from an oil well is shown in Figure 3.4 [10]. Coarse filtration of raw water is treated by dissolved gas flotation to reduce suspended solids and oil/grease. Pre-treated water (TDS = 10,000 mg/l) is treated in a multi-step membrane process followed by ion exchange (IX):

- UF for removing trace amounts of oil and reducing turbidity to <1.0 NTU
- NF for removing hardness and TOC
- Double-pass RO for reducing boron to <10 ppm, and TDS to 150 ppm
- IX for reducing boron concentration to <1 ppm if needed

The overall recovery was >80% with recycling of UF reject combined with RO reject for various applications. The RO permeate is suitable as boiler feed water and the IX effluent is suitable for irrigation with reduced boron concentration. Weak base anion resins are very effective in removing boron to below detectable limits; borate ion (BO_3^{3-}) selectivity is extremely high when the pH is >4.0. The resin is regenerated with 0.5–0.6% HCl or H_2SO_4.

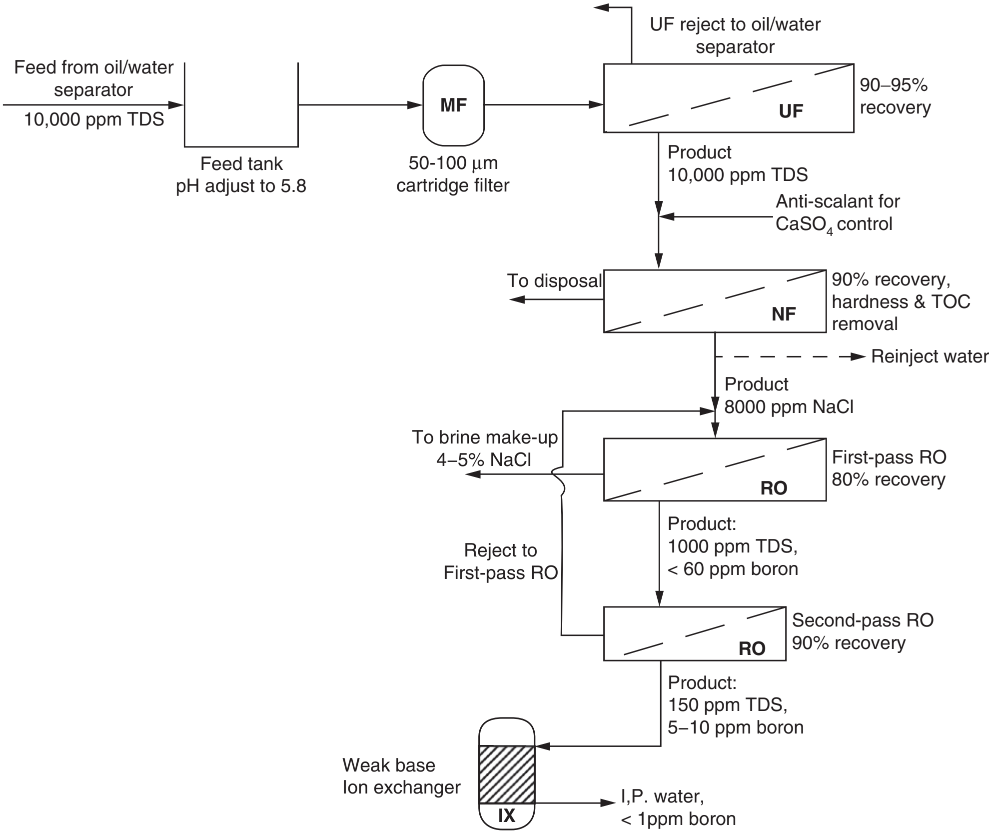


Figure 3.4 Process flow diagram for treating oilfield produced water. *Source: Adapted from [10].*

The world's first membrane-based produced water treatment plant was built in 2013 to process 7200 m^3/d (45,000 barrels/d) produced water from an oilfield in San Luis Obispo County, California. The feed water TDS is 7000 mg/l. The treatment process is OPUS® II technology, which consists of ceramic membrane pre-treatment followed by ion exchange and a two-pass RO system. Up to 20,000 bbl/d treated water is for surface discharge (TDS < 600 mg/l) and 25,000 bbl/d treated water is for use as once-through steam generation make-up (hardness < 2 mg/l as $CaCO_3$). Based on pilot studies the RO recovery was 80% in first-pass RO and 90% in 2nd-pass RO [11].

Reverse osmosis and NF processes are, however, not suitable for treating high salinity produced waters, i.e., TDS > 40,000 mg/l, because of very high osmotic pressures. Thermal processes such as mechanical vapour recompression (MVR) are the most robust, require minimum pre-treatment, and can treat feed waters with TDS > 100,000 mg/l.

The disadvantages of thermal processes are low capacity, very high energy consumption, high Capex and a large footprint. Nevertheless, MVC systems are being used to treat "frac" flowback and produced water in the high salinity range producing brines with salt concentrations of 18–20%.

A thermal evaporation system for treating produced water and flowback water entails chemical pre-treatment with a polyelectrolyte, acid and anti-scalant upstream of an induced gas flotation (IGF) unit [12]. The IGF unit removes suspended solids and traces of oil and grease before the pre-treated feed water flows to the MVR unit. The heat transfer surfaces in the MVR are arranged vertically in the evaporator chamber with the feed side of the plates completely submersed. Vapour evaporating from the liquid flows to a compressor where it is mechanically compressed and reintroduced on the opposite side of the heat transfer plates as heating steam. Distillate condensing between the plates is the product water while the small concentrated brine stream is continuously discharged as blowdown. The energy consumption of the system is 35.9 kWh/m^3 and the Opex is in the range of \$2.00 to \$2.50/bbl.

3.1.3 Zero liquid discharge

Zero liquid discharge (ZLD) is used to concentrate RO/NF reject in industrial wastewater plants. Most of the water in the concentrate is recovered as product by separating the salt from the water. ZLD systems include thermal evaporators, crystallizers, brine concentrators and spray dryers. The feasibility of using a thermal processes to recover brine salts from brackish water RO reject stream was evaluated in a pilot study [13]. The groundwater water TDS was 5067 mg/l. The RO reject was evaporated in a MVC unit where 95% of feed water was recovered as distillate. The remaining 5% was discharged as blowdown to the crystalliser in which water was separated from the more soluble (and recoverable) salts such as NaCl and $CaCl_2$. The salts left after crystallisation were ~85% (wt.) dry. The distilled water from the MVC and the crystalliser combined with the RO permeate amounted to ~95% product water recovery, which was essentially 100%, and 0% liquid waste was discharged. The data were used to calculate the annual treatment cost for producing 11,000 m^3/d water. The annual cost was about \$4.8 M (\$1.15/m^3) of which the cost of MVC + crystalliser was 69%, RO = 14%, land = 13%, and post-treatment = 4%; thermal process treated only 5% of the feed but was the most expensive.

ZLD is used in steam-assisted gravity drainage (SAGD) facilities in areas where adequate disposal wells are too far from the central processing facility [14]. However, the thermal unit had problems handling non-volatile organic compounds (humic acids and asphaltenes) that build up in the evaporator/crystalliser and contaminate the salt cake. The facility in Alberta, Canada had to install a second MVR unit making the process very expensive. Similar problems with organics were experienced at another facility that produced concentrated brine from the crystalliser.

One refinery in California recycles effluent from the biological treatment system using lime softening, followed by UF to remove suspended solids, and RO for desalting. The RO permeate is used as boiling feed water and cooling tower makeup. The RO reject is discharged to an evaporation pond. This system originally had problems because of organic fouling of the UF membrane – San Joaquin Valley crudes contain naphthenic acids that tend to foul membranes. Heavy oil crudes tend to have similar organic acids that must be dealt with in membrane systems [15].

A non-thermal ZLD process for treating brackish water RO reject is electrodialysis/electrodialysis reversal (ED/EDR). The salt rejection is 60–70% but recovery approaches 97% with multiple stages [3]. The benefits of ED over MVC are lower capital cost, lower energy consumption and much greater flow capacity; MVC range is 250–3000 m^3/d [15].

3.1.4 MVC-RO hybrid desalination

The application of MVC for treating industrial wastewater was discussed earlier in the chapter. Mechanical vapour compression systems are small distillation units with a capacity in the range of 250–3000 m^3/d [14]. Although they are small, expensive and energy-intensive units, they are often used to desalinate high salinity water, e.g., seawater and river estuary water in remote areas. In order to reduce the capital cost and energy consumption, RO-MVC hybrid systems provide a less expensive option:

1. RO-MVC system (Figure 3.5a): MVC evaporator treats high salinity RO brine concentrate (TDS ~ 67,000 mg/l). The overall recovery is 90%, and the MVR feed water is ~30% of the original raw stream flow rate.
2. MVC-RO system (Figure 3.5b): RO polishes ~60% of the "low quality" 200 mg/l MVC distillate, and ~40% of the distillate is by-passed for blending with the RO permeate to increase the product water TDS. The advantages of this process scheme are as follows: (i) minimal feed water treatment required because of MVC, (ii) RO feed flow is reduced by 33%, (iii) the size of the RO unit is reduced to a two-stage array from a three-stage array resulting in fewer membrane elements in case 1, (iv) because of the high quality of the distillate (RO feed water), the RO unit recovery is 90%, (v) RO high-pressure pump power is reduced by one-third, (vi) higher feed temperature and virtually no scaling potential results in high RO membrane flux, >30 $l/m^2/h$ instead of <15 $l/m^2/h$, and (vii) minimises brine concentrate volume. RO polishing would be required if the distillate is for drinking water applications. RO is used for removing trace amounts of any undesirable compounds carried over in distilled water.

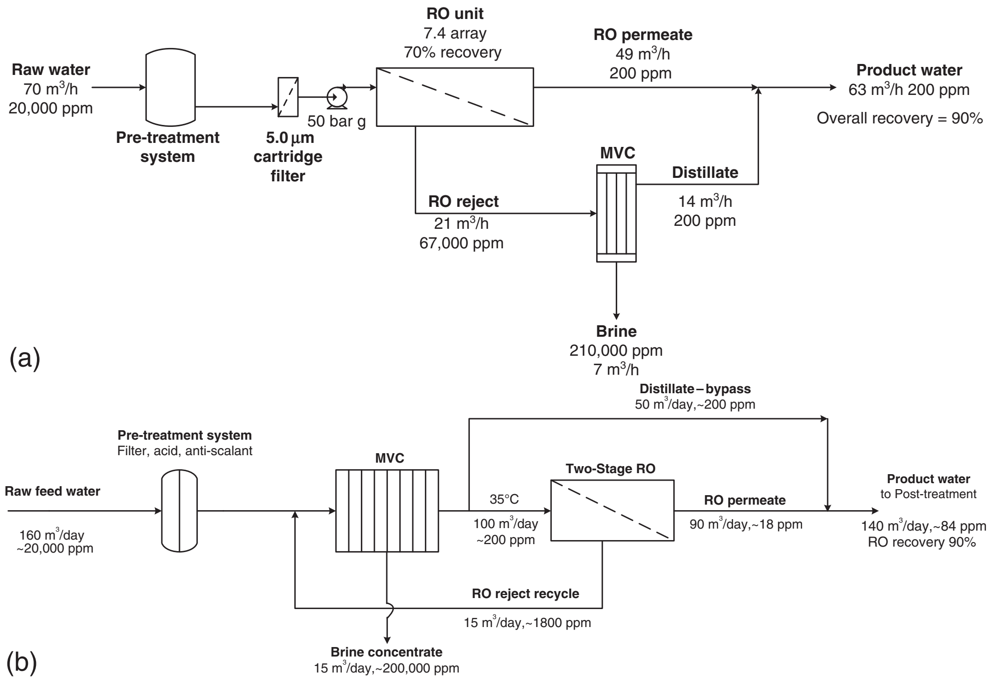


Figure 3.5 (a) Process flow diagram of a RO-MVC system. (b) Process flow diagram of a MVC-RO system. Activated carbon and calcite filtration post-treatment not shown.

3.1.5 Hybrid NF-RO-MSF seawater desalination process

Application of NF to soften RO feed water in hybrid RO-multistage flash (MSF) seawater desalination plants such as shown in Figure 3.6 is relatively recent [6]. In the pretreatment of high salinity seawater, for example, NF reduced total hardness from 7500 to

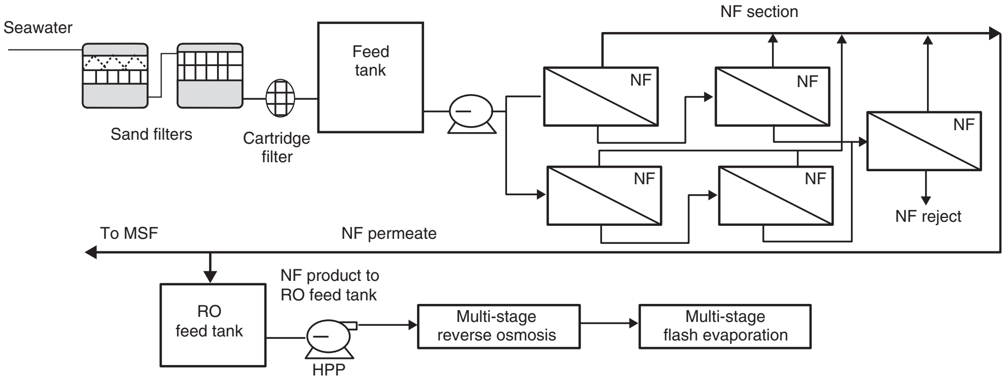


Figure 3.6 Seawater desalination using a NF-RO-MSF staged process. *Source:* [6].

220 mg/l, TDS from 45,460 to 28,260 mg/l, and chloride from 21,587 to 16,438 mg/l [16]. One alternative use of integrated NF-RO-MSF systems is blending RO reject stream with MSF recycle stream, using a portion of the heated MSF seawater as RO feed water, and using NF as a pre-treatment to increase recovery in MSF and RO processes [16].

NF softening minimises scaling potential thereby increasing RO product water recovery. Seawater RO recovery is also limited by osmotic pressure and organic fouling; SWRO plants, especially those treating water from open water intakes, are primarily fouled by organic and particulate matter [3]. NF membranes are very effective in rejecting organics (MW > 200 Da), particulates and colloids, and are also less prone to fouling than polyamide RO membranes because of different membrane chemistries as discussed in Chapter 1. Another factor that accounts for the lower fouling rate is the lower rejection of monovalent ions that constitute most of the ions in seawater and brackish water. The higher the salt rejection, the higher the ionic strength at the membrane/feed interface, which reduces the repulsive force between charged colloidal particles [16], so that the colloidal particles agglomerate. Larger aggregates, in turn, are more prone to depositing on the membrane surface than the smaller colloidal particles resulting in fouling.

A hybrid MSF and RO plant is in use at the 454,000 m^3/d Fujairah plant in the United Arab Emirates. The two systems operate in parallel, with the overall water production split 62.5% MSF and 37.5% RO [3]. The main advantage of this design is operations flexibility; while MSF plants are relatively flexible with changes of 25% production capacity possible, RO plants can be adjusted by as little as 5% production increments because of the modular design. Another advantage is that the distilled water with very low TDS is blended with the RO permeate to supply desalinated water with TDS in the range of 75–120 mg/l.

3.1.6 Salts recovery from seawater desalination plants

Brine concentrate stream from seawater desalination plants is typically discharged to the sea. However, the brine can be processed to recover salts for the chemical industry, e.g., Mg^{2+} salts in the NF reject stream and Cl^- salts in the RO reject stream, as shown in Figure 3.7 [10]. NF and RO system recoveries are 80% and 62.5%, respectively. NF membranes have a very high rejection of divalent ions, SO_4^{2-}, which is rejected together with equivalent amounts of the respective cations starting with the least soluble salt, Ba, Sr, Mg, Ca, Al, etc. Typical rejection of dissolved ions by NF membranes is as follows: sulphate, 99.9%; magnesium, 98%; calcium, 91%; bicarbonates, 56%.

The inorganic chemical industry has a use for such brines, e.g., NF permeate (RO concentrate in Lagoon 2) for chlorine production. Another potential use is NF concentrate (Lagoon 1) for Mg^{2+} production. A high market value of the brine streams from

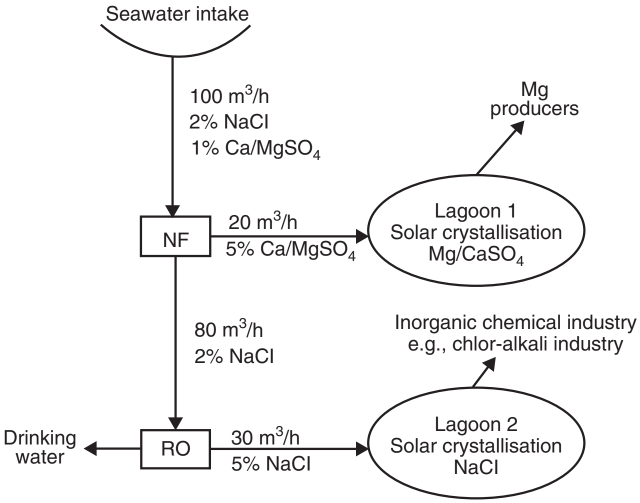


Figure 3.7 A multi-purpose integrated membrane process applicable for seawater desalination. *Source: [10].*

NF-RO or RO-MSF seawater desalination plants has a potential for significant reduction in the cost of drinking water:

- 1.5 ton of salt per 50 m^3 drinking water (Lagoon 2).
- Less discharge cost of salts. Use of the salt from Lagoon 1 for magnesium production.
- Less cleaning frequency (and cost) and longer life of RO membrane because of reduced fouling.
- Up to 30% higher production in thermal desalination plants because of increased top brine temperature.

3.1.7 Landfill leachate water treatment

Leachate from a landfill can be a major source of contamination of groundwater and surface water in the vicinity of the landfill by hazardous substances. The leachate contaminants are a combination of organic and inorganic compounds as shown in Table 3.1.

Table 3.1 Impact category of landfill leachate compounds

Compound/parameter	Environmental category
Cd, Ni, AOX	Human toxicity
Cu, Zn, Pb, Hg	Ecological toxicity (surface/groundwater)
Salts, chlorine, sulphide, ammonia	Ecological toxicity (surface/groundwater)
Nitrogen	Eutrophication
COD	Eutrophication

Source: [17].

The organic compounds are mostly fatty acids, fulvic acids and humic substances. The composition of the leachate changes with time; acidic and a comparatively high proportion of organic compounds during the first 3–5 years. The leachate is usually treated by a combination of several processes: (a) biological treatment; (b) chemical oxidation; (c) adsorption; (d) precipitation; (e) evaporation; (f) drying; (g) stripping; and (h) membrane processes such as UF and RO. An overview of various treatment methods is given in Table 3.2 [17].

Granular-activated carbon adsorption in combination with biological pre-treatment is the leading process for removing COD, and AOX. The process flow sheet with a membrane bioreactor (MBR) is shown in Figure 3.8a. Biological treatment is required for removing ammonia, COD and BOD. In the MBR system, MF or UF membranes are used to retain and concentrate the biomass. In addition to removing particulate matter such as pathogens, MBR enhances the performance of the biological system. First, the membrane unit increases the sludge residence time; and second, the membrane unit promotes the stability of the autotrophic microbial population that does the nitrification – the microorganisms display a slow rate of growth, and unlike in the conventional systems their concentration cannot be reduced to an unacceptable level. Additional advantages of the MBR process include lower ammonia level in the UF permeate (down to 5–15 ppm from 1200–1500 ppm in the raw leachate), and nitrogen concentrations up to 50–150 ppm. The COD in the permeate is high (500–1500 ppm) since UF membranes do not reject low MW compounds. The UF permeate is, therefore, treated in a carbon filter before disposing it safely while the UF reject is recycled to the biological stage. A variation of the process entails treatment of the UF permeate by NF instead of the activated carbon filtration before disposing the NF permeate safely, and the NF concentrate is recycled to the biological stage after it is treated in the carbon filter. This closed-loop

Table 3.2 Process combination for landfill leachate treatment

Option no.	**Treatment processes**						
1	BIO	UF	OX				
2	BIO	UF	ADS				
3	BIO	UF	RO		EVA	DRY	
4	BIO	UF	NF		EVA	DRY	
5	BIO	UF	NF	IX			
6	BIO	UF	NF	ADS			
7	FIL	RO	RO		EVA	DRY	
8	FIL	RO	NF	RO		DRY	N2
9	FIL	RO	RO			EXT	

FIL: filtration, e.g., sand filtration; BIO: biological treatment and nitrification/denitrification; UF: ultrafiltration for biomass retention; ADS: adsorption, e.g., activated carbon adsorption; OX: oxidation, e.g., ozonation; RO: reverse osmosis; NF: nanofiltration; IX: ion exchange; EVA: evaporation; DRY: drying; EXT: external concentrate removal; N2: nitrogen recovery, e.g., ammonia stripping. *Source:* [17].

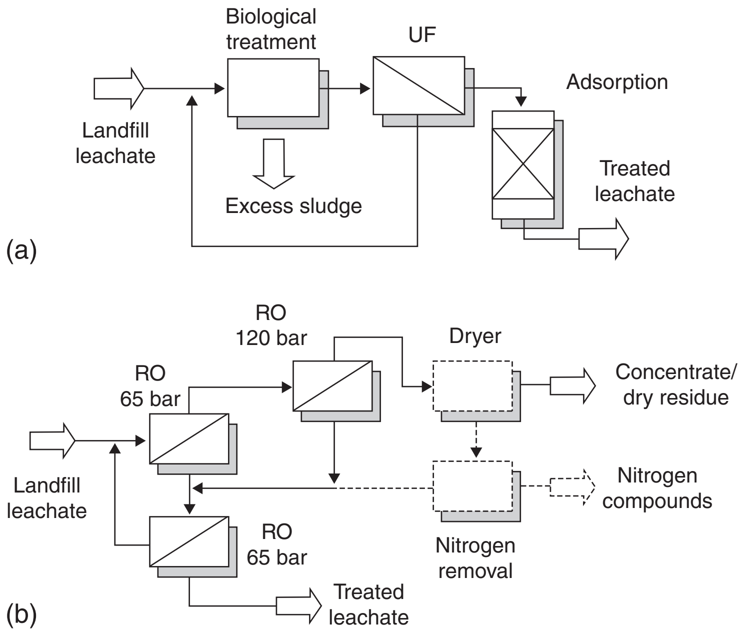


Figure 3.8 (a) A membrane bioreactor-based system for treating landfill leachates. (b) A multi-staged RO and reject RO integrated membrane system for treating landfill leachates. *Source:* [17].

system is designed to minimise the generation of sludge while achieving almost 100% treated leachate water recovery.

RO is the most widely used membrane process for leachate treatment because it rejects almost all the contaminants. Membrane processing made an early headway (1984) since the conventional processes could not meet the new stringent regulations [17]. Pre-treatment is essential to prevent membrane fouling that can be severe with these waters. These RO plants operate at 75–90% recovery and the 10–25% RO concentrate is processed by another RO system operating at 120 bar g to reduce the concentrate volume before it is disposed of. The flow sheet of a multiple RO system is shown in Figure 3.8b. The PRO permeate is treated in a second-pass RO unit to further purify the leachate before it is disposed of to surface water body.

3.1.8 Arsenic and nitrate-contaminated groundwater

Arsenic is a naturally occurring element that can be present in relatively high concentrations in surface water and groundwater. Inorganic arsenic is a toxic and carcinogenic compound that causes skin and various forms of internal cancer. The maximum allowable limit standard set by the World Health Organisation (WHO) is 10 ppb (μg/l). It is estimated that 33–77 million Bangladeshis are at risk due to arsenic contamination of their drinking water supplies where concentrations range from 10 to 14,000 ppb.

High concentrations of arsenic have also been found in other countries, viz. India, Taiwan, northern China, Thailand, Vietnam, Hungary, Argentina, Chile, Mexico and the southwest USA [18].

Arsenic removal methods include adsorption, IX, chemical precipitation, coagulation and membrane separation [19]. Since arsenite is uncharged, it is not removed by IX, and somewhat removed by coagulation. It is, therefore, necessary to oxidize the dissolved arsenic to the arsenate state before removal. RO membranes, on the other hand, reject both the arsenate and the arsenite. A hybrid membrane process that has been successfully demonstrated in the United States combines coagulation with MF [20]. The coagulation/MF process consists of the addition of an iron-based coagulant such as ferric chloride (10 mg/l) at pH of 6.8 followed by MF. The membrane hybrid process eliminates the flocculation step. A high MF flux of 153 $l/m^2/h$ was achieved with minimal fouling and long cleaning intervals.

The problem of high nitrate content in many ground waters was mentioned in Chapter 2. Nitrate concentrations greater than 50 mg/l in water are carcinogenic, and is becoming a serious health problem in heavily fertilised and irrigated farmlands. A NF/IX water treatment system is very effective in removing virtually all nitrates from drinking water [6]. In the NF/IX hybrid system, pre-filtered water flows through a NF membrane system, which removes all the multivalent ions and some of the monovalent nitrate ions. The NF permeate is then polished in an anion IX column where the nitrates are exchanged with chloride ions. NF pre-treatment increases the efficiency of the IX process since it removes dissolved organic carbon and divalent ions such as sulphate ions.

3.1.9 Treatment of acidic streams

Acidic solutions are commonly used in the winning and processing of metals resulting in the waste streams containing aids and metals [21]. Membrane technologies such as RO and ED are used commercially for metal and acid recovery from waste streams; for example, RO is used for recovering Cr, Cu, Cd, Zn and Ni from plating rinse waters, and ED is used for acid recovery from acidic pickling, anodizing and etching solutions. NF technology, on the other hand, is unique; it recovers the metals in the retentate while passing the acids in the permeate. This is because NF rejects acids poorly while retaining divalent ions and some monovalent ions. Because of low acid rejection, the osmotic pressure is low so that the acid plus water can be considered as the solvent.

A patented hybrid process that combines NF with IX (or diffusion dialysis) for separating heavy metals from acids is shown in Figure 3.9. The process can treat both strong and weak acids with high or low metal concentrations. The waste feed is a spent 20 wt% sulphuric acid solution containing 9.6 g/l aluminium. The NF permeate is purified acid. The NF membrane was Dow/Film-Tec NF45. The operating pressure was 34 bar g. Acid preferentially permeated the membrane at ~51% recovery. The NF concentrate

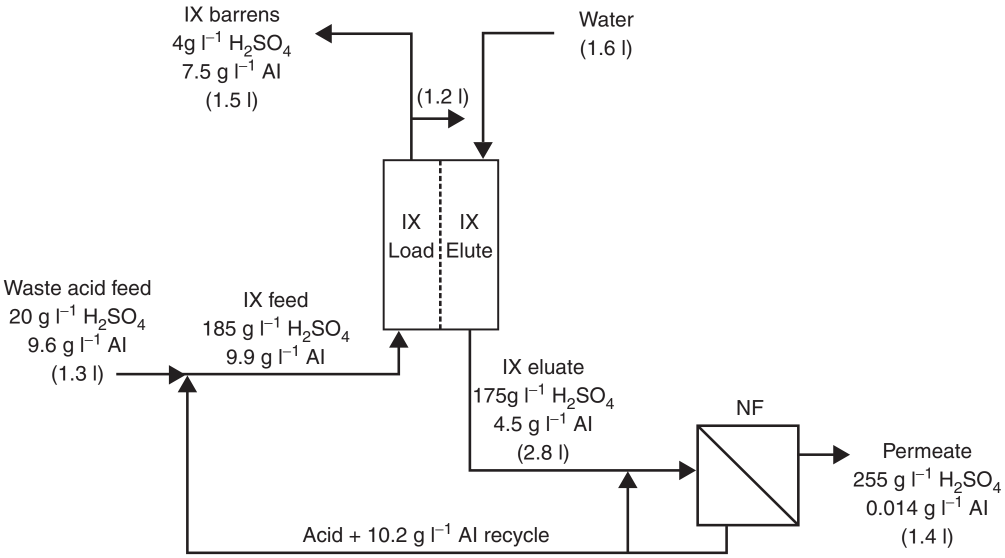


Figure 3.9 Process flow sheet for treating acidic waste streams. The NF-IX hybrid process treats acidic waste containing 20 wt% sulphuric acid and ~1% aluminium, separating the heavy metal from the acid. *Source: [21].*

contained 99.9% of aluminium in the original feed. The main advantages of the hybrid process are (a) much lower osmotic pressure for a standalone NF process and (b) higher purity achieved than with IX standalone process.

3.1.10 Dairy processing

The earliest application of membrane processes in the food industry and one of the largest is in the dairy industry where it is used for (a) the pre-concentration of milk for cheese manufacture and (b) the fractionation of cheese whey. Milk is a complex liquid consisting of 12.5 wt% total solids, 3.3% protein, 3.5% fat, 4.9% lactose and 0.7% ash. RO of cheese whey was commercialised in 1971, and the first UF/RO plant for fractionating cottage cheese was commercialised in 1972. By 1996 approximately 80,000 m^2 RO and 240,000 m^2 UF membrane area was installed for dairy processing [22], of which whey processing constituted 75%. In 1984 NF was introduced for simultaneous concentration and desalination.

A hybrid membrane system used for processing milk may entail MF, UF, NF/RO and ED. Cheese whey, a by-product during cheese production, was traditionally concentrated by evaporation and spray drying. Membrane filtration was successful because it not only reduced energy and processing costs, it also improved product properties; minimal protein denaturation as a consequence of lower process temperatures. Further, since UF both concentrated proteins and removed lactose and salt simultaneously, specialty products such as whey protein concentrates (WPC) and protein isolates could be produced [22,23]. Mass balance for an integrated UF/RO membrane process for cheese whey processing is shown in Figure 3.10.

In membrane processing of cheese whey, the whey is pre-treated with MF prior to UF instead of the less efficient centrifugation for removing small quantities of fat (soluble globules, 0.2–1.0 μm) and casein (fine particulates, 5–100 μm). Complete removal of these fines by MF nearly doubles the UF flux due to reduced concentration polarisation and fouling. Demineralisation of whey by removing monovalent salts in whey powders is necessary because they cause negative sensory quality whereas the divalent ions in the powder have a positive health benefit [22]. NF is well-suited for demineralisation since it retains divalent ions but not the monovalent ions. NF displaces other processes – evaporation (EV), RO and ED – as shown in Figure 3.11.

In a commercial process for the production of WPC powder, cheese whey (5 wt% solids) is concentrated by UF to 15–20 wt% solids. The UF retentate is evaporated and/or spray dried, producing WPC powder. Simultaneously UF reduces the liquid feed

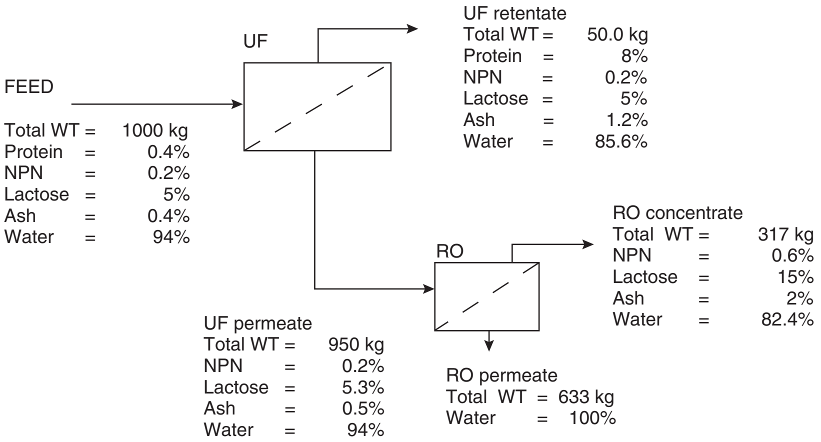


Figure 3.10 Mass balance for an integrated UF-RO membrane process. The process is based on a concentration factor of 20 for UF and three for RO. *Adapted from Ultrafiltration Handbook, Technomic, 1988.*

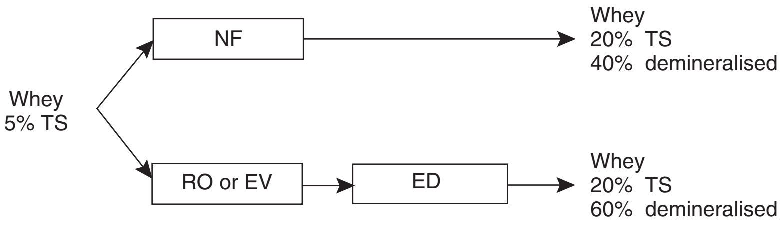


Figure 3.11 Various process schemes for whey processing.

volume by 90–95% prior to evaporation and drying thereby substantially reducing the energy load of the drying processes. The UF permeate (35 m^3/h) containing lactose is concentrated by RO for alcohol fermentation (17 m^3/h). The RO permeate flows (20 m^3/h) through a second-pass RO unit, producing demineralised water [24].

3.1.11 Sugar processing

Sugar production involves two distinct operations: (a) processing sugar cane or sugar beets into raw sugar and (b) processing the raw sugar into refined sugar. Cane and beet sugar extracts contain sucrose and undesirable amounts of polysaccharides, lignins, proteins, starches, gums, waxes, and other colloidal impurities that contribute colour and/or taste to the crystalline product and reduce product yield. The raw juice, therefore, is subjected to heating, liming addition and clarification to remove proteins and colloidal matter [25]. Sugar refining is a highly energy-intensive process; hence, membrane technology is highly attractive. However, because of high osmotic pressure and high viscosities, the role of membrane application is limited to dilute streams for clarification and purification at the juice extraction stage. Possible operations that could be replaced by UF or MF are shown in the dotted areas in Figure 3.12 [23]. UF and MF could be used

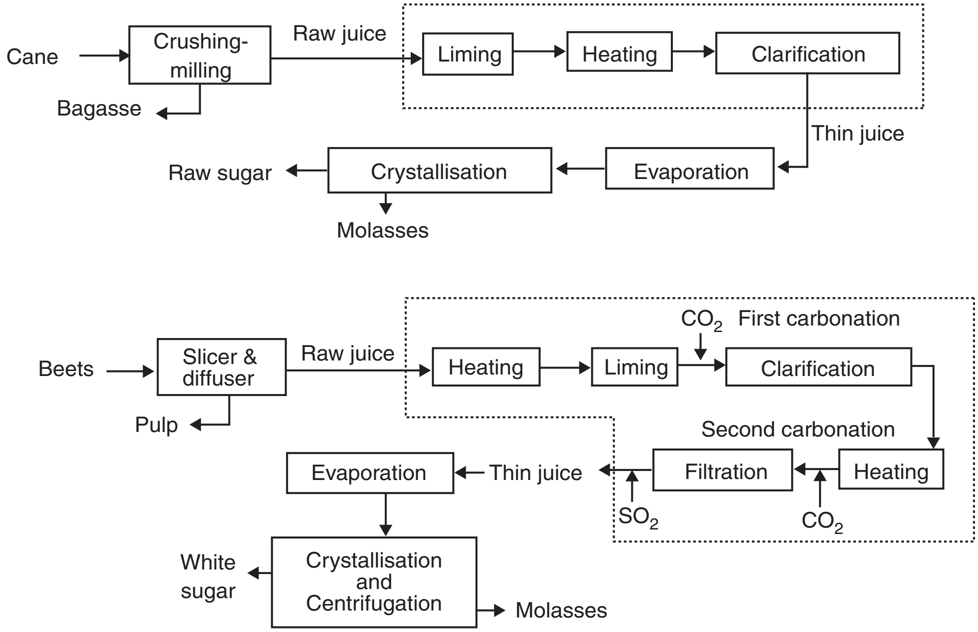


Figure 3.12 Sugar refining by membrane processing. Possible operations that could be replaced by MF or UF are shown in dotted areas. *Source: Cheryan, Copyright® 1998 from Ultrafiltration and Microfiltration Handbook by M. Cheryan. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.*

for removing these colloidal and macromolecular impurities with little or no addition of lime, carbon dioxide, or sulphite before the clarified juice is evaporated and crystallised. Further, removing macromolecules and reducing lime levels reduces fouling and scaling of the evaporators.

Cane sugar processing consists of the following steps: sugar cane is crushed, the juice is heated and filtered, then sent to a series of crystallisation steps to create crystals of raw sugar, followed by centrifugation to remove any remaining juice or syrup. The last step produces a small stream of remaining syrup called cane mill molasses containing up to 55% (wt.) sucrose and substantial amounts of invert sugar (glucose/fructose mixture) impurities. Sucrose is the fraction that becomes crystallised sugar, and has considerable commercial value but cannot be extracted economically because of the impurities. Several US patents [26] describe a process to recover sucrose from molasses and other syrups incorporating NF and MF. In this process, the molasses is pre-treated by MF and/or UF to remove colloids, polysaccharides and other high molecular weight impurities to prevent fouling of NF membranes. NF membranes retain more than 75% sucrose and small amounts of invert sugar while the permeate contains most of the invert sugar and less than 10% sucrose. The retentate flows back to the first crystalliser/centrifuge stage where it crystallises into raw sugar, and is then processed in a refinery to make refined sugar. The desugarised molasses is useful as animal feed. Although beet sugar contains no invert sugars, molasses can still be treated by the NF process.

3.1.12 Vegetable proteins

Conventional methods for producing soy protein concentrates and isolates consist of extraction, heat treatment, and centrifugation to separate the protein and fat from undesirable compounds such as oligosaccharides, phytic acid and trypsin inhibitors. Typically, the traditional methods are time consuming and the products sometimes have inferior functional properties possibly due to the denaturation of proteins during heating. Since the undesirable compounds are smaller in molecular size than proteins and fat components, proteins can be easily recovered and isolated by using UF membranes. Further, since UF separation does not involve heat and chemicals (used in extraction), the functional properties of the soy protein are superior. Typically, the UF membranes used are in the high MWCO range of 50,000–200,00 Da. Although the composition of the final soy product seems to be independent of the MWCO of the membrane, the flux is much higher. Furthermore, membrane processing results in higher yields because the whey proteins are also recovered. These proteins contribute to superior functional properties [23].

3.1.13 Edible leaf protein concentrates

Leaf protein is a valuable and renewable source of protein. It has been extensively investigated as a possible solution for world hunger, protein deficiency and starvation. Of the leafy plants grown as forages, alfalfa is dominant because of its high productivity, high nutritive value, and low production costs [27]. Leaf juice contains up to 5% protein (20% dry basis), which is recovered by heat coagulation at 80°C. Leaf protein consists of a chloroplastic or green protein fraction (65–75%) and a mixture of cytoplasmic and chlorophyll-free protein or white protein (25–35%). The chloroplastic fraction is a mixture of proteins with MW > 65,000 Da, while the cytoplasmic protein is a mixture of two proteins exhibiting a MW between 10,000 and 65,000 Da [28]. Whole leaf protein concentrate (LPC) is a dark green product, which is very low in fibre, and high in protein and xanthophyll [27,29]. Xanthophyll gives the LPC special value as a chicken feed ingredient, since it is this pigment that gives egg yolks and broiler skins their golden yellow colour.

Whole LPC has been unacceptable as a food because of its colour and flavour characteristics [27]. The green protein can be separated from the white protein by selective heat coagulation [29]. Fractionation by heat, however, denatures the protein. Preparing the white proteins in soluble form is most desirable, since solubility and other functional properties of undenatured protein are important for many food applications. Recovery and fractionation of alfalfa protein by membrane UF is, therefore, a preferred method [28,29,30]. The UF process removes 80–90% of the water containing non-protein soluble components such as low molecular weight amino acids, sugars, minerals, vitamins and phenolic bitter-tasting pigments. Ultrafiltered protein concentrates also contains more amino acids than heat precipitated ones. The spray-dried white protein is water soluble, cream-white in colour, and tasteless. During UF of whole juice, a 7–8% protein level is critical for the separation efficiency. Exceeding these levels causes a rapid decrease in the flux with a simultaneous decrease in the rate of protein concentration due to severe fouling, as discussed in Chapter 2. UF of chloroplastic-free juice, by contrast, was efficient even up to 19% dry matter starting with a clear juice containing 2.5–3.5% dry matter [28].

An alternate approach, therefore, has been to separate the green protein from the white protein by heat coagulation at 55°C, centrifuge the product to separate the coagulated green protein from the brown liquor containing white protein, and recover the white protein by UF using a 10,000 Da MWCO membrane (Figure 3.13). One hundred gallons of fresh juice squeezed from 1.1 tons of fresh crop produces 4.5 kg of food grade spray-dried LPC and 22 kg of feed-grade LPC [28]. However, even a mild heat treatment causes some denaturation of the protein.

An integrated membrane process based on MF-UF-diafiltration is shown in Figure 3.13: a backwashable dead-end MF with a pore size of 5.0 μm to separate the green fraction at pH 8.0 followed by UF to recover the white fraction and purification of the white fraction using diafiltration (DF). MF with a pre-coat traps the chloroplastic fraction producing a chlorophyll-free brown liquor. The pre-coat material can be diatomaceous earth or corn starch. The latter is preferred since the filter cake is useful as

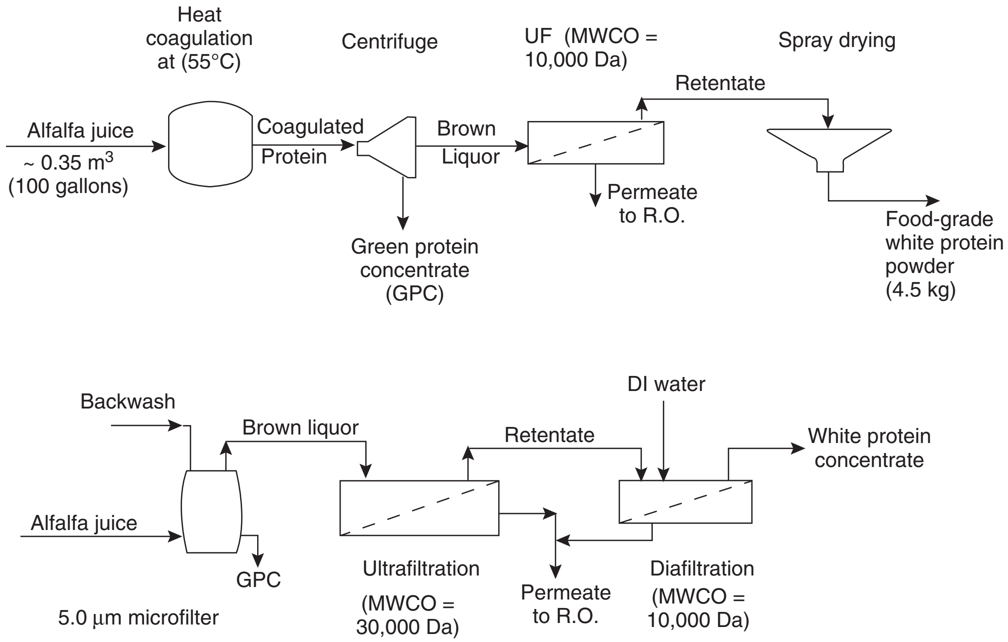


Figure 3.13 Hybrid membrane process schemes for recovering leaf proteins.

cattle feed. The efficiency of the process can be increased by adding a body feed of the coating material at very low concentrations (5%). Because of its unique design, the MF cartridge is not subject to internal pore blockage unlike like the traditional dead-end MF cartridge. The backwash cycle is very fast (<1 min) and efficient. The filter elements are durable with a 7–10 year life and use a variety of materials for making serrated disc elements including nylon, polypropylene and stainless steel.

Green plants and especially alfalfa also hold promise for growing therapeutic proteins genetically [31]. Genetic engineering makes it possible to custom-design a green plant to produce a desired product in the seed, leaves, fruit, root, or sap, and grow these modified plants on farms. The modified plant alfalfa crop is harvested before the plant's blooming season and seed production stage followed by extraction and recovery of the protein.

3.1.14 Vegetable and corn oil processing

In conventional chemical processing of vegetable oils, crude oil is recovered from the mechanically expressed vegetable seed by solvent extraction using hexane, as shown in Figure 3.14 [22]. The miscella (a mixture of extracted oil and solvent) from the extractor contains 60–70% solvent, which is recovered by distillation and reused. Purification of crude oil consists of removing components that are harmful and are not wanted in the final product, the pure oil. These components are phosphatides (gums and lecithin),

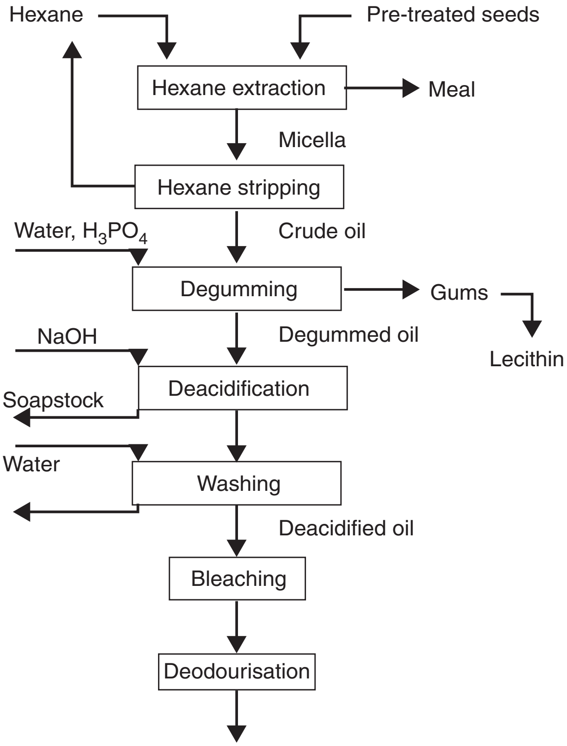


Figure 3.14 Schematic diagram of conventional chemical processing of vegetable oils. *Source: [22].*

free fatty acids, pigments, and volatile odouriferous materials. These materials are removed successively in steps termed degumming, refining, bleaching and deodourising.

The conventional technology is energy intensive, uses large amounts of water and chemicals, and generates heavily contaminated effluents. Membrane processing tackles these drawbacks and also removes phospholipids and free fatty acids. Further, hexane removal by distillation after degumming increases the distillation efficiency. Energy savings and wastewater (high BOD acidic waste) elimination are estimated to be 10–20 trillion BTU/yr and 20–25 million gallons/yr, respectively. Additional energy savings are possible when RO is used to remove hexane instead of distillation [24,32]; the solvent-rich stream that exits the RO unit is recycled to the extractor and the oil-rich stream is processed by distillation to recover the remaining solvent. Energy savings of 2 trillion BTU/yr are estimated for the hybrid membrane-distillation operation in the US domestic edible oil industry.

Phospholipids (4.5 wt% of crude oil) are among the most abundant surfactants found in nature. At concentrations higher than the critical micellar concentration, surfactants form micelles, which are then easily rejected by UF membranes, as discussed in

Chapters 1 and 6. Phospholipids have hydrophilic polar heads and hydrophobic nonpolar tails and form reverse micelles in organic solvents such as hexane. Moreover, the micelles bind low molecular weight impurities such as free fatty acids, sugars, amino acids and colour compounds [33]. Because of the formation of micelles, triglycerides are also fractionated from phospholipids. The latter is then easily purified to produce a valuable product, lecithin, oil-free. Since the micelles are estimated to have pseudo-molecular weights of 200,000, it should be possible, therefore, to recover lecithin oil-free using UF membranes with MWCO of $\geq$20,000.

An integrated membrane process may involve the following unit operations [23]:

- Degumming – Hexane-resistant UF membranes (PA, PS, PVDF, PI, PAN, or inorganic) with a MWCO of 20,000 Da and molecular sizes of 20–200 nm.
- Deacidification – Hydrophilic UF membranes (PAN) with a MWCO of 30,000 Da in the first stage to remove free fatty acids (permeate) followed by a hydrophobic membrane in the second stage to process the retentate containing triglycerides from the first stage.
- Removal of metals – Ceramic UF membranes with pore sizes of 0.01–0.02 μm for recovering the nickel catalyst and reducing the nickel level in the product to 1–10 mg/l.
- Dewaxing – Ceramic MF filters with pore diameters of 0.05–1 μm operated in conjunction with periodic timed backwashing.

A processing scheme shown in Figure 3.15 [34] includes two or more dead-end cartridge MF stages using increasingly fine filters to prevent fouling of the downstream UF membranes, followed by a feed-and-bleed (F&B) filter. The retentate from the F&B filter is recycled back to the extractor, whereas the permeate flows to several UF stages to separate the phospholipids from the oil/solvent mixture. The permeate from the first UF stage contains less than 200 ppm phospholipids and is evaporated to remove the solvent

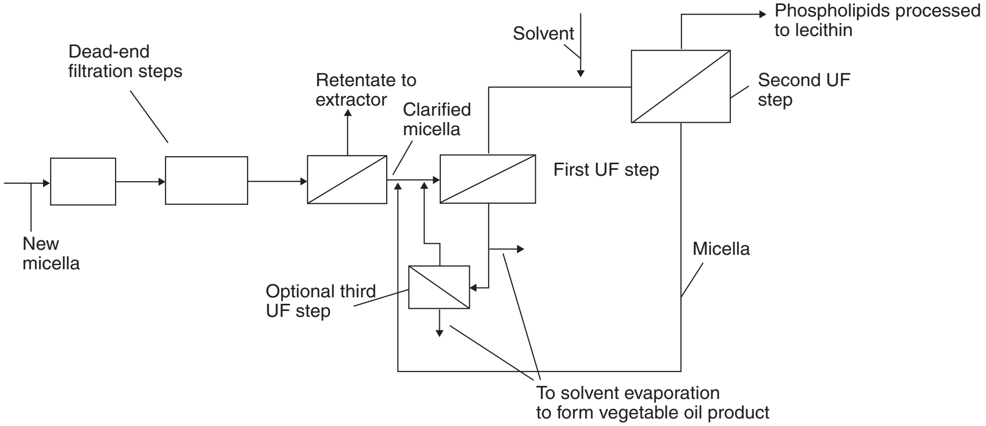


Figure 3.15 Processing of vegetable oil miscella in a hybrid membrane system.

and produce pure vegetable oil. The phospholipid content may be reduced to less than 5 ppm by adding a third UF stage. The second UF stage retentate contains concentrated phospholipids (25 wt%) and is further processed to make lecithin, a food additive.

Wet milling of corn accounts for more than 75% of the corn processed for food, feed and industrial chemicals in the United States. The corn wet milling process is quite energy and capital intensive. Corn is also the main feedstock of ethanol ($>1.5 \times 10^9$ gal per year). Since ethanol is used as an oxygen additive in petrol for clean burning, an energy efficient technology for processing corn makes the overall process more efficient. A conventional corn refining process is shown in Figure 3.16. The unit operations that could be replaced with membrane processes MF, NF, UF, RO are marked as I, II, III and IV, respectively.

3.1.15 Fruit juice and wine processing

A conventional process of producing final juice product is shown in Figure 3.17. In the manufacture of clear juice, the pressed fruit juice is pasteurised and treated with pectinase (an enzyme) to hydrolyse the pectin and reduce cloudiness. Next, a fining agent such as gelatin is added during the preliminary clarification step followed by holding and decanting. The juice is filtered using diatomaceous earth as a filter aid to remove suspended solids, colloidal particles, proteins and condensed polyphenols. The final clear juice is pasteurised again, if necessary. The process involves several batch operations that are both time consuming and labour intensive [23]. Membrane processes are used to replace the holding, filtration and decantation steps as shown in the figure. Membrane processing produces higher quality juice due to reliable and consistent removal of haze-forming components including suspended solids, colloidal particles, proteins and polyphenols with a turbidity of 0.1–0.3 NTU as compared to 2–5 NTU for conventional processing.

Processing of citrus juices by integrated membrane processes are shown in Figures 3.18 and 3.19. In the case of debittering (Figure 3.18), fresh or reconstituted citrus juice that has been de-oiled and pasteurised is ultrafiltered to remove the pulp [23]. The clarified permeate containing sugars, bitter compounds (limonin, naringin, hesperdin, polyphenols) and off-flavour compounds flows through an adsorbent resin column that contains an adsorbent macroreticular resin with no functional groups. The resins are designed to remove these compounds. The debittered juice is recombined with the UF concentrate containing the pulp to produce the blended and refined citrus juice product. The hybrid process is cheaper than the traditional process using centrifuge-cum-hydrophilic adsorbent system.

Another application of membrane processes in the production of citrus juice concentrates, as shown in Figure 3.19. UF is used to separate the pulp (retentate) from the serum (permeate). The serum fraction contains sugars and flavour compounds. The pulp fraction

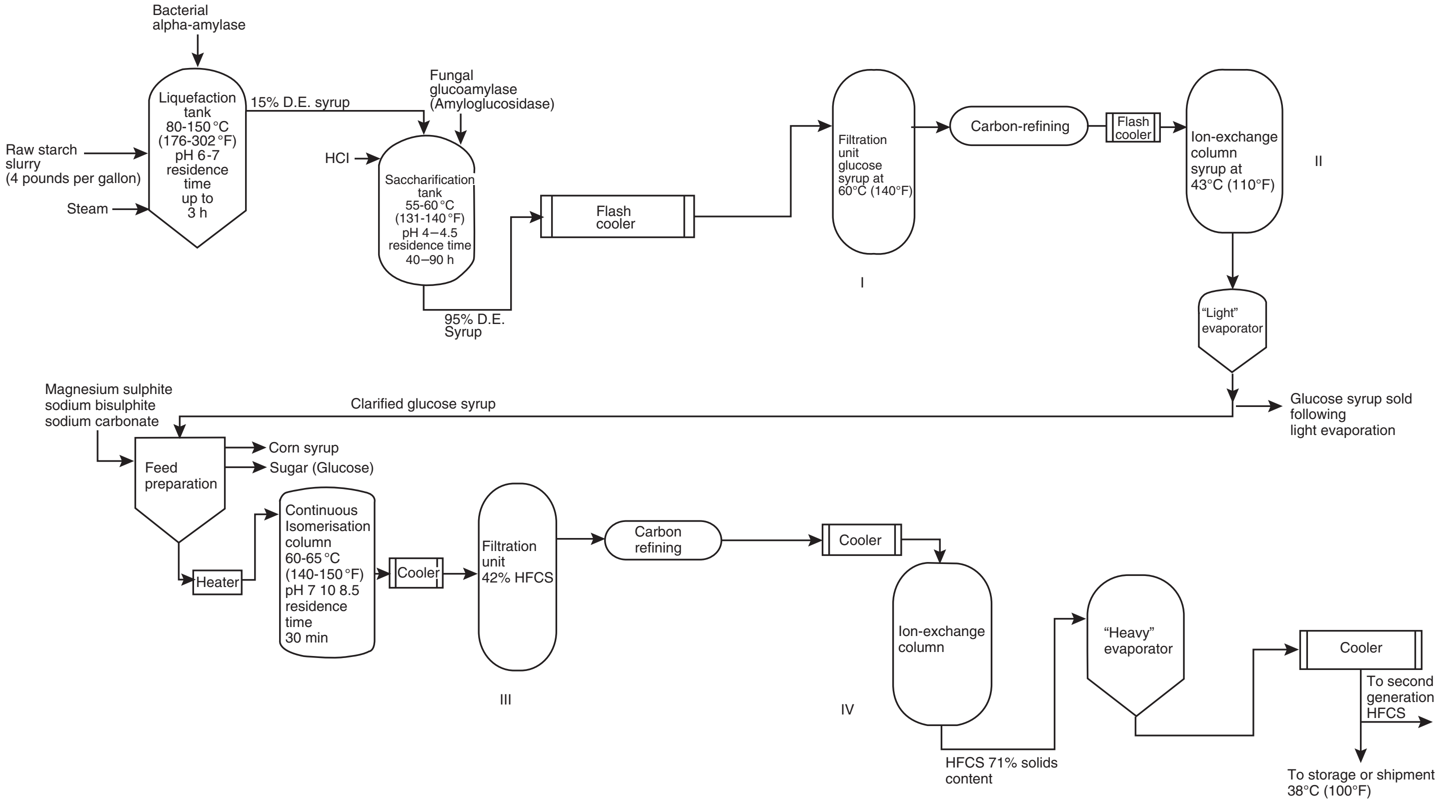


Figure 3.16 Corn refining process steps. I, II, III and IV operations could be replaced with membrane processes. *Adapted from Biotechnology in Industry, Butterworth, 1983.*

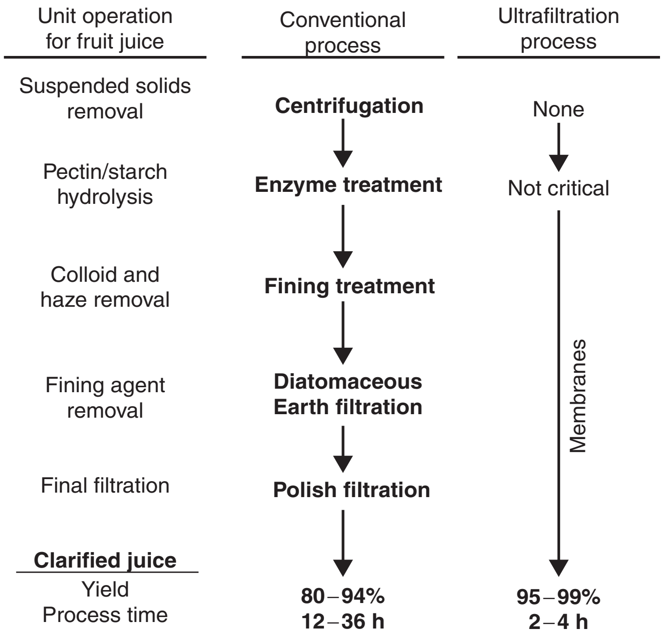


Figure 3.17 Manufacture of apple juice by conventional and membrane processes. *Source: Cheryan, Copyright® 1998 from Ultrafiltration and Microfiltration Handbook by M. Cheryan. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.*

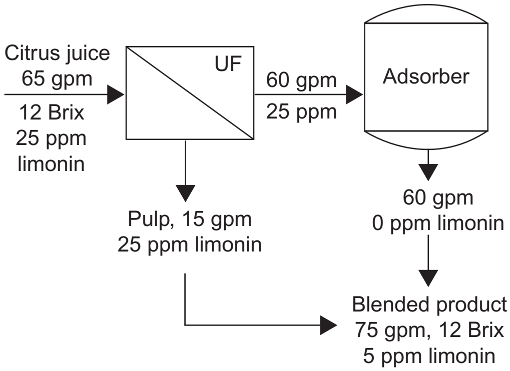


Figure 3.18 Processing of citrus juices by a hybrid membrane process. *Source: Romicon.*

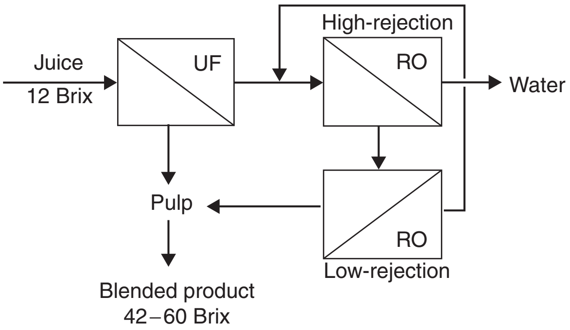


Figure 3.19 Concentration of fruit juices by an integrated membrane process. *Source: Cheryan and Alvarez, Memb. Sci. Tech., Academic Press (1995).*

contains some soluble solids, all insoluble solids, pectins, enzymes, orange oils and microorganisms. The UF permeate (90–95% of the feed volume) is concentrated in a two-stage RO unit. The concentrated serum is blended with the UF concentrate to produce a highly concentrated juice (42–60° Brix). Prior to mixing with the RO concentrate, the UF pulp fraction (5–10% of the feed volume) is pasteurised for improving stability by destroying spoilage microorganisms.

Membrane processes have also been used for producing juice concentrates without loss of quality that occurs during evaporation [23,24]. Specifically, evaporation results in the loss of various volatile alcohols, esters, and aldehydes, resulting in a significant deterioration in quality, aroma and flavour of the concentrated product.

Wine processing by a hybrid membrane process is shown in Figure 3.20. The first UF unit removes microorganisms, colloids, and high molecular weight materials. The MF step removes yeast used for fermentation. The second UF unit is used for sterilising prior to bottling. Membrane pore size plays a crucial part in the retention of colour and aroma compounds. UF membranes with MWCO of between 100,000 and 500,000 Da are best [23].

3.1.16 Recovery of flavour compounds by osmotic distillation

Osmotic distillation (OD), sometimes called “isothermal membrane distillation,” is a membrane process in which a liquid phase (usually an aqueous solution) containing one or more volatile components flows across one surface of a microporous membrane whose pores are not wetted by the liquid, while the opposing surface is in contact with a second non-wetting liquid phase (usually an aqueous solution) in which the volatile components are soluble or miscible [35]. The device is similar to the membrane contactor (MC) discussed in Chapter 1, which contains hollow fibre membranes that are hydrophobic (non-wetting). Unlike MC used for degasification, the feed to be concentrated flows in the shell side of the membrane element, while the brine strip solution flows in the lumen side.

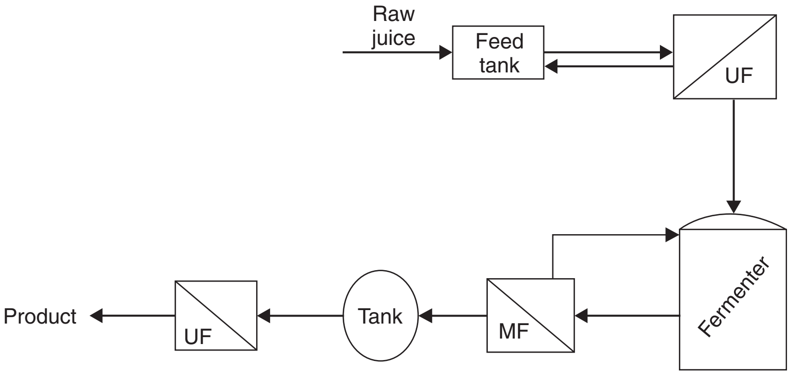


Figure 3.20 Wine production by a hybrid membrane system. *Adapted from Cheryan.*

The device or process is best suited for concentrating dilute solutions containing non-volatile solutes (relatively low concentration) of moderate to high molecular weight such as sugars, polysaccharides, carboxylic acid salts and proteins with limited stability to high temperature and shear stress. Process flow sheet for a juice concentration unit is shown in Figure 3.21. The process incorporates partial batch recycling on the feed side to minimise large feed viscosity changes in the MC and continuous countercurrent recycling with evaporative re-concentration of the brine strip stream [35]. The MC modules can be arranged in a series, parallel, or series-parallel array.

The OD process is more expensive than evaporation (EV), UF, or RO processes for concentrating aqueous mixtures. However, OD can selectively remove water relative to other low-molecular weight solutes yielding products of superior quality especially when volatile solutes such as flavours and fragrances are involved. Usually with most liquid foodstuffs, the maximum acceptable concentration achieved by (EV/UF/RO) is 30%. Hence, a hybrid process involving pre-concentration of the feed by RO followed by further concentration of the RO concentrate by OD is a logical extension for recovering a higher concentration product at lower processing cost. A typical hybrid process is shown in Figure 3.22. The process flow sheet includes an MF or UF stage to pre-treat the feed for removing suspended solids and colloids and thus minimise fouling of RO/OD membranes. Another potential application includes dealcoholisation of ferments, i.e., removal

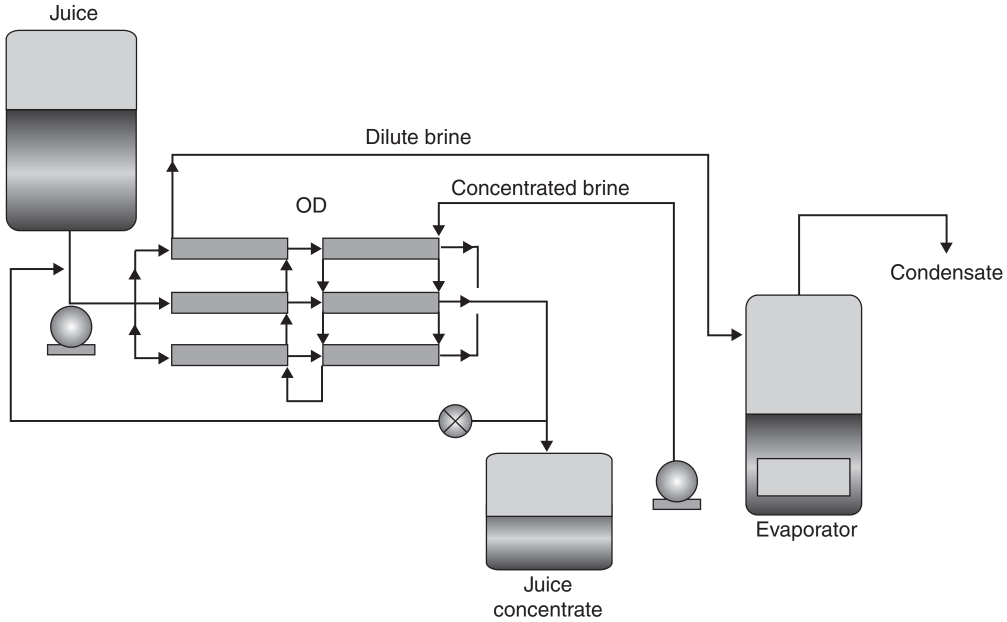


Figure 3.21 Hybrid osmotic distillation schematic for juice concentration. *Source: Hogan et al., Reproduced with permission from Chemical Engineering Progress, July 1998. Copyright® 1998, AIChE.*

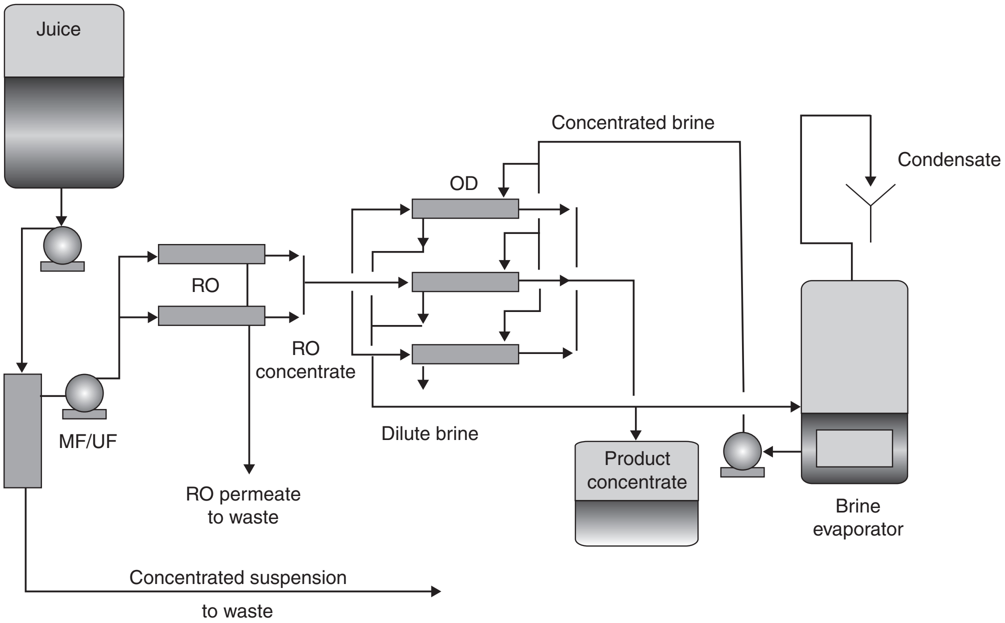


Figure 3.22 Hybrid osmotic distillation schematic for biological products. *Source: Hogan et al., Reproduced with permission from Chemical Engineering Progress, July 1998. Copyright® 1998, AIChE.*

of ethanol from fermented beverages such as beer and wine. In this hybrid process food-grade (190 proof) ethanol can be recovered from the strip solution using a rectifying column. Similarly, OD can be used for the selective removal of organic volatiles from aqueous solutions in the pharmaceutical industry; for example, removing or recovering a part of the organic solvent from the product-rich supernatant used in the extraction of intracellular products from fermentation broths.

3.1.17 Bioprocessing

Bioprocessing or biotechnology is used in the production of pharmaceuticals, foods, flavours, fuels and chemicals with the aid of a biocatalyst such as an enzyme, microorganisms, plant cell, or animal cell in a bioreactor. It also involves genetic engineering for the manipulation of plants, animals, and microorganisms such as yeasts, bacteria and fungi. Downstream processing is required to remove impurities, bulk-volume reduction and simultaneous concentration of the desired product from the bioreactor. Various steps deployed during downstream processing for recovering the final product in protein production are illustrated in Figure 3.23 [36,37]. Protein recovery is sensitive to operating conditions because their function depends on the integrity of the delicate 3D tertiary structure.

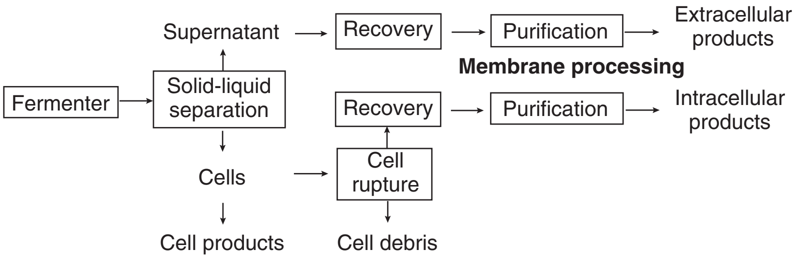


Figure 3.23 Major process steps in downstream processing. Membrane processes may include MF, UF, RO, and/or ED for concentration, separation and purification.

Most pharmaceutical substances are manufactured in batch processes by (a) chemical synthesis, (b) fermentation, (c) isolation and recovery from natural sources, and (d) a combination of the above. Fermentation broths are usually very dilute and contain many complex compounds as given in Table 3.3 [23]. Because of the dilute and impure nature of the broths and sensitivity to operating conditions, MF, UF and NF are well-suited for downstream processing, i.e., separation, isolation, purification and recovery of the product. Several membrane applications in bioprocessing are illustrated in Figure 3.24 [23] including gas separation (GS).

NF technology is used in the pharmaceutical and biotechnology industry to recover antibiotics from fermentation processes. A schematic flow diagram of NF separation for recovery of 6-APA is shown in Figure 3.25 [10]. 6-Aminopenicillanic acid (6-APA, MW 216 Da) is an intermediate in the manufacture of synthetic penicillin and can be manufactured by an enzymatic process. A medium-sized plant produces 15–20 tons of mother liquor per day. NF (solvent stable membrane is used) separates the 6-APA (in the retentate) from the other liquor at 60–80 kg/d and is recycled to the extraction unit, thereby minimising product losses (recovery is 90–95%).

Table 3.3 Fermentation broth component concentration

Component	Concentration (%w/w)
Bacteria or yeast (ethanol, lactic acid broths)	1–5
Fungi (citric acid, penicillin production)	1–3
Animal cells (mammalian tissue culture)	0.1–5
Acetic acid in fermentation broth	0.2–5
Lactic acid in fermentation broth	8–10
Citric acid in fermentation broth	5–10
Extracellular enzymes	0.5–1
Vitamins	0.005–0.1
Antibiotics	1–5
Ethanol	7–10

Source: Cheryan, Copyright® 1998 from Ultrafiltration and Microfiltration Handbook by M. Cheryan. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.

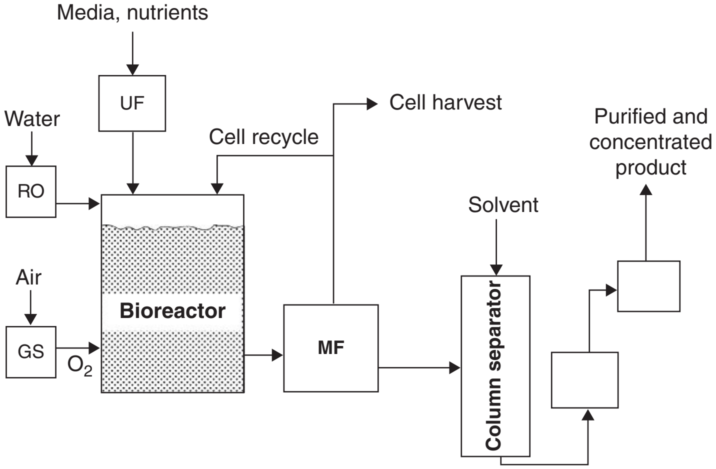


Figure 3.24 Bioprocessing by hybrid membrane systems showing upstream and downstream membrane processing steps. *Adapted from Cheryan.*

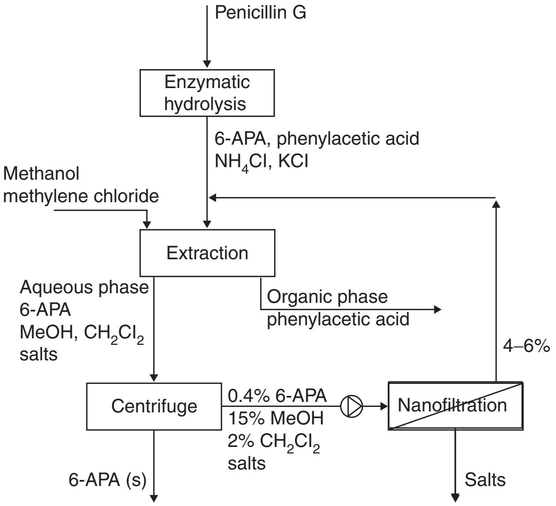


Figure 3.25 Pharmaceutical drugs recovery with a hybrid membrane system. *Source: [10].*

3.1.18 Membrane recycle bioreactors

A process flow diagram for producing ethanol and lactic acid from cheese whey by fermentation with the aid of a membrane recycle bioreactor (MRB) is shown in Figure 3.26 [23]. The UF permeate (WPC in the retentate) contains lactose, non-protein nitrogen and dissolved salts and is then concentrated by RO to the desired sugar

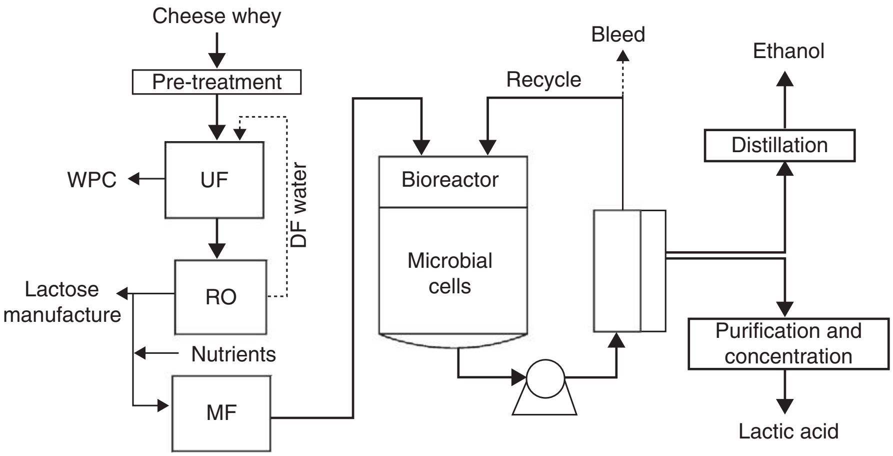


Figure 3.26 Processing of cheese whey using multiple membrane systems and a membrane recycle bioreactor. *Source: Cheryan, Copyright® 1998 from Ultrafiltration and Microfiltration Handbook by M. Cheryan. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.*

concentration for fermentation (2–3 times for lactic acid and 4–5 times for ethanol). The bioreactor or fermentor contains a suspension of the microorganism (biocatalyst). In the case of ethanol production by yeast, a cell concentration of 90 g/l is optimal, whereas lactic acid production requires a cell concentration of 60 g/l. MRBs offer the advantage of conducting fermentations in continuous mode instead of in batch mode, resulting in lower capital costs, better process control and improved productivity [23,37].

The MRB shown in Figure 3.26 consists of a reaction vessel and a membrane (UF or MF) module. The biocatalyst is suspended in the main reaction vessel, and the feed is pumped into the reaction vessel at the same rate as the permeate (product) flow rate. The reaction mixture is pumped continuously through the membrane module where the products of the reaction and other low molecular weight compounds are removed in the permeate, while the biocatalyst and other rejected compounds are recycled back to reaction vessel for further reaction. MRBs generate higher product concentration because of higher cell concentrations that allow high dilution rates with complete substrate utilisation. UF membranes with a MWCO of 10,000–100,000 Da are used to retain the enzymes, and MF membranes are used when microbial cells are involved.

3.1.19 Dehydration of ethanol

Dehydration of ethanol has been the most successful and important application of membrane pervaporation [2, 38]. Pervaporation (PV) is used to remove the ethanol product from fermentation broth thus preventing product inhibition. The data from ABE (acetone, butanol, and ethanol) production from xylose substrate using C-acetobutylicum in a conventional fermenter indicates that butanol production reached a maximum value after 90 h and dropped after 260 h. In the case of a bioreactor-PV hybrid process, butanol production reached a maximum after 300 h, and the high value was maintained due to the continuous removal of the product by the PV membrane unit [38].

Ethyl alcohol concentration in the fermentation broth varies between 5% and 10%. Ethyl alcohol is concentrated and dehydrated by a distillation process. However, ethyl alcohol forms an azeotropic solution with water at ethyl alcohol concentration of 95.6 wt%, and distillation becomes ineffective at removing the trace amount of water. Because of the formation of azeotropes, azeotropic distillation with an additive, normally either cyclohexane, or benzene, needs to be applied. The energy consumption of this dehydration process is very high. The PV process, therefore, has been considered as an alternative separation process for breaking the azeotrope. However, the one-step PV membrane concentration of ethyl alcohol is not considered economically feasible. According to the vapour phase-liquid phase ethyl alcohol concentration diagram for a commercial polyvinyl alcohol/polyacrylonitrile composite PV membrane, distillation is more favourable than PV for the concentration of ethyl alcohol up to 85 wt%, while PV is more effective for concentrating ethyl alcohol from 85% to 99 wt% or higher. The steam consumption of the PV-distillation process is 2.7 kg/kg of dehydrated ethyl alcohol as compared to 4.0–6.0 kg/kg of dehydrated alcohol [38].

3.1.20 Flue gas desulphurisation by membrane gas absorption

Membrane gas absorption (MGA) is a gas–liquid (G–L) contacting device that uses a microporous hydrophobic hollow fibre membrane element similar to the membrane contactors discussed earlier. The hydrophobic membrane barrier separates the gas phase from the absorption liquid phase. The gas to be separated diffuses through the gas-filled pores of the membrane and is absorbed in the liquid. Absorption is based on physical absorption or by a chemical reaction. Both phases should not mix in order for the operation to be efficient.

Environmentally unacceptable compounds such as SO_2, NO_x, CO_2, H_2S, NH_3, HCl, O_3 and Hg are typically removed by conventional G–L contactors such as packed towers. MGA is an alternate to conventional G–L contactors [39]. A process flow sheet of a MGA pilot plant with a capacity of 100 m^3/h is shown in Figure 3.27. Biogas containing hydrogen sulphide from an anaerobic digester at a potato starch production plant is combusted in a steam boiler. The boiler flue gas contains sulphur dioxide, which is recovered (up to 95%) in the membrane absorber unit as a bisulphite, which can be reused in the production plant. Thus, not only does the MGA technology mitigate the acid rain problem but it also recovers bisulphite, which is used as a production ingredient.

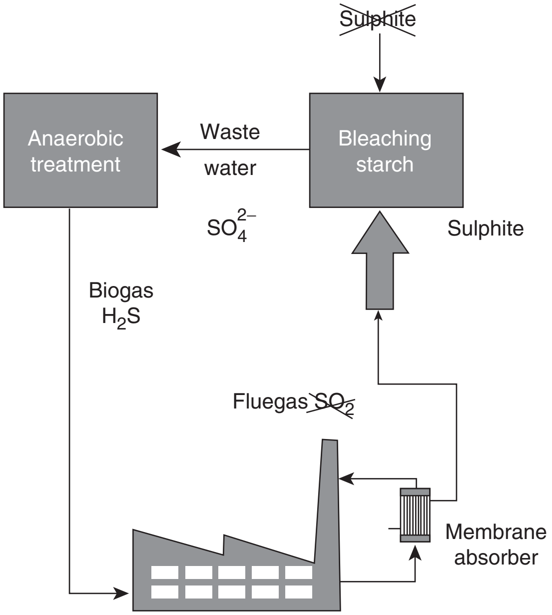


Figure 3.27 Flow schematic of flue gas desulphurisation by membrane gas absorption. *Source: [39].*

3.1.21 Fuel cell integrated membrane desalination

Membrane desalination plants, especially seawater RO plants, are energy intensive. One option for reducing energy consumption is to use dual-purpose plants that provide both electricity and waste heat for heating RO feed water. Membrane productivity increases with feed water temperature albeit at a slight penalty in product water quality. Higher productivity, in turn, means fewer membrane elements to achieve the same product water flow rate, resulting in reduced Capex and Opex.

Among the many options of dual-purpose plants is integration of fuel cells power plants with RO desalination systems. A schematic diagram of a fuel cell integrated RO hybrid system is shown in Figure 3.28, where the fuel cell stack heat is used to pre-heat RO feed water [40]. Fuel cells are electrochemical engines that convert the available chemical free energy in a fuel, usually hydrogen and oxygen (air), to electrical energy directly without going through the heat-exchange process. A typical fuel cell power plant consists of a fuel processor that reforms the fuel, e.g., natural gas or methanol to hydrogen, a multi-cell fuel cell stack, a power conditioner that converts fuel cell d.c. power output to a.c. power, and a heat exchanger (for heating during start-up and for removing heat due to irreversible losses during operation).

Energy consumption and performance data of fuel cell integrated seawater RO (SWRO) and brackish water RO (BWRO) systems are given in Tables 5.4 and 5.5.

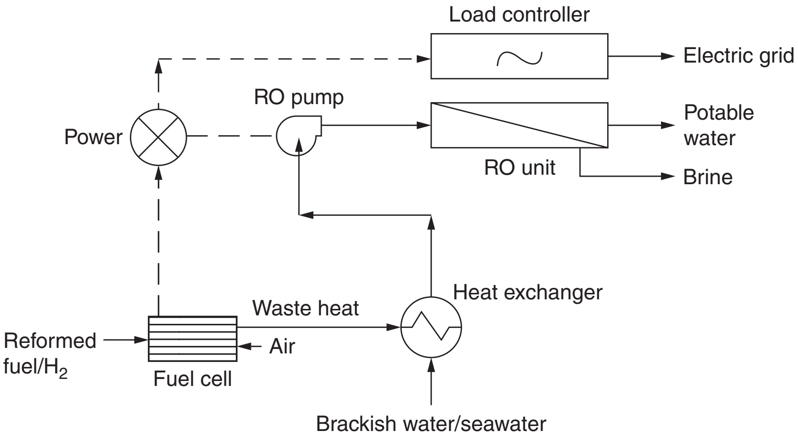


Figure 3.28 Schematic diagram of a fuel cell-RO system. *Source: [40].*

The analyses shows that raising the RO feed water temperature from 20 to 30°C reduced the RO plant energy usage by 7–11%, albeit with a drop in product water TDS; the product water quality decreases slightly with rise in temperature due to higher osmotic pressure, and because solute (ions) flow through the membrane has a higher activation energy than water flow. On-site, standalone distributed fuel cell power plants integrated with on-site RO desalination plants are ideally suited for supplying both power and potable water to rural and remote communities, and at the same time eliminating the costly installation of power transmission lines and water distribution piping.

3.1.22 Seawater desalination by ion-concentration polarisation

Ion-concentration polarisation (ICP) is an electrochemical transport phenomenon that occurs when an ion current is passed through ion-selective membranes. An ion depletion zone evolves when a potential drop is applied across a nanochannel containing fixed charges, which thereby prevents ionic species from flowing into a freshwater reservoir. A continuous stream of seawater is divided into desalted and concentrated streams [41]. Both salts and larger particles (cells, viruses and microorganisms) are pushed away from the membrane (a nanochannel or nanoporous membrane), which significantly reduces the possibility of membrane fouling and salt accumulation, thus avoiding two problems that plague RO and ED. The process was capable of continuous desalination of seawater with a salt rejection of ~99% at 50% recovery using seawater samples. The energy power consumption was <3.5 kWh/m^3, which is comparable to SWRO, but the process is significantly less complex and costly. The process does not require high-pressure pumping/recirculation and can eliminate charged species ranging in size from small salt ions to large particles or cells without fouling the membrane. Since the ICP desalination process does not require high-pressure pumping, it can be powered with batteries and used in small-scale mobile applications. The process may be suitable for small-scale use in remote regions, because minimal pre-treatment of the feed is needed, and the necessary equipment is lightweight and easy to use.

3.1.23 Low-energy electrochemical process for seawater desalination

Seawater desalination is energy intensive. The energy consumption of state-of-the art SWRO desalination plants is three to four times higher than the theoretical minimum energy of ~1.06 kWh/m^3 at 50% recovery and 35,000 mg/l TDS [46]. A low-energy electrochemical process was developed by Siemens WT (now Evoqua WT). In field tests with a 50 m^3/d unit in 2010–2011 in Singapore, the energy consumption was ~1.8 kWh/m^3 inclusive of pumping, desalting, pre-treatment, and post-treatment [42]. Seawater feed from an open intake flows through a coarse screen and is chlorinated before it flows to a UF unit. The UF product water flows to a three-stage ED unit. The ED product water is treated by electrodeionisation (EDI). The energy consumption of a commercial plant would be slightly higher than 1.8 kWh/m^3 achieved in the demonstration unit. This is the most promising process to date vis-à-vis energy consumption for seawater desalination.

3.1.24 Sea salt recovery from seawater by electrodialysis

A special application of ED is the concentration of salt from seawater for the production of table salt in Japan [43]. The ED plants concentrate the salt content from 35,000 mg/l in seawater to 180,000–200,000 mg/l. The ED reject (brine concentrate) is further concentrated by evaporation and crystallisation to produce salt crystals. ED is used as a pre-concentration step since its energy consumption is substantially less than the thermal steps. Large plants with a capacity of 20,000 to more than 200,000 tons of salt per year are in operation in Japan. A TSX-200 ED unit contains 3500 cell pairs in a stack. The cell pair area is 2 m^2 and the cell thickness is 0.4 mm. Titanium is used for the anode and the cathode is plated with Pt. The production capacity of the TSX-200 unit is ~30,000 tons NaCl per year.

Hydrochloric acid is added to the seawater to decompose HCO_3^- and CO_3^{2-} ions and prevent $CaCO_3$ scale formation. A part of desalted seawater is supplied to the anode chambers. In order to prevent damage to the membrane by Cl_2 and HClO generated by the reaction at the anode, a perfluorinated IX membrane is used between the cathode chamber and the adjacent stack. Hydrochloric acid solution is supplied to the cathode chamber to neutralise OH^- ions generated by the cathode reaction. A wash system is provided for washing the inside of the desalting cells with acid or chemical reagents that dissolve the adhered substance. In order to prevent $CaSO_4$ precipitation and increase current efficiency, the membrane surfaces are treated to give monovalent permselectivity, i.e., applying a thin electrolyte layer of opposite charge to the IX membrane on the surface facing the seawater solution [43]. Because the Donnan exclusion effect is much stronger for multivalent ions than univalent ions, the polyelectrolyte layer rejects multivalent ions but allows monovalent ions to pass relatively unhindered.

3.2 WATER DESALINATION

Brackish water desalination was the first successful application of RO with the first large-scale plant built in the late 1960s using cellulose acetate membranes. The first seawater RO (SWRO) was built in 1973 with the advent of high permeability polyamide membranes. By 1993, the SWRO total capacity had reached 56,800 m^3/d. In 2008, membrane desalination constituted 50% of total desalination capacity of which 45% was RO and 5% was EDR, and the rest 50% was thermal. However, 80% of all desalination plants were membrane – 90% RO and 10% EDR. Desalination dominates the RO market and breaks down to 51% desalination, 35% industrial and 14% residential/commercial and non-desal water [44]. In 2012, the global desalination capacity exceeded 60 M m^3/d with more than 60% produced by RO membranes. The global water production by desalination in 2016 is projected to be 100 M m^3/d, twice the rate of global water production by desalination in 2008 [45,46].

Seawater RO desalination vis-à-vis thermal desalination has grown rapidly in the last decade for several reasons: (i) energy consumption for SWRO is about one-half of multiple effect distillation, the most efficient thermal desalination process, and (ii) high reliability membrane operation with a greater than 95% on-line factor because of longer membrane life and effective pre-treatment. At present RO is the most energy-efficient technology for seawater desalination [45,46]. Membrane systems are also compact and modular. A process block diagram of a typical SWRO plant – 35,100 mg/l feed water TDS operating at 70 bar g and ~50% recovery – is shown for illustration purposes in Figure 3.29 (see also Figure 5.1). A photograph of a large desalination plant is shown in Figure 5.5.

Seawater RO membrane desalination has become a viable process since its inception in 1970 for several reasons:

- A substantial reduction in the cost of desalinated seawater from US\$1.75/m^3 to <\$1.00/m^3 in the last 20 years. The cost for BWRO product water is US\$0.25–0.75/m^3.
- Substantial reduction in specific energy consumption from 8 kWh/m^3 in 1980 (16 kWh/m^3 in 1970) to 3–4 kWh/m^3 today. The figure for BWRO is 0.3–1.0 kWh/m^3 [3].
- Membrane life up to 5 years and reliable performance with minimal supervision.

Some notable recent developments include:

- Hybrid membrane systems combining RO and MSF for seawater desalination in dual-purpose plants for the cogeneration of water and electricity where the RO plant

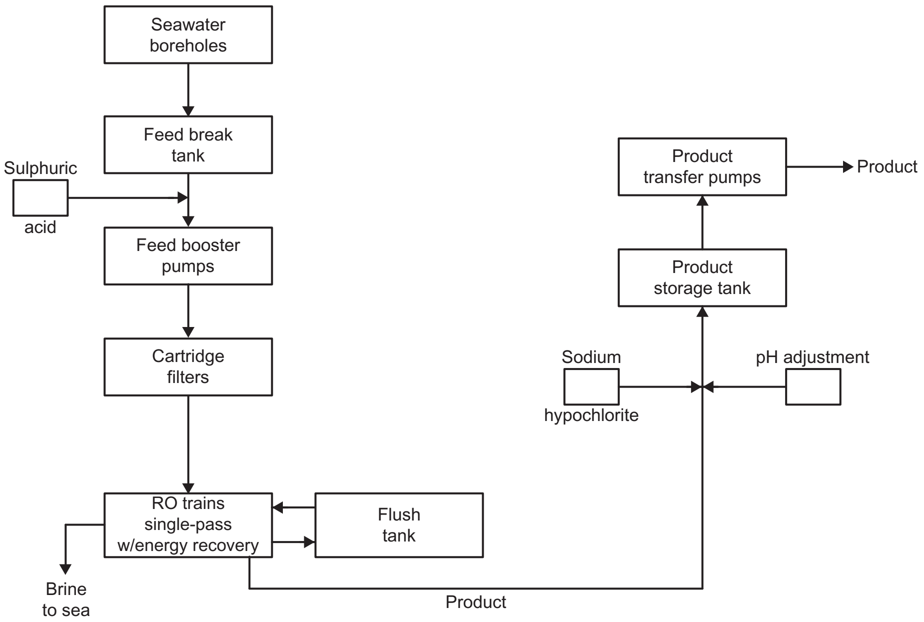


Figure 3.29 A seawater RO plant process flow schematic. The membrane plant uses boreholes for raw seawater intake. Sulphuric acid and 5.0 μm cartridge filter are used for pre-treatment. Post-treatment includes decarbonation, lime addition for pH adjustment and sodium hypochlorite injection for chlorination. The plant includes an automatic system for flushing the membranes and an energy recovery device.

can provide water when the electricity needs are low. Further, by blending higher TDS RO product water (300–400 ppm) with MSF distillate (25 ppm), water production can be more economical for potable water production [3,47,48].

- Integrated membrane system systems deploying MF, UF, NF or some combination of these for RO feed water pre-treatment instead of conventional pre-treatment. For example, it has been shown that hollow fibre UF membrane systems are more efficient and cost-effective for RO brackish water and seawater plants [3,48,49]. MF/UF are very effective in removing fines and colloidal particles, oil is effectively removed by UF, and NF is very effective in removing hardness and low molecular weight organics.
- Electrodialysis/electrodialysis reversal (ED/EDR) represents 3% of all the desalination capacity in the world [48]. It is, however, used mainly for desalinating brackish water. It can achieve 95% water recovery with minimal chemical feed. However, it can only reject ionised matter. Substances such as colloids, silica and boron at $\mathrm{pH} < 8.0$ are not removed. A triple-membrane system using UF-EDR-RO has been very effective in producing purified water for power plants [50]. In this integrated system, UF is used for removing suspended solids and macromolecules;

EDR removes bulk of dissolved ions; and RO removes the remaining dissolved ions, silica and the smallest organics.

- Energy consumption of SWRO plants operating at 40–45% product water recovery and with energy recovery currently is about 3–4 kWh/m^3. There is a major emphasis in the desalting community to reduce the energy consumption to <2.0 kWh/m^3 and make the process less expensive.

The salient features of SWRO and brackish water RO (BWRO) desalination processes that determine plant design and influence capital and operating costs are summarised below. Several RO desalination plant case studies are subsequently discussed to illustrate systems design and operation.

1. Feed pressure: 50–80 bar g for SWRO vs. 20–30 bar g for BWRO.
2. Feed water TDS: Seawater = 33,000–45,000 mg/l; brackish water = 1000–10,000.
3. Feed water quality: Seawater – fairly consistent; brackish water – variable (Table 3.4).
4. Feed water treatment: Relatively simple for SWRO because of low water recovery, high ionic strength and low concentration of bicarbonate ions. High boron concentration can be an issue. Pre-treatment is elaborate for biologically active seawaters such as the Arabian Gulf region. For BWRO, relatively complex because feed water quality is site-specific. Seawater intake type has a major impact on pre-treatment requirements and cost.
5. Product water recovery: 35–50% in the case of SWRO vs. 65–80% for BWRO. Permeate flux: 10–12 l/m^2/h in the case of SWRO vs. 17–20 l/m^2/h for BWRO.
6. Product water TDS: 300 ppm (33,000 ppm seawater) vs. <80 ppm (2500 ppm brackish water). SWRO membrane salt rejection >99.7%.
7. SWRO product water specifications: TDS < 400 mg/l; chloride level <100 mg/l; and WHO standard boron level of <0.5 mg/l. Meeting the WHO boron standard requires additional treatment. The boron concentration in seawater is 3–5 mg/l.
8. Membrane array design: Usually one-pass, single-stage for SWRO because of low recovery vs. typically single-pass, two-stage for BWRO [3,51].
9. Ancillary equipment: Energy recovery for SWRO for systems larger than 40 m^3/h product water capacity; reduces energy consumption by more than 40%. Energy recovery is not economical unless the reject pressure is >20 bar g and product water recovery is <80%.
10. Critical parts material: High corrosion-resistant duplex stainless steel for high-pressure SWRO plant parts.

Overall, membrane desalination costs have dropped due to the development of high rejection and high productivity membranes (development of a chlorine-resistant polyamide membrane is needed), improved process controls, and lower energy consumption. Higher productivity elements consisting of higher surface area and denser membrane packing yield higher quantities of product water. Additional cost savings are possible with newer RO feed water pre-treatment processes; for example, by replacing conventional pre-treatment with UF/MF membrane filtration, developing more efficient RO pumps

Table 3.4 Composition of representative brackish waters in the US and seawater

Item/ion[a]	WM[c]	CL[d]	TUL[e]	FM[f]	RG[g]	OC[h]	SW[i]
Cations							
Calcium	204	129	420	299	163	140	400
Magnesium	91.7	89	163	36	51	10	1252
Potassium	8	–	2.3	–	–	35	–
Sodium	804	521	114	216	292	300	10,561
Strontium	3.1	–	–	–	–	–	–
Anions							
Bicarbonate	433	161	270	334	275	275	140
Boron	–	2.8	0.14	–	0.23	0.8	4
Chloride	1090	262	170	87	492	350	18,980
Fluoride	–	–	–	–	0.08	0.8	1.4
Nitrate	–	–	10	25	1.5	1.0	1.5
Phosphate	0.13	–	–	–	–	1.0	–
Sulphate	902	1260	1370	960	336	350	2650
Other						–	–
Silica (SiO$_2$)	32	49	22	–	35	10	–
Iron	0.35	1.2	–	0.02	0.03	0.3	1.4
Manganese	0.48	–	0	–	0.03	0.1	4
pH	7.95	7.7	7.2	7.4	8.1	8.0	7.8
TDS	3628	2478	2410	1880	1611	1400	33,990
Alkalinity[b]	355	133	221	274	226	226	115
Hardness[b]	850	692	1750	898	616	391	6133

[a] Ion as mg/l.
[b] Ion as CaCO$_3$.
[c] Welton-Mohawk, Arizona.
[d] Coalinga, California.
[e] Tularosa, New Mexico.
[f] Fort Morgan, Colorado.
[g] Rio Grande, Texas.
[h] Orange County, California.
[i] Seawater.
Source: Cabibbo et al.

and higher efficiency energy recovery devices, and employing novel plant design configurations [3,52]. Although the Capex of membrane filtration is 20–30% higher than conventional pre-treatment, it produces guaranteed higher quality (less fouling) RO feed water including SDI <3, turbidity <0.1 NTU and high retention/rejection of microorganisms (bacteria and algae), thereby ensuring lower operating and maintenance costs.

Creative engineering solutions have also contributed to the increased viability of seawater desalination. Where possible, SWRO plants are being located in less saline (10,000–20,000 ppm) bays that are fed by significant fresh surface water run-off or near river estuaries. Lower salinity source allows for operation at lower feed pressure reducing energy consumption and higher recoveries. In turn, this reduces the size of the pre-treatment equipment and lowers plant capital costs. The London desalination plant shown in Figure 5.5 draws water from the Thames River estuary and operates at 75% recovery.

3.2.1 Seawater RO desalination

Water shortages around the world have provided an impetus for the construction of many large SWRO desalination plants since 2000. Some of the recent large SWRO plants include Ashkelon, Israel (325,000 m^3/d); Fujairah, UAE (170,000 m^3/d); Perth, Australia (140,000 m^3/d); Tuas, Singapore (136,000 m^3/d); Carboneras, Spain (120,000 m^3/d) Point Lisas, Trinidad (115,000 m^3/d), Tampa Bay, USA (95,000 m^3/d) and Hamma, Algeria (200,000 m^3/d) [3,46,52]. The plant in Perth is the largest desalting plant powered by renewable (wind) energy. The world's largest SWRO desalination plant (540,000 m^3/d) in Sorek, Israel was commissioned in 2013. It is the first large desalination plant using 40 cm diameter spiral-wound elements, which are vertically mounted. Specifications of several large plants are detailed in Table 3.5 [53,54]. Seawater desalting costs are now in the range of \$0.5–0.8/m^3. However, both the capital cost and energy consumption of SWRO plants are still high, and further work is needed to expand the application and make the process affordable [46,55].

The minimum amount of energy (theoretical minimum energy) required to separate pure water from saline water is independent of the desalination technology. The theoretical minimum energy for SWRO for 35,000 mg/l TDS seawater and at a recovery of 50% is 1.06 kWh/m^3 (as the salinity of feed water or water recovery increases, so does the minimum energy required for desalination). The actual energy consumption, however, is higher because desalination plants are finite in size and do not operate as a reversible thermodynamic process [46]. Additional energy – >1 kWh/m^3 – is consumed by the intake, pre-treatment, post-treatment, and brine discharge stages of the desalination plant. Hence, it is quite unlikely that the actual energy of a SWRO plant can drop below 2.2 kWh/m^3. If it is achieved, it would be a major improvement over the current value of 3–4 kWh/m^3 but still more than double the theoretical minimum value. Various aspects of energy consumption and costs of membrane plants are discussed in Chapter 5.

Dual-purpose plants

One option for reducing energy consumption is to use integrated systems, e.g., a thermal desalination system coupled with a single-stage SWRO system. The rationale for developing integrated energy-water systems is to reduce capital cost, energy consumption and the cost of desalinating seawater since nearly 70% of a SWRO plant operating cost is due to energy consumption. Further, by blending higher total dissolved solids RO product water (200–400 ppm) with thermal distillate (25 ppm), water production can be more economical for potable water production.

Table 3.5 Specifications of several large seawater RO desalination plants

Item	Fukuoka – Japan	Sydney Water – Australia	Hadera – Israel	Sorek – Israel
Total capacity	50,000 m^3/d	250,000 m^3/d	347,942 m^3/d	540,000 m^3/d
Feed water TDS	35,000 mg/l	41,000 mg/l	40,700 mg/l	40,800 mg/l
Product water TDS	350 mg/l first-pass 200 mg/l second-pass	115 mg/l	300 mg/l	300 mg/l; 20 mg/l Cl
Product recovery	60%	45%	41%	∼45%
Feed water temperature	12–30°C	16–24°C	15–30°C	27°C
RO membrane array	Partial second pass for boron removal	2-pass	2-stage, partial 2-pass	4-stage, partial 2-pass
2nd-pass design	Similar	Similar	Similar	Similar
Membrane module	Hollow-fibre HPRO[a], Toyobo; 20 cm spiral-wound LPRO[a]	20 cm dia spiral-wound Dow/Film-Tec	20 cm diameter spiral-wound Dow/Film-Tec	40 cm diameter spiral-wound, Dow/Film-Tec; Hydranautics spiral-wound
Membrane polymer	Cellulose triacetate	TFC polyamide	TFC polyamide	TFC polyamide
Operating pressure	82 bar g first pass; 15 bar g second pass	60 bar g at 16°C	69 bar g	–
Energy consumption	–	3.25 kWh/m^3	4.0 kWh/m^3	<4.0 kWh/m^3
Energy recovery device	–	Calder DWEER	ERI PX	Calder DWEER
Seawater intake	Infiltration intake	2.5 km tunnel, velocity cap	Submerged open sea	Submerged open sea
Pre-treatment system	Ultrafiltration, acid	DAF, acid, ferric chloride coagulant, polymer, 2-stage dual media filtration	Acid, ferric chloride coagulant, polymer, dual media filtration	Ferric chloride coagulant, dual media filtration
Post-treatment system	Lime remineralisation, NaOH pH adjustment, NaOCl chlorination	Lime stabilisation	Lime stabilisation, CO_2, pH adjustment	Lime stabilisation
Brine disposal	Ocean	2.5 km tunnel with multi-port diffusers	Blended with power plant cooling water, discharged to sea	Multiport diffusers
Capital cost	–	$933 million	$425 million	$600 million
Water cost	–	–	$0.63/$m^3$	$0.585/$m^3$
Start-up date	January 2006	April 2010	May 2010	August 2013

[a] HPRO: high-pressure RO; LPRO: low-pressure RO.

Source: Based on [53,54].

An attractive option is co-location of SWRO plants with conventional power plants for utilising power plant waste heat and using the power plant cooling water as the SWRO plant feed water [46,55]. A co-located SWRO plant draws heated seawater from the cooling water loop for its feed supply and then discharges the concentrate stream back into the cooling water loop at a point downstream of the feed withdrawal point [55]. Membrane productivity increases with feed water temperature, albeit at a slight penalty in product water quality. Warmer temperature results in reduced RO feed pressure and concomitant power consumption [40]. An increase in permeate flux of up to 60% was reported when feed water temperature was increased from 20 to 40°C, possibly due to changes in membrane morphology and higher solvent flow as discussed in Chapter 5. However, in the 30–40°C range, higher membrane permeability is adversely affected by higher osmotic pressure and higher salt passage, as shown in Figure 1.11.

The advantages of colocation are as follows [55]:

1. Reduced RO feed pressure because warmer water is less viscous resulting in lower operating costs.
2. Use of the existing power plant ocean intake and outfall structures, thus precluding the need to construct separate such infrastructure for the SWRO plant and saving a substantial portion of the desalting plant capital cost.
3. Dilution of the SWRO concentrate stream prior to ocean discharge, which resolves a key ecological concern. Although the RO reject TDS (~70,000 ppm) is at least twice that of feed TDS, the return cooling water flow is one to two orders of magnitude greater than the concentrate flow, thus diluting the concentrate to near seawater levels as illustrated below. By comparison, without the utilisation of the cooling water dilution, the salinity of the concentrate discharge would be twice the ambient salinity.

A 0.19 M m^3/d SWRO plant operating at 50% recovery draws 0.38 M m^3/d feed (35,000 ppm TDS) from the power plant cooling loop and discharges the concentrated brine (70,000 ppm TDS) stream at 0.19 M m^3/d. If the cooling water intake is 5.7 M m^3/d, the ultimate ocean discharge is 5.51 M m^3/d of seawater at ~36,200 ppm TDS based on blending of 0.19 M m^3/d of RO brine concentrate [55]. Thus, the discharged salinity is only 3.5% higher than ambient salinity.

A few potential limitations of colocation are: (a) the power plant must provide more cooling water than the SWRO plant can process, (b) RO membranes can be fouled by iron, copper, or nickel in cooling water and (c) the RO feed water must be cooled if the temperature is >35°C.

Energy recovery

In SWRO plants large flow rates of concentrated brine (50–60% of feed) are discharged at high pressure. This pressure energy recovery from the high-pressure brine stream is critical to the economic viability of the RO desalination process. One of the first major studies addressing energy recovery was reported in 1969. Subsequently, a major feasibility study on energy recovery at SWRO and BWRO plants was done in 1980 [56]. Typically, in the case of SWRO plants 25–40% of energy can be recovered depending on the type of recovery device used [55,57,58]. One of the energy recovery devices in use is the Pelton Wheel turbine, which transforms potential energy in the brine stream to high-pressure RO pump shaft power, as shown in Figure 3.30a. The advantage of the Pelton wheel is the flat efficiency curve in a wide range of concentrate flows. One of the largest Pelton Wheel systems in the world is installed at the Point Lisas plant in Trinidad. These turbines achieve efficiencies of 88–90%. A more recent energy recovery type is the isobaric chamber device or pressure exchanger, which facilitates the exchange of energy in the brine stream directly to the incoming seawater, as shown in Figure 3.30b. Since the

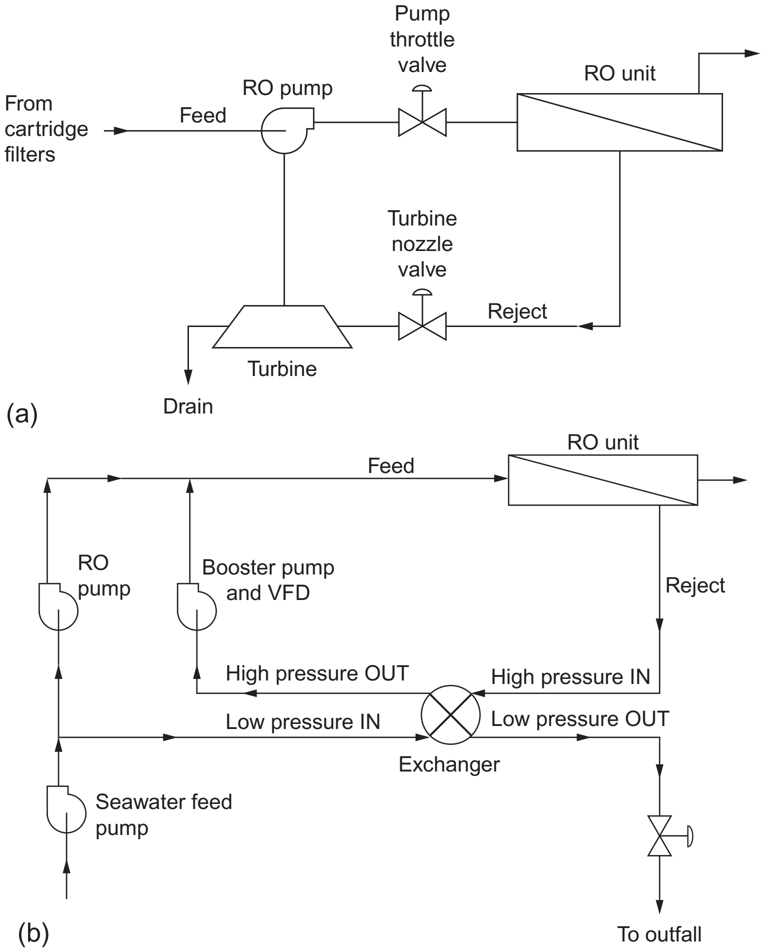


Figure 3.30 (a) A hydraulic turbine energy recovery system. (b) A pressure exchanger isobaric chamber energy recovery system. *Source: [40].*

pressure exchangers are positive displacement devices (direct energy transfer), high energy recovery efficiencies of 94–96% are achievable. The pressure exchanger system can maintain these high efficiencies independent of the operating conditions that need to be adjusted with time to maintain the same product water recovery. However, there is one drawback; because of mixing of feed and brine, the RO feed water TDS increases by 4–6% [51].

Seawater intake

Besides marine life, seawater contains particulate and colloidal matter as well as biological contaminants and some hydrocarbons that require filtration to prevent fouling of RO membranes by particulate matter. Seawater RO plants use beach wells (bore holes) or open intake surface water. The main difference between the two is the quality of raw water that flows to the RO plant. Water obtained from beach wells gets filtered through porous media and most of the organic matter is removed. Since beach well water is of better quality, both the pre-treatment requirement and operating costs are reduced. Unfortunately, beach wells have limited capacity and cannot provide enough water for large plants. Most large SWRO plants, therefore, use open seawater intakes [52].

Alternate SWRO system designs

Although single-pass, single-stage RO systems have been the workhorse of SWRO plants, several large plants have deployed variations of two-pass designs as detailed in Table 3.5. Various multi-pass design options are possible. The simplest design consists of a two-pass system, where the first pass is a high-pressure SWRO membrane array and the second pass is a low-pressure RO "polishing" step (see Figure 2.21). The first RO pass typically operates at a 35–45% recovery, while the second pass can operate at recoveries > 80%. The seawater RO plant in Fujairah, Saudi Arabia operates with a similar setup, except the second-RO pass is split into two RO units in series; the reject from the second set two passes is recycled back to the RO feed stream, and the overall recovery of the RO system is 41%. The feed water contains 38,000–38,500 mg/l TDS, and the resulting permeate TDS is 75–120 mg/l [3].

Another type of two-pass SWRO system takes advantage of the variation in permeate TDS along a membrane element and the pressure vessel. Typically, a pressure vessel houses 6–7 elements in series. As the permeate passes through the membranes, the remaining feed water or concentrate becomes more concentrated. As the feed/concentrate TDS increases, the salt passage through the membrane increases, thus increasing the permeate salinity. Therefore, the permeate produced in the first membrane element has a lower salinity than the permeate produced in the last (reject exit) membrane element. The alternate two-pass design takes a portion of the higher-salinity permeate as the feed to the second pass, while the lower-salinity permeate is collected directly as product water [3,51]. The Tampa Bay, Florida RO plant takes advantage of this alternate two-pass design; the overall energy consumption of the RO system is lower because only a portion of the first-pass permeate is pumped to the second pass.

More complex multi-pass SWRO systems include the system used in Ashkelon, Israel, which uses four RO passes in series to treat seawater from an open water intake in the Mediterranean Sea (40,700 mg/l TDS). The permeate must be produced with less than 0.4 mg/l boron and 20 mg/l chloride. Thus, a series of passes with changes in pH was necessary to obtain the required permeate water quality. The first pass has a recovery of 45% and is operated at neutral pH. Permeate from the feed end is collected as product, while permeate from the concentrate end is collected and flows to the second pass, which operates at 85% recovery and $\mathrm{pH} > 8.5$ to achieve greater boron removal. The concentrate from the second pass continues to the third stage, also operated at 85%, but at low pH. The objective of the third pass is to achieve higher recovery without salt precipitation. However, the boron removal in the third pass is minimal at low pH, and a fourth pass (high pH, 90% recovery) treats the third pass permeate for boron removal. Overall, the recovery is approximately 44%, and the plant uses 25,600 SWRO membranes and 15,100 BWRO membranes [3,51].

One design for increasing recovery is sequencing of RO/NF membrane elements in the pressure vessel, which typically contains six membrane elements. The salt concentration and the osmotic pressure in the last membrane element (#6) is greater than in the first element (#1) and, hence, the flux is the lowest based on the well-known equation (see Chapter 1):

$$J_{\mathrm{w}} = A(\Delta P - \Delta\pi).$$

The modified design involves using elements of different rejection and productivity characteristics; for example, high rejection SWRO elements (#1–4), a low rejection BWRO element (#5) and a NF element (#6) with the last two elements rated for higher productivity.

Case studies – Several examples of small and large SWRO plants are described below

Case study I. The process flow diagram of a small SWRO plant is shown in Figure 3.31. The plant design is typical of a SWRO plant. The operating conditions are as follows:

- Feed water flow rate: 2200 $\mathrm{m^3/d}$ at 70 bar g
- Permeate flow rate: 1000 $\mathrm{m^3/d}$
- Product water recovery: 45%
- Feed water TDS: 38,000 mg/l
- Product water TDS: 325 mg/l at >99% salt rejection
- Energy consumption: 5.8–6.0 $\mathrm{kWh/m^3}$ (small plant value)

The feed water source is a seawater infiltration well located in porous volcanic rock about 100 m from the shoreline. The well is dosed with sodium bisulphite (SBS) for disinfection

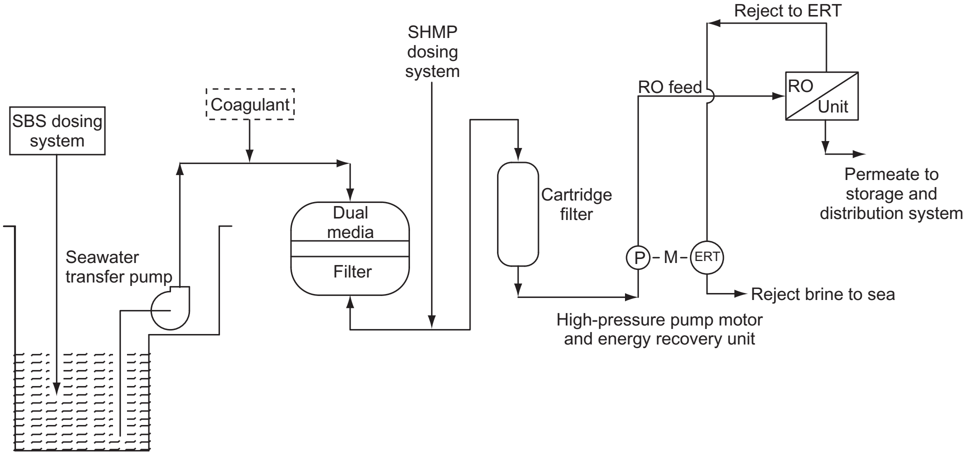


Figure 3.31 Process flow diagram of a seawater RO membrane plant integrated with a hydraulic energy recovery turbine. *Source: Desalination 82 (1991) 31.*

(30–40 ppm), and seawater is transferred from the well to three media filters operating in parallel (one filter on standby) by two centrifugal pumps. Sodium hexametaphosphate (SHMP) anti-scalant is injected upstream of the 5.0 μm cartridge filter in the media filters effluent to prevent precipitation of magnesium sulphate. The SHMP dosage is based on a 5–10 ppm level in the RO feed water. Coagulant dosage upstream of the sand filters is 1–2 ppm, if required. The Silt Density Index (SDI) values, an indicator of colloidal fouling, were consistently in the range of 0.5–1.0, indicating the feed water is very clean because it coming from a beach well.

The RO feed water is transferred by the high-pressure pumps (one pump is in operation, and the other is on standby) to the RO membrane unit. The high-pressure, multistage submersible centrifugal pump is connected to an energy recovery turbine (ERT). The pump-motor-turbine-set enables the recovery of energy from the high-pressure brine reject stream. The high-pressure brine drives the turbine (reverse-running pump) mounted on a common shaft with the electric motor and the RO high-pressure pump. The high-pressure feed seawater is piped to the RO vessel rack. The membrane unit is a two-stage array (12:6): stage 1 consists of 12 pressure vessels in parallel and stage 2 contains 6 pressure vessels also in parallel. Brine from the first stage pressure vessels is collected in an intermediate manifold and flows to the second-stage pressure vessels. The reject from the second stage is piped to the ERT from which it discharges to an outfall in the sea.

Each pressure vessel contains six polyamide TFC seawater (Dow/Film-Tec 30) spiral-wound elements, 20 cm diameter × 100 cm long, producing 1000 m^3/d. The feed water TDS is about 38,000 mg/l. Since 45% is recovered as product water, the TDS of the RO reject is 69,000 mg/l, and the osmotic pressure of the reject brine stream is nearly 54 bar.

This means the effective driving force at the end of the RO unit is only 16 bar, since the feed pressure is ~70 bar.

Case study II. The process and instrumentation diagram (P&ID) of a SWRO system is shown in Figures 3.32 and 3.33. The one-pass RO unit is a single-stage array (6:0) consisting of six parallel pressure vessels with each pressure vessel containing six spiral-wound TFC membrane elements connected in series. The permeate flows to the product water storage tank. High-pressure reject flows to the hydraulic ERT before it flows back to the sea. The ERT transfers the recovered energy to the high-pressure RO pump. The system design conditions are as follows:

- Feed water flow rate: 1400 m^3/d at 75 bar g
- Permeate flow rate: 490 m^3/d
- Product water recovery: 35%
- Reject flow and pressure: 910 m^3/d at 72 bar g
- Feed water TDS: 30,000 mg/l
- Product water TDS: 300 mg/l at >99% salt rejection

The feed water pre-treatment for this SWRO plant in the Mediterranean is minimal: multimedia filtration for removing particulate matter larger than 20.0 μm, acid injection for reducing pH to less than 6.0 to prevent calcium carbonate scaling, sodium metabisulphite injection for dechlorination, and 5.0 μm cartridge filtration for protecting the RO modules from particulate fouling. Cartridge filter is a standard feature for all RO systems. Post-treatment includes a product water drawback tank to protect the membranes when the system is not in operation and addition of lime solution to the product water for raising the pH to 7.5–8.0 to prevent corrosion of downstream piping and equipment since the pH of the permeate is typically ~5.5–6.5.

Case study III. Fukuoka SWRO is the largest desalination plant in Japan with a capacity of 50,000 m^3/d. It was commissioned in 2005–2006. The plant specifications and operating conditions are given in Table 3.5 [53,54]. The plant is of special interest because of its various different design features and performance [59]:

- A large seabed filter intake system with a maximum capacity of 103,000 m^3/d. The seabed filter reduces the SDI to <2.5.
- SWRO product water recovery is ~60%, the highest in the world.
- Hollow-fibre cellulose triacetate (CTA) seawater RO membranes (HOLLOSEP HB10255FI). Virtually all desalination plants use spiral-wound thin-film composite polyamide (PA) membranes/elements. Hollow-fibre RO membranes are only supplied by Toyobo (the largest SWRO plant using CTA hollow-fibre membranes is in Rabigh, Saudi Arabia, capacity = 205,000 m^3/d).

High product water recovery was achieved with Toyobo's advanced modules design and with high permeability CTA membranes. Further, CTA membranes are tolerant to residual chlorine in feed water up to 5 ppm compared to 2 ppm for cellulose acetate (CA) and <0.1 ppm for PA membranes [59]. This prevents biofouling, which is a major advantage.

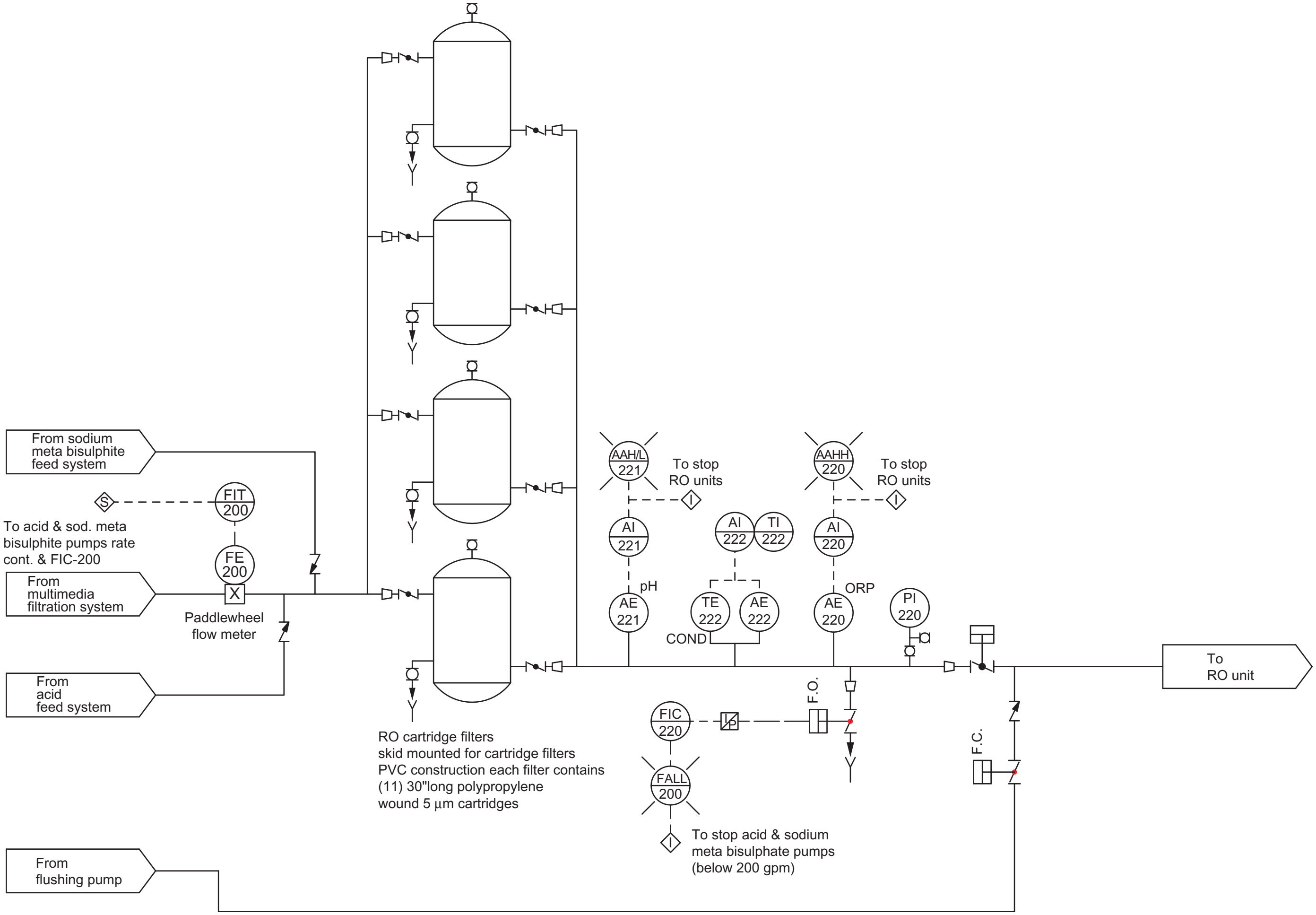


Figure 3.32 A P&ID of a dead-end cartridge microfiltration pre-treatment system for a seawater RO plant.

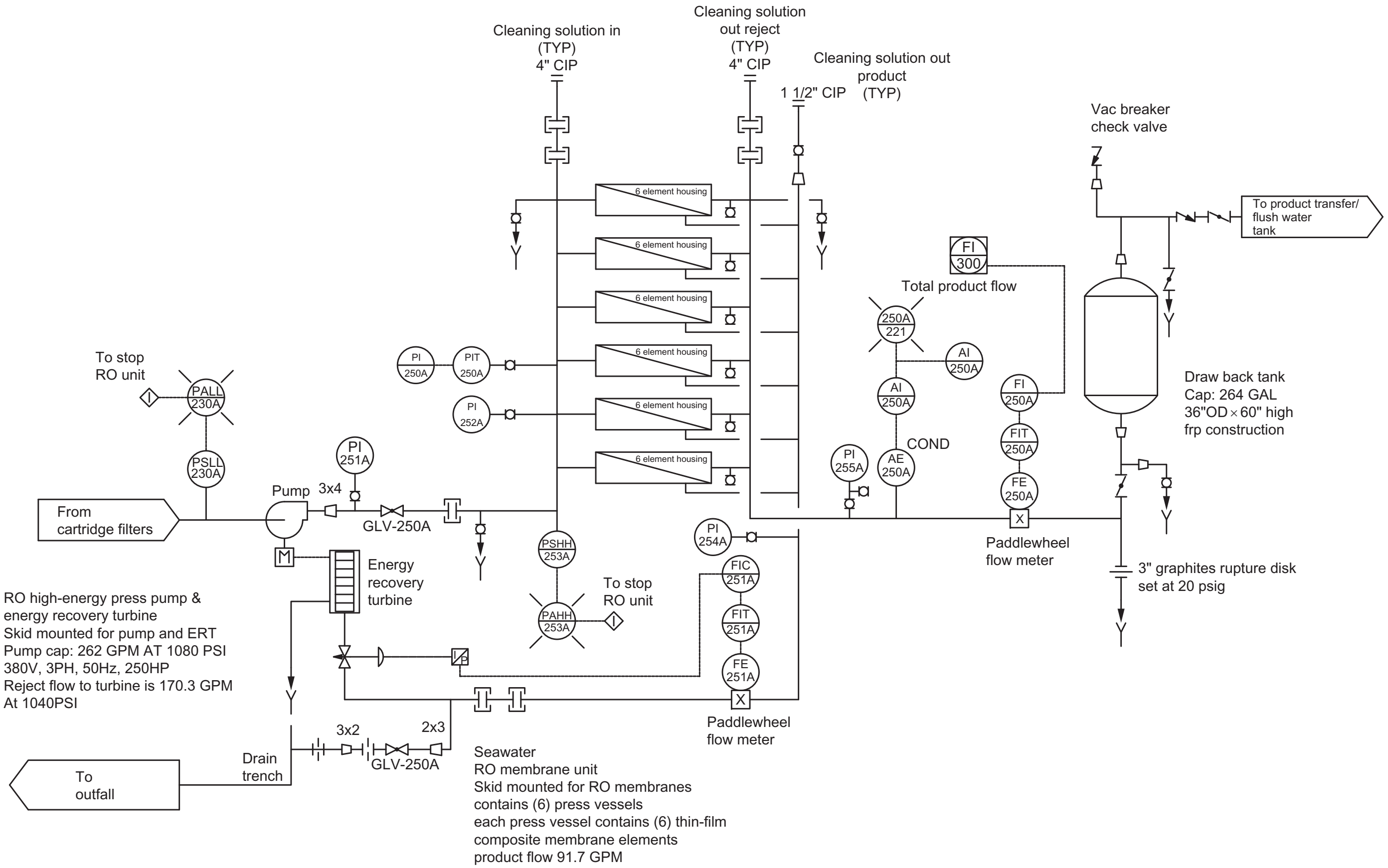


Figure 3.33 A P&ID of a seawater RO single-stage membrane system.

In general, CA/CTA membranes are also less prone to fouling because they are more hydrophilic and less hydrophobic than PA membranes, and the membrane surface is not rough (e.g. see Table 2.10).

The Fukuoka plant uses UF membranes for pre-treatment. The RO system consists of a high-pressure SWRO section and a low-pressure RO (LPRO) section. The LPRO system is the second-pass RO unit that treats SWRO permeate (see Figure 2.21b) when required; for example, to reduce boron in RO product water. The LPRO membranes are spiral-wound. The SWRO system has five units, each with a capacity of 11,988 m^3/d. SWRO feed water is treated with acid to lower the LSI value and prevent carbonate scaling. The LPRO pH is raised to >9.0 with caustic soda to enhance boron rejection; at $pH > 9.0$ boron is ionised resulting in much higher rejection.

Case study IV. The Gold Coast (Queensland) SWRO desalination plant was commissioned in 2008–2009 to supply up to 27% of the average demand for the Brisbane/Gold Coast region, which had been facing severe drought conditions. The plant built at a cost of $1.06B has a capacity of 125,000 m^3/d [60]. The seawater TDS range is 34,000–39,000 mg/l, $TSS = 10 \pm 5$, turbidity = 8 NTU, boron concentration = 5 mg/l, and design temperature range, 17–28°C. Higher salinity and temperature are experienced during warmer months. The SDI is 20 ± 10.

Seawater supply is from an intake 20 m below the water surface, about 1.5 km offshore and 2.2 km from the RO plant. The supply tunnel is about 70 m below the ground surface. The pre-treatment train includes chlorination, polyelectrolyte and ferrous sulphate coagulation/flocculation, acid dosage, dual-media filtration, anti-scalant addition, acid, cartridge filtration and sodium metabisulphite (e.g. see Figures 3.31 and 3.32]. The RO system is a two-pass unit. Post-treatment includes CO_2 and lime treatment and chlorination with sodium hypochlorite. The desalinated product water TDS is ~220 mg/l with maximum boron concentration of 1 mg/l.

The RO system consists of nine first-pass and three second-pass skids. The RO membranes are 20 cm spiral-wound TFC polyoxide type. The membrane pressure vessels have side-entry front/rear permeate ports. The high-pressure first-pass SWRO unit is supplied by a multi-pump system (three on-line, one on-standby). The SWRO feed pressure is 60 bar g TDH (total delivery head). The second-pass RO unit treats the first-pass permeate and, therefore, operates at much lower feed pressure. The SWRO unit deploys dual work exchanger energy recovery devices. The plant is among the most energy efficient in the world, with an average efficiency of 3.58 kWh/m^3. The ERDs recover about 97% of the energy required to convert seawater to product permeate.

In 2009 the plant was named Global Membrane Desalination Plant of the Year by Global Water Intelligence. Since December 2010 the plant has operated intermittently, depending on the changing water needs and drought conditions; for example, during the 2012–2013 floods it operated at full capacity to meet critical drinking water needs in some Brisbane suburbs.

3.2.2 Brackish water RO desalination

Brackish water RO (BWRO) plants tend to be smaller in production capacity than seawater RO plants, but a greater number of BW RO plants (48% of the total number of plants) are in operation worldwide than SWRO plants (25%) [3]. The feed water is either groundwater or surface water. Many plants produce between 500 and 10,000 m^3/d of RO product water. The production range of BWRO plants in the US is 200–76,000 m^3/d, and the range of feed water TDS is 500–8500 mg/l. More than 1200 desalination plants operate in the United States, which has 16% of the world's desalination capacity [48]. Most of the brackish desalination plants (80%) in the US use RO technology. The remaining are divided between ED and NF. Ninety-six percent of the more than 300 municipal desalination plants in the US are located inland. The BWRO plants are typically single-pass and two-stage.

The largest brackish water RO (BWRO) plant in the US (Yuma, Arizona) was built in 1991 and operated in 1992. Although it has been on "ready reserve" since 1993, it was operated again in spring 2007 for 90 days successfully. The 270,000 m^3/d BWRO plant is designed to treat agricultural drainage water and divert the RO product water to the Colorado River to lower the river's salinity before it flows to Mexico [61]. The plant was reactivated in May 2010 to launch a 1-year pilot run. The RO plant consists of 9360 CA membrane elements as follows: approximately two-thirds of the spiral-wound elements are Koch (Fluid Systems), 30 cm diameter × 150 cm long with a surface area of 117 m^2, and one-third are Hydranautics, 20 cm diameter × 100 cm long with a surface area of 33 m^2.

Most brackish water RO plants require extensive pre-treatment as discussed in Chapter 2. Feed water quality of brackish waters in the US southwest is given in Table 3.4. The intensity of pre-treatment depends on the quality of feed water as detailed in Table 3.6. Feed water constituents that affect pre-treatment design are summarised below [62,63]:

1. Ground waters usually have very low SDI values, and cartridge filtration is a generally sufficient pre-treatment. Cartridge filters of 5.0–10.0 μm nominal pore size are typically used. Increasingly, cross-flow MF and UF is being used. Surface waters may have SDI as high as 200 requiring more rigorous pre-treatment. A rough guide is that waters with SDI less than six can be passed through deep-bed media filters. SDI values in the 6–50 range require coagulation with cationic polyelectrolytes, followed by clarification. Coagulation with aluminium sulphate (alum) or ferric salts, followed by sedimentation and media filtration, is suitable pre-treatment when SDI is greater than 50.
2. The fouling tendency of colloids can be reduced in some instances by increasing their zeta potential, thus reducing their tendency to adhere to surfaces as discussed in Chapter 2. Methods used to achieve this include softening the feed water by IX, NF and/or dosing the feed with a polymeric dispersant.
3. The most common precipitates encountered in brackish water desalination are calcium and magnesium carbonate, sulphates of calcium, barium, and strontium,

Table 3.6 Pre-treatment options for brackish water desalting plants[a]

Feed water/product water recovery	Reverse osmosis (RO)	Electrodialysis (ED)
Tularosa, NM	Ion exchange, acid, SHMP	Ion exchange
70%	Lime, soda ash, SHMP	Lime, soda ash, acid
80%		
Rio Grande, TX	Acid	Acid
70%	Acid, SHMP	Acid
80%		
Fort Morgan, CO	Ion exchange, acid, SHMP	Minimum
70%	Ion exchange, acid, SHMP	Ion exchange, acid
80%		
Coalinga, CA	Acid	Minimum
70%	Acid, SHMP	Minimum
80%		
Welton-Mohawk, AZ	Lime, acid	Lime, acid
70%	Lime, acid	Lime, acid
80%		
Orange County, CA	Acid	Acid
70%	Acid	Acid
80%		

[a] Based on feed water chemical analysis in Table 3.4.

and silica. Well water may have special problems associated with components that are soluble under reducing conditions but form insoluble substances when oxidised by contact with air. Manganese, ferrous salts and hydrogen sulphide fit in this category.

4. Since brackish waters usually contain high levels of calcium, sulphuric acid dosing is commonly used to prevent calcium carbonate precipitation. This increases the potential for calcium sulphate scaling, which may become the limiting factor in determining product water recovery. If the calcium or magnesium concentrations are high, cation exchange or lime-precipitation softening should be employed before acid dosing.
5. Precipitation of sulphates can be prevented by dosing with polyelectrolyte crystallisation inhibitors such as SHMP. Its effect is to hinder the rate of crystallisation, rather than to prevent it altogether. SHMP is almost totally rejected by RO membranes and has little or no effect on the permeate quality. The RO module feed/reject channels must be flushed before shutting the RO system down.
6. Polymers are also used to inhibit calcium carbonate precipitation; for example, Flocon®, Aqua Feed®, Belgard®, and Aquakreen®. Use of these polymers can reduce the need for acid dosing. The advantages over SHMP are that they are more stable against thermal and hydrolytic degradation, making dilution procedures less critical. These advantages are particularly useful in small installations, but the use of such polymers has become established in large plants as well.

7. Silica precipitation is a serious problem. The formation of insoluble silica compounds is not easy to predict accurately, as the solubility is strongly dependent on temperature and pH, as discussed in Chapter 6. Silica compounds, once formed, are difficult to remove – particularly from CA membranes, which are not tolerant to high pH cleaning solutions. Silica, soluble and colloidal, can be removed by the lime-precipitation process, but because of the relative cost and complexity of the process, this is generally avoided if possible.
8. The concentration of ferrous ions that can be tolerated by most membranes depends on the concentration of dissolved oxygen. If dissolved oxygen is less than 0.1 mg/l, brine may contain up to 4 mg/l ferrous ions. If the brine is oxygenated, the iron concentration should be below 0.05 mg/l. Contact with air should be avoided or the water should be aerated followed by filtration or clarification.
9. Well water may contain dissolved hydrogen sulphide. At $\text{pH} \geq 8$, a significant portion of the hydrogen sulphide is present as sulphide ions, which oxidised to elemental sulphur by either oxygen or chlorine. This can be prevented by acidifying the water. Under acid conditions, the hydrogen sulphide passes through the membrane into the product water, which then requires degasification. The release of hydrogen sulphide gas can cause corrosion and environmental problems.

Case studies

Feed water composition of several brackish waters in the southwest United States are given in Table 3.4. This region is drought prone, and with a rapid growth in population, the situation is worsening [3,48]. Membrane pre-treatment options for RO and ED designed plants operating at 70% and 80% water recovery are given in Table 3.6 [64]. The design data show that the pre-treatment required for Rio Grande, Coalinga and Orange County is minimal using in-line acid and anti-scalant dosage, whereas it is elaborate for Tularosa, Fort Morgan, and Welton Mohawk. The data also show that 80% recovery is achievable even in the case of the last three feed waters with well-designed pre-treatment systems. Process flow sheets based for these feed waters are shown in Figures 3.34–3.37. Sample RO performance process flow sheets based on the membrane manufacturer's projections at 70% product water recovery for Welton-Mohawk and Rio Grande are shown in Figure 3.38, illustrative of RO unit design calculations.

The Welton-Mohawk RO unit is a two-stage array (29:15) comprised of 44 pressure vessels. Each pressure vessel contains six polyamide TFC water spiral-wound elements, 20 cm diameter × 100 cm long, producing 3820 m^3/d (~700 gpm) permeate. The membrane (Hydranautics CPA2) average flux is 17.9 $l/m^2/h$ (lmh). The initial operating pressure is 17 bar g. The reject brine flow rate is 1636 m^3/d (~300 gpm). The product water TDS is 90 mg/l and the pH is 4.9 units. The feed water pH is lowered to 6.0 with sulphuric acid to prevent calcium carbonate scaling. An anti-scalant (5–10 ppm) is also

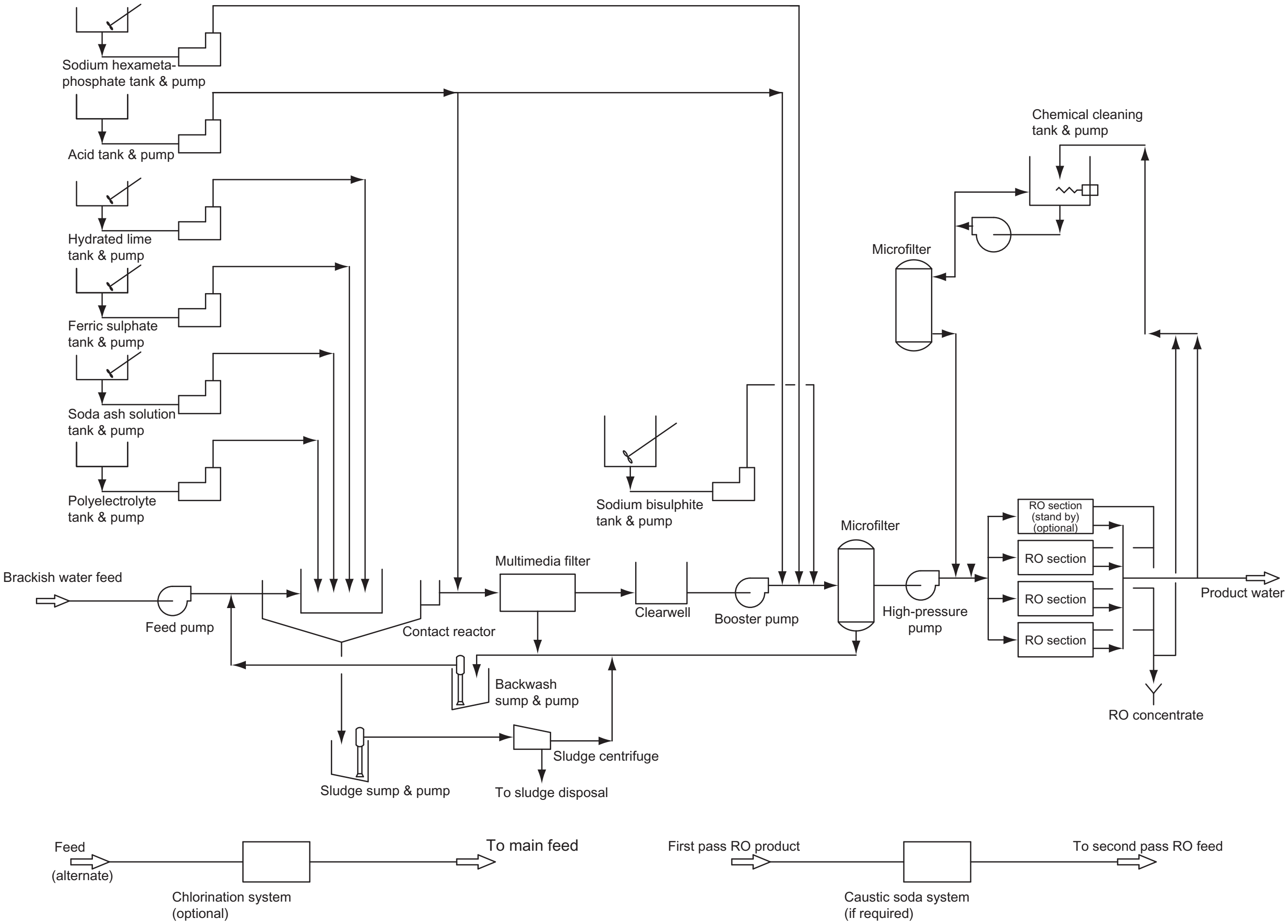


Figure 3.34 Lime pre-treatment system plus a RO membrane brackish water desalination plant process flow sheet. *Source: Cabibbo et al.*

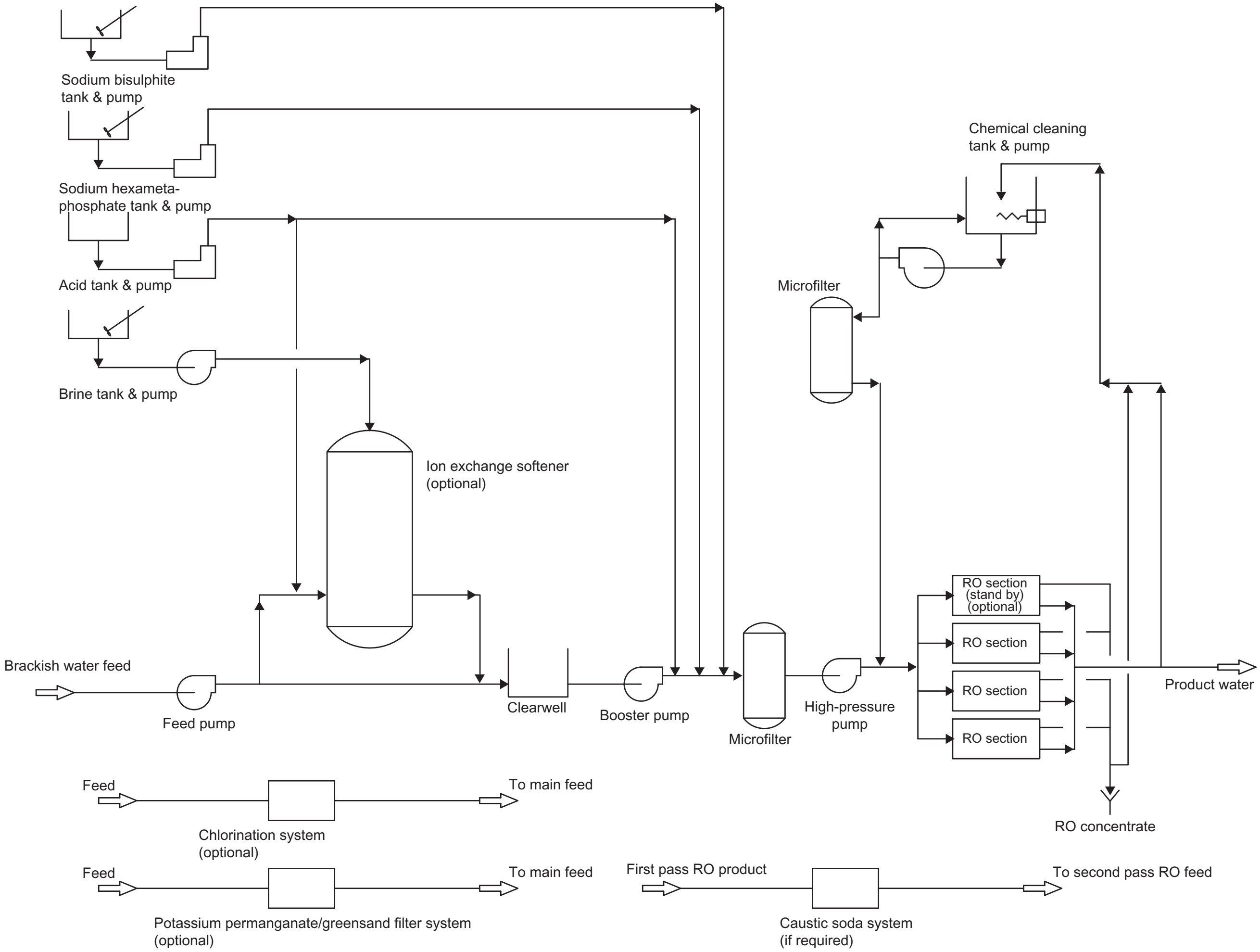


Figure 3.35 Acid pre-treatment system plus a RO membrane brackish water desalination plant process flow sheet. *Source: Cabibbo et al.*

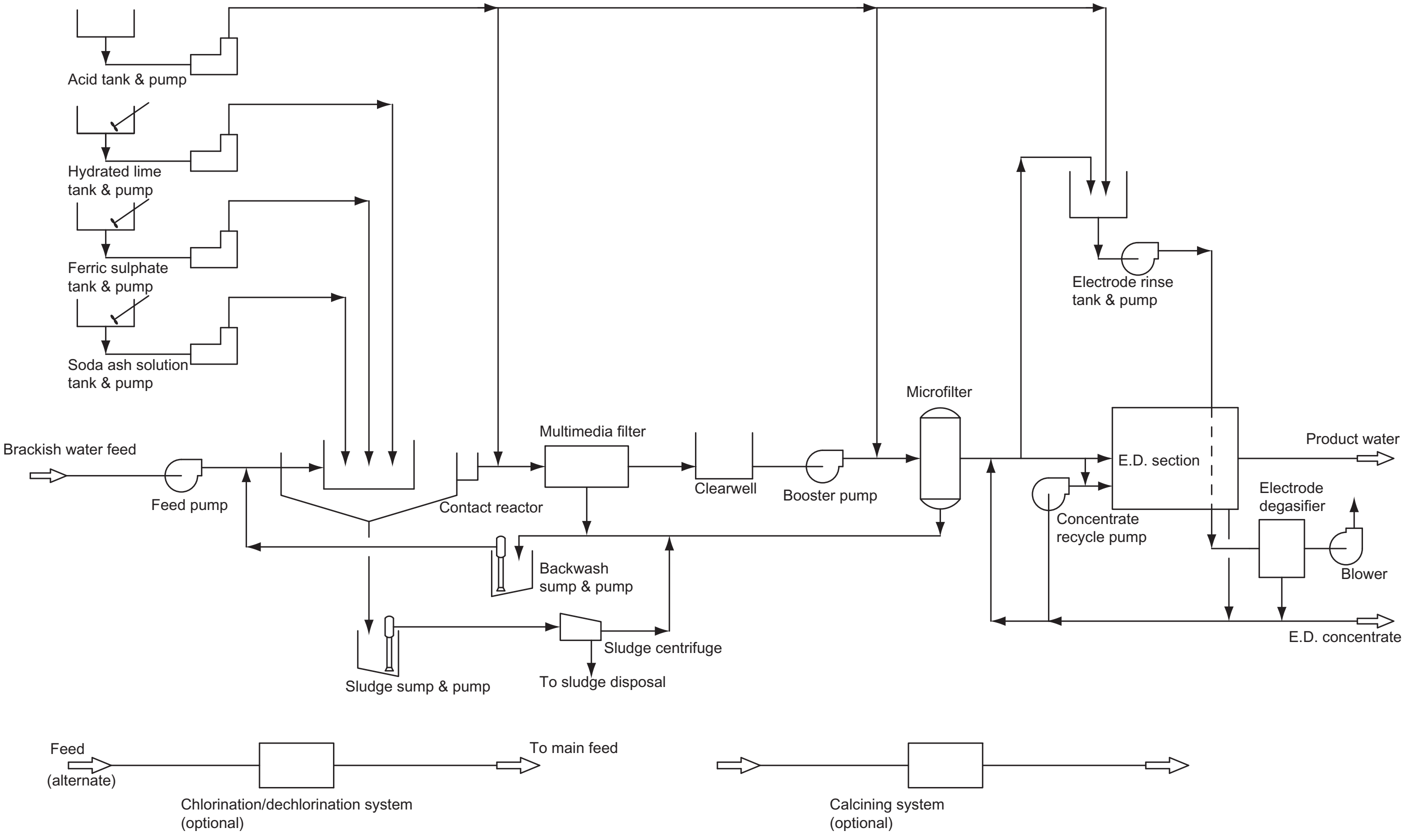


Figure 3.36 Lime pre-treatment system plus an ED membrane brackish water desalination plant process flow sheet. *Source: Cabibbo et al.*

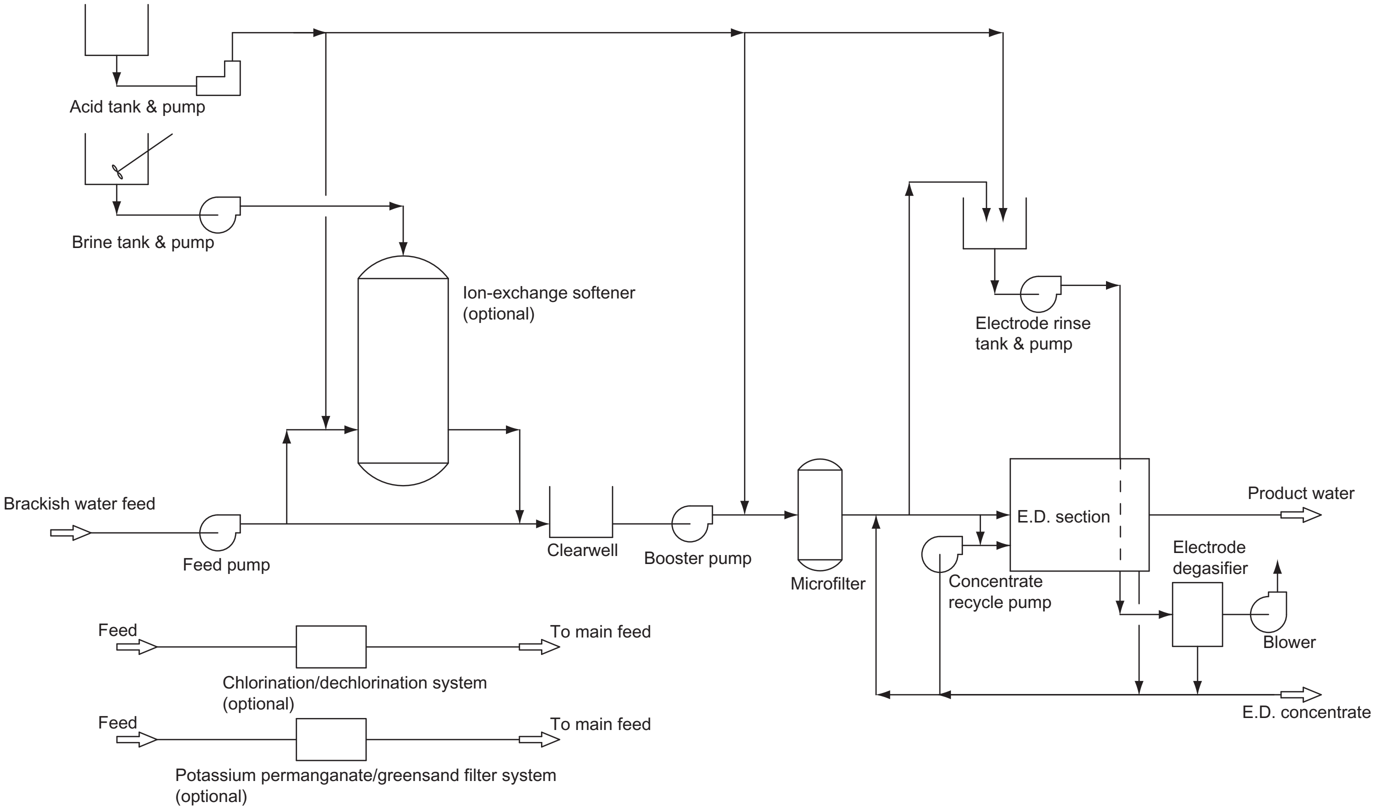
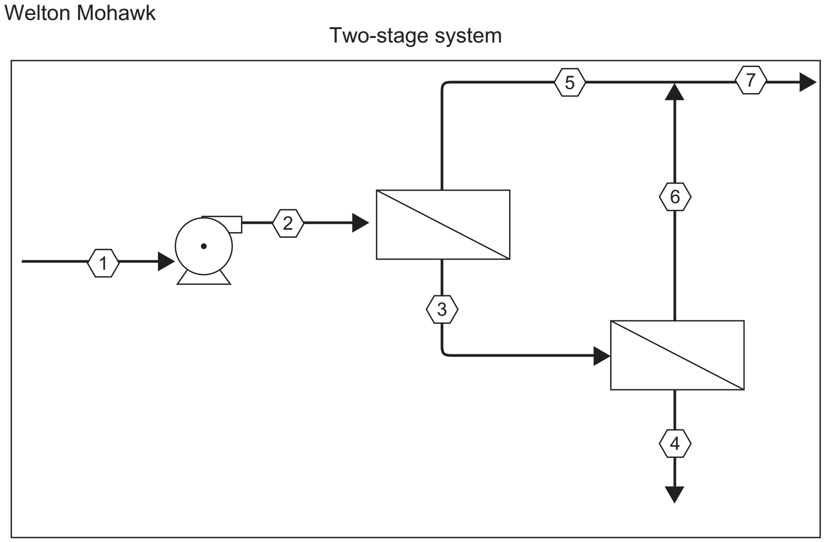
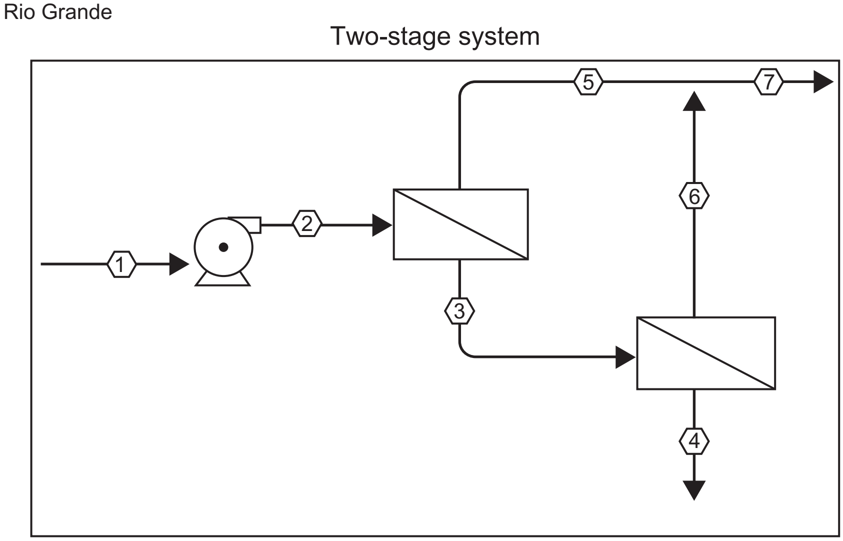


Figure 3.37 Acid pre-treatment system plus an ED membrane brackish water desalination plant process flow sheet. *Source: Cabibbo et al.*



	1	2	3	4	5	6	7
Flow (gpm)	1000.0	1000.0	428.3	300.0	571.7	128.3	700.0
Pressure (psi)	0.0	154.2	140.4	123.8	0.0	0.0	0.0
TDS (ppm)	3728.4	3694.8	8553.8	12105.7	55.2	245.9	90.1

(a)



	1	2	3	4	5	6	7
Flow (gpm)	1000.0	1000.0	386.7	300.0	613.3	86.7	700.0
Pressure (psi)	0.0	73.3	58.2	41.6	0.0	0.0	0.0
TDS (ppm)	1656.5	1622.4	4097.3	5111.9	62.0	586.1	126.9

(b)

Figure 3.38 (a) Process design flow schematic of a brackish water RO membrane system. Welton-Mohawk site. (b) Process design flow schematic of a brackish water RO membrane system. Rio Grande site.

required to prevent calcium sulphate scaling. The product water is remineralised and pH is raised to 7.5 with lime or caustic soda.

The Rio Grande RO unit is a two-stage array (26:14) comprised of 40 pressure vessels. Each pressure vessel contains six polyamide TFC water spiral-wound elements, 20 cm diameter × 100 cm long, producing 3820 m^3/d (~700 gpm) permeate. The membrane (Hydranautics ESPA4) average flux is 17.9 lmh. The initial operating pressure is 14 bar g. The reject brine flow rate is 1636 m^3/d (~300 gpm). The product water TDS is 127 mg/l and the pH is 5.5 units. The product water is remineralised and pH is raised to 7.5 with lime or caustic soda.

3.2.3 Brackish water desalination by electrodialysis

Desalination of brackish water is the largest single application of ED/EDR. It is mainly used in small to medium size plants with capacities 100–20,000 m^3/d with brackish water salinity in the range of 1000–5000 mg/l [65]. For brackish waters with TDS < 5000 mg/l, ED is more economical than RO, as discussed in Chapter 5. Reverse osmosis is considered to have an economic advantage when the TDS is >10,000 mg/l. Other advantages of ED over RO are high water recovery, long useful life of membranes, operation at temperatures up to 50°C, and less susceptible to fouling and scaling due to process reversal (EDR). A comparison of pre-treatment required for six brackish waters in Table 3.6 shows that ED requires less pre-treatment than RO. This is also evident when the pre-treatment options for RO shown in Figures 3.34 and 3.35 are compared with for ED in Figures 3.36 and 3.37. Feed pre-treatment is minimal when EDR instead of ED is used since the reverse polarity operation reduces membrane fouling and scaling.

Since the ED/EDR ion-exchange membranes are resistant to chlorine, they are more robust than RO membranes for water reuse applications since these feed waters have higher levels of organic matter that typically foul RO/NF membranes. The chemical and mechanical stability of IX membranes guaranties a long useful life even in feed waters with aggressive and oxidising components. Compared to thermal distillation discussed earlier in the chapter, the energy consumption and capital cost of ED are significantly lower [65]. EDR modules/stacks are shown in Figure 3.39.

Several examples of treatment of municipal waters by ED/EDR are described below (see also Chapter 5). All the cases discussed demonstrate why ED/EDR was preferred to RO or NF.

Case study I. The city of Suffolk, Virginia, USA selected EDR instead of RO for treating well water with TDS ~ 700 mg/l. Both RO and ED are suitable for reducing high levels of fluoride, 4.6 mg/l (4.0 mg/l max.) and reducing sodium to 50 mg/l for potable water. However, EDR was selected because the volume of brine concentrate discharge was an important consideration [43]. The product water recovery of ED was 94% vs. 85% for RO. For the 14,240 m^3/d plant, the brine concentrate from the RO plant would

Figure 3.39 EDR modules. *Source: MemBrain-MEGA.*

have been 2136 vs. 855 m^3/d from the ED plant, i.e., the brine volume from the RO plant would have been 2.5 times higher.

Case study II. EDR was selected over RO to treat river water for drinking water in Barcelona, Spain, commissioned in 2008 [43]. The feed water TDS is 2000 mg/l and contains high levels of bromide, which along with dissolved organic matter, are a precursor for chlorination disinfection by-products called trihalomethanes (THMs). The THMs of concern are $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$ and $CHCl_3$. The product water recovery is 90% with salt rejection equal to 60–80%. The ED system reduces bromides by 80% and achieves a THM formation potential below the maximum allowable limit of 100 μg/l. The plant consists of nine EDR units with a capacity of 200,000 m^3/d. It is the largest EDR plant in the world, and one of the largest brackish water desalting plants. Dual-media filters effluent flows through activated carbon filters and then through 5.0 μm cartridge filters to the ED stacks: 576 GE EDR Mark 4-2 membrane stacks, 64 stacks per unit. Chemical dosing includes anti-scalant and HCl for scale control if necessary. Post-treatment includes remineralisation with lime and CO_2. The brine concentrate is transferred to the Mediterranean – river estuary. The selection of EDR over RO was based on the following pilot tested results:

- No additional pre-treatment required over the existing pre-treatment facility
- EDR performance independent of seasonal variations in river water temperature and salinity
- 90% recovery
- Lower remineralisation and power costs than RO

Case study III. One of the first ED desalination plants in the US was commissioned in 1974 in the state of Oklahoma to supply drinking water to local communities. At the time of start-up, the 11,400 m^3/d rated plant was the largest membrane desalination plant in the world [66]. The raw water from the Foss Reservoir was low salinity brackish water with TDS equal to 1600 mg/l but very high in hardness, 900 mg/l as $CaCO_3$, and turbidity 2–5 NTU. Pre-treatment included cold-lime softening, media filtration and acid dosage to reduce the pH to 7.5–9.0. Chemical treatment in the clarifier included lime addition to remove some of the calcium, ferric chloride for coagulation, a polyelectrolyte to improve flocculation, chlorine for disinfection and copper sulphate to control algae in the summer (e.g. see Figure 3.36]. Activated carbon filters were used to dechlorinate the water for protecting the anion-exchange membranes (AE). In the mid-1980s, the styrene divinyl-benezene AE membranes were replaced with acrylic-based membranes that were tolerant to continuous exposure to free chlorine residual of 0.3–0.5 ppm, and the carbon filters were disconnected. The acrylic-based cation-exchange (CE) membranes installed in 1974 were still in operation in 2003, proving the longevity of the CE membrane. Post-treatment included sodium carbonate addition, chlorination and ammonium sulphate dosage to convert the free chlorine to chloramines.

The ED system consisted of three trains each rated for 3800 m^3/d. Each train contained 24 ED stacks arranged as six stacks operating in parallel and four stacks operating in series. The design recovery was 68–70%. Higher recovery was constrained by $CaSO_4$ solubility, which was based on $2.25 \times K_{sp}$, the solubility product (see Table 6.9). SHMP anti-scalant was injected to inhibit $CaSO_4$ and $BaSO_4$ precipitation and scaling. Sulphuric acid was added to the concentrate and the negative electrodes to prevent $CaCO_3$ scaling. Lime softening results in water with low bicarbonate levels, which resulted in low dosage of acid. In general, ED is more tolerant to colloidal fouling than RO but the ED system did not experience any colloidal or biological fouling.

In order to increase recovery and prevent $CaSO_4$ scaling, the ED system was replaced with EDR in the late 1980s based on several years of pilot testing. The recovery increased to 78% with $BaSO_4$ super-saturation ($137 \times K_{sp}$) as the limiting factor. Higher recovery resulted in the plant capacity increasing to 17,000 m^3/d product water from 11,400 m^3/d. The new plant installed in 2003 has the same number of membrane stacks, 72, but each stack has twice the active area. The new system also installed variable frequency drives for feed and concentrate pumps to reduce power consumption. The design power consumption was 0.87 kWh/m^3 at 3°C and 1.29 kWh/m^3 at 2°C, and included energy consumption for the feed concentrate and product recycle pumps. The maximum $CaSO_4$ saturation in the concentrate was $3.76 \times K_{sp}$ and the $LSI < 2.1$. In the 1980s it was decided to upgrade the ED plant. NF and EDR technologies were evaluated for upgrading. After several years of pilot tests, EDR was selected based on the following results [66]:

1. NF recovery was 67% with lime softening vs. 78% recovery with EDR without softening.
2. NF capacity was limited to 14,500 vs.17,000 m^3/d for EDR with the existing pre-treatment system.

3. Dechlorination of feed water required for NF. Not required for EDR.
4. Biological fouling was a severe problem in the case of NF. None in the case of ED/EDR.
5. Colloidal fouling of NF membranes when the SDI was high. Not an issue with ED/EDR.
6. Lime softening required for NF because of $CaSO_4$ fouling. EDR design did not depend on lime softening.
7. Lower capital cost and least risk of problems with EDR compared to NF. The overall cost of the EDR desalting plant was $7.7 M in 2003.

ED/EDR industrial water desalting

Desalting of industrial process water and wastewater treatment are other important ED applications. Industrial water processing includes demineralisation of boiler feed water and desalination of contaminated industrial water for reuse. A typical application of industrial water reuse is the recycling of cooling tower blowdown water. Electrodialysis is particularly suited since high recovery rates up to 95% can be achieved, which results in savings of feed water costs and in a reduction of waste water discharge. Furthermore, ED membranes can be operated at temperatures up to 50°C, which is in the range of most cooling systems. Very often toxic or valuable components such as heavy metal ions can be removed to avoid pollution of the environment and save disposal costs by recycling valuable materials [43,65].

Case study I. An integrated EDR-RO membrane plant in GEAM, Dolní Rožínka, Czech Republic treats high salinity wastewater from a tailing pond of uranium mine and is contaminated also by other sources [67]. Feed water contains a wide scale of pollutants: inorganic salts (mostly Na_2SO_4), heavy metals, uranium and low and high molecular organic compounds. There are two water sources: sludge bed water and drainage water. The membrane plant pre-treatment is as follows: precipitation of Ca and Mg by lime and soda ash, sedimentation, sand filtration, sorption of heavy metals and uranium in an ion-exchange column, oxidation, sorption of oxidation products on activated carbon, and acidification by H_2SO_4. The pre-treated water ($TDS = 35{,}000$ mg/l) flows to the EDR system at 65 m^3/h. Partially desalted ED permeate (12,000 mg/l) flows to the RO unit at 50 m^3/h. The RO permeate flow rate is 35 m^3/h and the TDS is 180 mg/l (salt rejection $> 98\%$). The RO permeate quality is below the effluent limits for safe discharge to the local river at 35 m^3/h. The recovery of the ED and RO units is 77% and 70%, respectively. The RO reject is recycled and mixed with ED feed water. The ED concentrate ($TDS = 100{,}000$ mg/l, flow rate $= 15$ m^3/h) is evaporated followed by crystallisation to recover Na_2SO_4 salt.

The EDR system consists of 30 stacks – two trains of five parallel lines with three stacks in series, countercurrent operation, feed-and-bleed mode. There are 200 membrane pairs in each stack with an effective membrane area of 5000 m^2. The RO unit contains 20 spiral-wound TFC membrane elements, 20 cm diameter × 100 cm long with an effective membrane area of 840 m^2.

Case study II. An EDR plant in Žiar nad Hronom, Slovakia treats highly alkaline water (pH 13–14) from an aluminium production plant [67]. The wastewater contains about 10,000 mg/l NaOH as well as high concentrations of inorganic salts, heavy metals and high molecular organics; Na^+, $Al_3{}^+$, OH^-, $CO_3{}^{2-}$ are the main constituents. Heavy metals include Cr, As, Mo and V. The ED plant pre-treatment includes neutralisation by H_2SO_4, sand filtration, acid decarbonisation and cricket (pressure) filtration. The pre-treated water (TDS = 37,000 mg/l) flows to the EDR system at 15 m^3/h. Partially desalted ED permeate TDS is 6000 mg/l and the recovery is ~80% with the flow rate at 12 m^3/h. Sodium sulphate salt in ED concentrate (TDS = 180,000 mg/l, flow rate = 3 m^3/h) is recovered by evaporation and crystallisation.

The EDR system consists of 12 stacks – four parallel lines with three stacks in series, countercurrent operation, feed and bleed mode. There are 200 membrane pairs in each stack with an effective membrane area of 2000 m^2. The feed water temperature is 30–35°C.

3.2.4 High recovery/brine treatment membrane processes

RO membrane plants are used extensively for brackish water (TDS = 1000–10,000 ppm) desalination and industrial water (TDS < 1000 ppm) desalination. Typically, these plants operate at 65–80% product water recovery so that 20–35% of feed water is wasted as concentrated brine. Pre-treatment costs and brine concentrate management are major issues limiting the construction of more inland RO desalination plants [46,48]. Traditional methods of brine disposal include deep well injection, surface discharge, evaporation ponds and sanitary sewers. All these methods use waste water, which is a byproduct of treated water (e.g. groundwater) that consumes energy for its purification. Thermal zero liquid discharge process is used to treat small streams but is both capital and energy intensive as discussed earlier and is not a suitable process for medium to large brackish water plants [46,48]. Integrated RO/EDR and NF/EDR systems can address these issues since EDR can achieve higher recovery under fouling and scaling condition and is resistant to silica scaling and chlorine residual unlike polyamide RO membranes. Data analysis demonstrated that in the case of inland brackish water desalination, higher overall recovery results in reducing costs of treated water and brine disposal [68].

Integrated membrane processes

The simplest case is the dual-membrane system; the primary RO (PRO) reject/brine stream is purified in a brine RO (BRO) unit operating at recoveries of 50–70%, as shown in Figures 2.21 and 5.2 [69]. The brine recovery system membrane processes were modelled using Hydranautics Membrane Solutions software v.2007 and Dow/Film-Tec ROSA software 6.2. The brine TDS was between 1300 and 6600 mg/l. The membranes were PA thin-film composite (TFC). The spiral-wound elements were either 10 cm diameter × 100 cm long or 20 cm diameter × 100 cm long, with three to six elements per pressure vessel mounted in series (e.g. see Figure 2.19). Feed water treatment included anti-scalant addition and pH adjustment with acid to 6.5–6.8 to maintain the LSI < 1.8. Based on membrane manufacturer's recommendations, the saturation limits with anti-scalants are as follows: $BaSO_4 = 6000\%$, $SrSO_4 = 800\%$ and $CaSO_4 = 230\%$. The silica precipitation/scaling limit can be raised to 300 ppm with a dendrimer anti-scalant (Professional Water Technologies, Vista, California).

The PRO and BRO unit recovery was 75% and 50%, respectively, and the overall recovery was 87.5% with the BRO feed (PRO reject) composition as TDS = 1300 ppm, hardness = 825 ppm, $SO_4 = 360$ ppm, and silica = 16 ppm. The BRO unit was a one-stage array with three pressure vessels (3:0) in parallel and three elements per pressure vessel (9 elements total). The RO elements were Hydranautics ESPA1 (40 cm dia.). The recovery of the BRO unit increased from 50% to 70% when a small portion (<20%) of the BRO reject stream was recycled to the BRO unit inlet, as shown in Figure 3.40 [69]. Reject recycle provides additional fluid flow above the membrane, thereby reducing concentration polarisation and achieving higher flow. Thus, the overall water recovery was 92.5%. The BRO unit was a two-stage, 3:2 parallel pressure vessel array with three elements per pressure vessel (15 elements total). The RO elements were Hydranautics ESPA2+ (20 cm dia.). The average flux was 17–20 lmh.

The water recovery was increased to 95% using a triple membrane process; a NF unit was added to purify the BRO reject stream, as shown in Figure 3.41 [69]. The PRO, BRO and NF unit recovery was 75%, 60% and 50%, respectively, resulting in the overall water recovery of 95%. The BRO feed (PRO reject) composition was TDS = 6650 ppm,

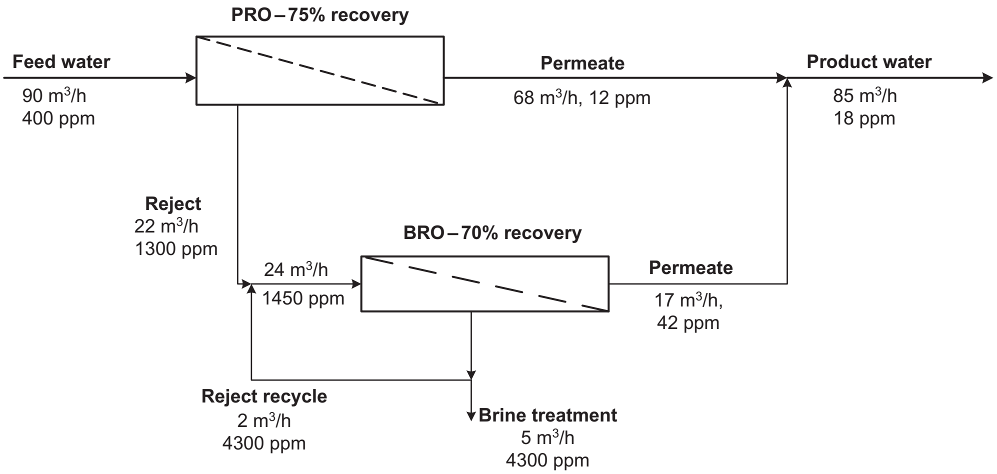


Figure 3.40 Process flow schematic of a high-recovery RO-BRO system with reject recycle.

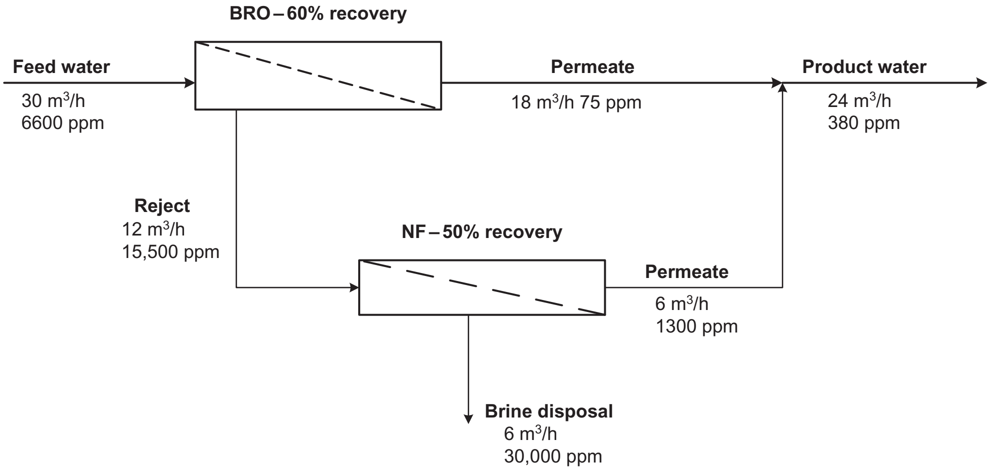


Figure 3.41 Process flow schematic of a high-recovery PRO-BRO-NF system. Feed water is PRO reject (PRO not shown). BRO-NF recovery is ~80%.

hardness = 2427 ppm, alkalinity = 796 ppm, SO_4 = 808 ppm, and silica = 60 ppm. The BRO unit was a three-stage, 3:2:1 parallel pressure vessel array with three elements per array (18 elements total). The NF unit was a two-stage, 2:1 parallel pressure vessel array with three elements per array (9 elements total). The RO elements were Dow/Film Tec BW30-400/34i (20 cm dia.), and the NF elements were Dow/Film Tec NF90-400 (20 cm dia.). The average flux was 17–20 lmh.

Zero discharge desalination (ZDD)

Zero discharge desalination technology was developed to reduce the volume of brine concentrates from brackish water RO/NF desalination plants [70]. ZDD is based on electrodialysis metathesis (EDM). The EDM stacks use the same types of anion and cation-exchange membranes as used in conventional ED stacks, but there are four membranes and solution compartments in the repeating unit of an EDM stack. In the process, ZDD converts sparingly soluble $CaSO_4$ to soluble $CaCl_2$ and Na_2SO_4 so that the volume of the original RO concentrate can be reduced to a very small volume of highly concentrated salt solutions without precipitation of salts. The solubilities of NaCl, $CaCl_2$ and Na_2SO_4 at 33°C are 27, 50 and 31 g/100 g solution. By contrast the solubility of $CaSO_4$ is ~2 g/100 g of solution. In field pilot tests, ZDD increased the recovery of RO system from 80% to 97% producing potable water from a brackish well while the brine concentrate volume was reduced to about 2% of the volume of RO/NF feed water.

Hybrid membrane processes

Another process entails using electrodialysis to treat RO reject from brackish water. A RO-EDR-Crystalliser/settler-UF-WAIV hybrid process achieved 98% recovery in pilot studies [71]. Potential for scaling on the brine side of the ED unit was prevented by acidification, using a EDR unit instead of ED, and a side loop crystalliser, which prevented build-up of scaling compounds. Settlers, in-line MF and a side-loop UF prevented suspended solids from returning to the EDR unit. The process was demonstrated in a series of more than 80 pilot batch experiments with RO concentrate of raw brackish groundwater from the Negev Highland, Israel. The water – brackish groundwater – was concentrated from 3000 to over 100,000 mg/l TDS while producing the desalted water that could be blended with the RO permeate. This super-concentrate from the EDR unit was further concentrated in a wind-powered WAIV unit that brought final brine TDS to ~30%. The process was promising for recovering mineral salts such as magnesium as well. The process is capable of treating large volumes from brackish water desalination plants.

It was shown that in the case of low TDS brackish feed waters, integrated membrane operations can achieve product water recoveries of 92–95% with minimal chemical treatment. In the case of high TDS brackish waters, hybrid processes have been investigated such as softening the PRO reject stream with lime or sodium hydroxide to raise the pH to 11, thereby reducing hardness and silica ion concentration in brine RO (BRO) feed water [72]. Chemical softening is commonly used in large-scale systems, whereas IX softening is generally restricted to flow rates <100 m^3/h and hardness <1000 ppm. The cost of softening PRO reject water including costs of softening equipment, softening chemicals and sludge handling is lower than for softening PRO feed water since the reject volume is less (20–35% of PRO feed water). Chemical softening of PRO reject to remove scaling compounds makes it possible to achieve very high recoveries in a brine RO unit. The BRO reject is further concentrated with EDR or WAIV to achieve 97–98% overall product water recovery.

3.3 HIGH-PURITY WATER PRODUCTION

Pure water refers to water that meets the specific needs of a given process or product; for example, (a) deionised water for medium pressure boilers, battery make-up, renal dialysis make-up, (b) purified water for cosmetics, chemical manufacturing, beverage water, (c) USP water for pharmaceuticals, vial washing, tissue culture, water for injection, (d) high-purity water for high-pressure boilers, combined heat and power systems, metals finishing, and (e) ultrapure water for microelectronics rinse water, supercritical boilers [73,74]. The definition of ultrapure water (UPW) differs from pure water or deionised water. Generally speaking, pure water refers to water that meets the specific needs of a given process or product; for example, in pharmaceutical applications removal of organisms or pyrogenic substances is of utmost importance, whereas in textile washing removal of hardness, iron and manganese is essential. For microelectronics the purity requirements are the most stringent of all the water production requirements in the general industry and require ultrapure water, e.g., resistivity ≥18.2 MΩ-cm [73]. High-purity water (resistivity 1–10 MΩ-cm) is also used in the metals finishing industry to rinse the metal surface clean of any dirt or chemicals prior to the plating operation. High-purity annual sales are about $6 billion. Power plants are the single largest user of high-purity water. Water treatment for the power generation industry for both utility and non-utility producers is estimated at more than 30% of all industrial water treatment sales.

In the last 20 years RO has replaced demineralisation by two-bed (cation-anion) IX (DBIX) prior to mixed-bed IX polishing (MBIX). Higher operating costs for IX systems combined with lower operating costs and increased confidence in operating membrane systems helped RO systems to be adopted. RO-IX treatment is more cost-effective than the DBIX-MBIX, especially when the feed water TDS is greater than 350 mg/l [75]. Hybrid systems based on feed water and product water purity may include RO combined with MF, UF, MBIX, EDI, ozone and UV. Integrated RO + EDI systems use 95% less chemicals than ion exchange. Increasingly, EDI is either complementing or replacing mixed-bed ion-exchange (MBIX) deionisers depending on the quality of product water required [74,76].

The water source of most high-purity water plants is city water or municipal water, which has undergone pre-treatment. The raw water source may be ground water or surface water with TDS in the range of 200–1000 mg/l. Municipal treated wastewater TDS is typically 100–300 mg/l. Feed water pre-treatment for high-purity water plants, therefore, is minimal unless brackish water is used as raw feed water.

3.3.1 Boiler water treatment

Power plants require high-purity make-up water for producing steam to drive turbines and generate electricity. In thermoelectric power plants steam is generated at a pressure of 40–200 bar g with the power generation efficiency increasing with steam temperature and pressure.

HPW needs to be devoid of contaminants such as sodium, chloride, or silica in the steam [73] since increased volatility of salts and silica at high temperatures and pressures, results in; for example, silica carryover into the steam phase. When the steam pressure is reduced in low-pressure turbines, silica precipitates on the turbine blades resulting in corrosion that can weaken and damage the turbines. Organic impurities decompose in the steam-water circuit to produce carbon dioxide and organic acids including acetic, formic, and glycolic that can cause corrosion [74]. Typical make-up water quality requirements are given in Table 3.7 [76]. The requirements vary depending on the type of boiler system and are published by many authorities such as the American Society of Mechanical Engineers (ASME, 1994) [73]. Steam generation in chemical process plants such as oil refineries, pulp-and-paper production, and food processing, on the other hand, does not require water of the same purity since steam is used for process heating. Instead,

Table 3.7 Typical make-up water specifications for high-pressure boilers

Parameter	Value
Conductivity, μS/cm at 25°C	≤0.1
Silica, ppb	5–10
Sodium, ppb	2–5
Chloride, ppb	2–5
Sulphate, ppb	2–5
TOC, ppb	≤100

Source: [76].

low pH corrosion of the condensate return lines is a problem. This is resolved by removing bicarbonate and carbonate alkalinity from the feed that prevents the formation of carbon dioxide and its passage to the condensate lines [73].

A typical make-up water process flow schematic diagram for producing HPW for steam generators is shown in Figure 3.42. It takes about 2 m^3 of high-purity water to produce 1 MWh of electricity. In order to minimise the overall water consumption, the make-up is combined with purified condensate steam, as shown in the figure, to provide boiler feed water. In the case of utility boilers, most of the steam is usually returned as condensate and less than 5% make-up water is required. However, for some industrial cycles there is little or no return condensate so up to 100% make-up is necessary. Since condensate has been purified by prior evaporation, in many cases it can be directly mixed with the make-up water to supply it to the boiler, as shown in the figure. Most high-pressure boilers (>60 bar g) deploy a condensate polishing system to remove the dissolved impurities and filter out the suspended solids such as corrosion products of iron and copper and occasionally organic material [77]. Sodium cycle strong cation ion exchange or MBIX is generally used to remove these contaminants depending on the level of purity required. The contaminants in the feed water

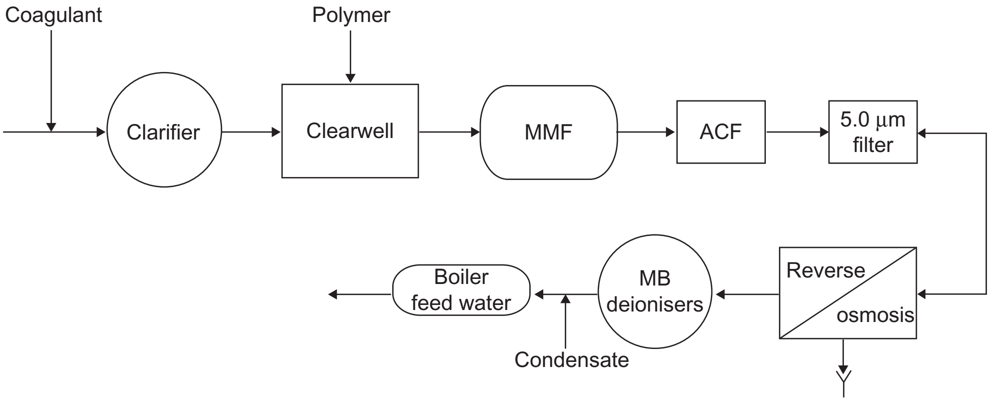


Figure 3.42 A typical boiler water treatment hybrid membrane system process flow schematic.

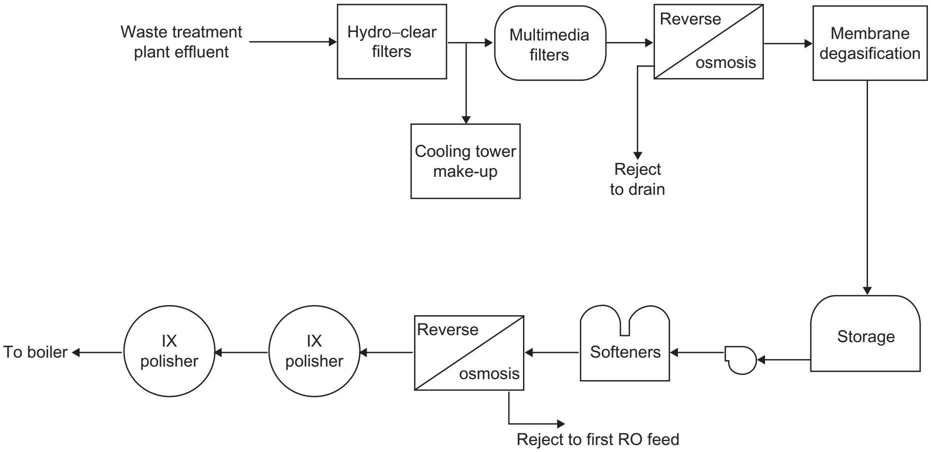


Figure 3.43 Process flow schematic for power plant boiler water production from a municipal wastewater effluent plant. *Source: USFilter.*

get concentrated in the boiler. Hence, a small portion (<5%) of the water in the boiler is drained (blowdown) to maintain the water quality. High-purity make-up water is fed to the boiler to make up for losses due to blowdown, evaporation and system leaks.

Case study. With increasing focus on water conservation and tighter pollution control regulations, power plants have to rely on reclaimed water in many cases. Reclaimed water generally means treated effluent from municipal wastewater treatment plants. A process flow schematic of one such water treatment plant producing high-purity water from reclaimed water at a 550-MW combined cycle power plant in New Jersey (USA) is shown in Figure 3.43 [78]. Waste treatment effluent is filtered and sent to the cooling towers. A small portion of the pre-filtered water flows to three multimedia filters at 114 m^3/h. Sodium bisulphite is added to filtered water and pumped to the first-pass RO unit. More than 98% of dissolved solids are removed. The RO permeate flows through a bank of membrane degasifiers, which remove dissolved CO_2 to reduce the ionic load on anion resins of MB deionisers downstream. Dissolved oxygen is also removed since oxygen in boiler water with trace amounts of chlorides or solids can cause pitting corrosion of metal surfaces [74]. The second-pass RO unit reduces the TDS and the purified water is polished by MB ion exchange to produce deionised water. The water treatment system supplies 70 m^3/h high-purity water to the steam generator with conductivity <0.2 μS/cm and silica <10 μg/l. Reusing reclaimed water reduced the power plant's dependence on potable water with savings of ~2200 m^3/d of city water to the local community.

3.3.2 Microelectronics rinse water

Ultrapure water is used in the microelectronics industry for applications such as rinsing and washing wafer surfaces between chemical etching steps and immersion lithography [73,79]. A large semiconductor fabrication facility typically uses 160 m^3/h of ultrapure water. The amount of UPW required to produce one 150-mm wafer is about 5 m^3. A method of manufacturing a VLSI (very large integrated circuit) is shown in Figure 3.44 [38]. There are four steps where UPW is used as shown. Why is water of extremely high quality required in the washing process of the semiconductor industry? A simple explanation is that without very high-purity water, short-circuiting is a real risk resulting in lower yields of the wafers. In 1984, the level of water purity was based on microcircuits with 2.0 μm line spacings. By 1995, the spacing had decreased to 0.3 μm, and to 0.07 μm by the year 2010.

Advanced wet cleaning processes have evolved to meet the challenges of manufacturing semiconductor devices with smaller geometries and higher performance. New materials and manufacturing processes, larger wafer size, line width shrinkage to 0.03 μm by 2015 and environmental concerns are the driving forces behind new cleaning/rinsing methods [79,80]. Very fine filtration with hydrophobic membrane filters with high efficiency for

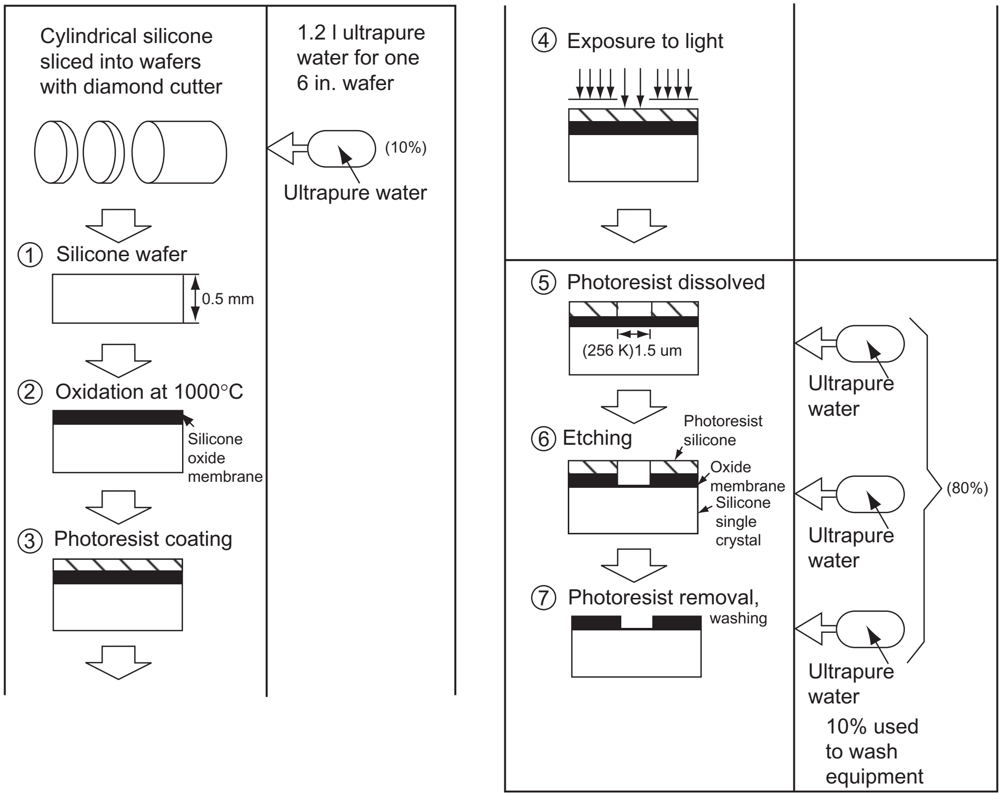


Figure 3.44 Ultrapure water applications during the manufacture of a VLSI wafer. *Source: Matsuura, Copyright® 1994 from Synthetic Membranes and Membrane Separation Processes by T. Matsuura. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.*

bubbles removal and particle retention is critical for removing particles down to 0.03 μm. Dissolved gases in UPW can create bubbles as in the case of gases/bubbles generated by the UV oxidation process. Dissolved gases must be removed to ppb levels. The role of UPW is, therefore, expanding from conventional wafer rinsing to advanced applications such as [80] (a) immersion optical lithography, (b) gasified UPW for wafer cleaning, (c) humidification with UPW of ultra clean air in the lithography environments where control of organics in the air is critical, and (d) new specialty chemical formulations for wet etch and cleans.

The microelectronics industry has also developed 65 nm circuits by switching from dry lithography to wet immersion lithography using UPW between the imaging lens and resist surface. This requires that the purified water quality must be maintained at the highest level of clarity (i.e. low absorbance) and purity (i.e. parts per trillion or ppt levels contaminants) to ensure high transmission of imaging radiation through water [79]. Newer UPW systems must, therefore, be able to efficiently remove dissolved gases and bubbles, urea, boron, particles, TOC, non-volatile residue as well as ionic and organic extractables from process equipment to prevent imaging defects. Refractive index of water is a critical parameter that can be influenced by these contaminants. Organic contaminants are undesirable as they can absorb deep UV energy and cause defects. Hence, TOC needs to be reduced from ppb levels to ppt levels. A UV-IX process was developed that achieves ppt levels of TOC by breaking down most organic molecules into carbon dioxide and water [80]. Further, removal of ions in the immersion system is accomplished with the aid of MBIX deionisers operating in series with silica and boron purifiers. These systems use strong IX resins for removing most metals and weakly dissociated silica and boron. Silica in HPW typically exists in the dissolved form and colloidal form. The IX purifier is effective in removing anionic silica and boron.

Case study. The hybrid membrane plant described in this case study provides 15 m^3/h UPW for a fab manufacturing facility. The high-purity water plant consists of a pre-treatment section, a two-pass RO unit, and a post-treatment section similar to the one shown in Figure 3.45. Raw (city) feed water is surface water with the following major constituents: bicarbonate = 183 mg/l; chloride = 61 mg/l; sulphate = 83 mg/l; silica = 14 mg/l; potassium = 3 mg/l; and sodium = 147 mg/l. City water is pre-filtered water with TDS ~500 mg/l. The treatment steps follow the sequence given below:

Filtered city water ⇒ Carbon filter ⇒ IX softener ⇒ Double-pass RO ⇒ 185 nm UV
⇒ Series MC ⇒ Primary MBIX ⇒ DI water tank ⇒ 1.0 μm filter
⇒ 185 nm UV ⇒ Polishing MBIX
⇒ 254 nm UV ⇒ 10, 000 MWCO UF ⇒ UPW to distribution loop
⇒ A portion of UPW recycled to DI water tank

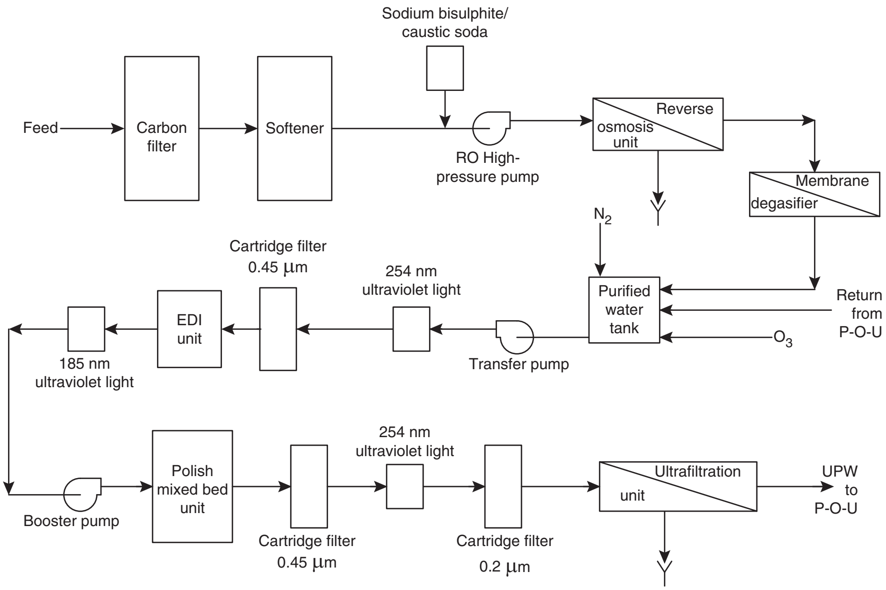


Figure 3.45 Process flow schematic of a typical ultrapure water system used in semiconductor manufacturing (5.0-mm cartridge filter upstream of RO pump not shown).

Dechlorinated and softened water flows to the RO skid through a 5.0-µm (nominal pore size) cartridge filter. The cartridge filter removes resin fines, particles and complexed colloids necessary to protect the RO membranes from particulate fouling. The RO membranes are thin-film composite (TFC) polyamide RO membranes (20 cm diameter × 100 cm long spiral wound elements) with rejection ~99%.

The first-pass RO unit is a three-stage (2:1:1) array and the recovery is 75%. The permeate flows to the second-pass RO unit and the reject flows to drain. The second-pass RO unit is a two-stage (1:1) array operating at a recovery of 90%. The reject flows back to the first-pass RO pump inlet. The second-pass permeate conductivity is <0.2 µS/cm. The overall recovery of the double-pass RO system is ~69%. Caustic soda solution is injected in the second-pass feed water line (first-pass permeate) to raise the pH from 6.0 to 8.0. At alkaline pH, free CO_2 in water is converted to sodium bicarbonate, which is easily rejected by the RO membrane.

The TOC level in the RO permeate can vary between 50 and 500 ppb. For producing UPW, therefore, various techniques are required to eliminate residual organic contaminants. Irradiation with 185 nm UV light is very effective in oxidising residual organic matter (TOC), thereby reducing the organic load on anion resins in the MBIX deionisers downstream. Ultraviolet irradiation also renders more than 90% bacteria ineffective. This is especially important since the MBIX units operate at neutral pH and are capable of supporting bacteria proliferation. Other oxidation processes include hydrogen peroxide and ozone. Direct feed of ozone followed by irradiation with 254 nm UV light is also very effective in reducing TOC levels to <5 ppb [73].

The RO product water is degasified in a membrane contactor, which removes any traces of dissolved gases from water with nitrogen flowing in the permeate side as sweep gas. Degassed water flows to primary MBIX deionisers. The resistivity of double-pass RO and MBIX polished/DI water typically is ≥16.0 MΩ-cm. Hence, further treatment is required for ultrapure water to meet the water quality specifications given in Table 3.8.

DI water is irradiated in a 185 nm UV light to further reduce the TOC level. The primary impact of oxidation is conversion of organics to carboxylic acids, which results in a drop in resistivity [73]. The UV effluent is, therefore, polished in a secondary MBIX producing UPW with resistivity = 18.2 MΩ-cm. The MBIX effluent flows through a bacteria reducing 254 nm UV unit to deactivate bacteria and destroy any traces of organic matter. The irradiated water flows through ultrafiltration (UF) membrane elements. The polysulphone UF membranes (MWCO of 10,000 Da) act as final barrier for reducing the particle count. The final product water (UPW) is monitored continuously for silica, dissolved oxygen, particle count, TOC and resistivity before it flows to the point-of-use (POU). A portion of the POU supply water recycles to the DI water tank to ensure there is no stagnant water in the distribution loop. All piping used in the polishing loop is polyvinylidene fluoride (PVDF), which has a lower coefficient of friction than stainless steel. Low friction and high flow velocities of 3–5 m/s in the UPW distribution loop prevent microorganisms (bacterial and fungi) from growing and adhering to the pipe walls. PVDF piping is also 30–35% cheaper than 316 L SS because it does not require steps such as passivation of SS components.

Table 3.8 Microelectronics UPW specifications

Parameter	Value
Resistivity	≥ 18.2 MΩ-cm
Particles	
> 0.2 μm	<10 count/l
> 0.5 μm	<1 count/l
Bacteria	<1 cfu/100 ml
Total organic carbon	<2 μg/l
Dissolved oxygen	≤2 mg/l
Calcium	<2 μg/l
Cations (each)	<0.2 μg/l
Chloride	<0.1 μg/l
Anions (each)	<0.2 μg/l
Silica (dissolved)	<3 μg/l

Source: Ultrapure Water.

3.3.3 USP grade water

The United States Pharmacopoeia (USP) has three general specifications for water quality that are applicable to medical and pharmaceutical uses, namely, "USP Water for Injection" (WFI), "USP Purified Water" and "Drinking Water" [81]. The primary difference between WFI and PW is the tolerance of microorganismas and endotoxins. Sterile WFI is the most demanding and expensive to produce. It is used for the final purification steps of parenteral products or where water is expected to have direct contact with human blood. Standard USP water specifications for pharmaceuticals manufacturing are conductivity = 0.2–1.0 μS/cm at 25°C; pH 5.0–7.0; TOC level <500 ppb; and bacteria count <100 cfu/100 ml. WFI also requires bacteria count <10 cfu/100 ml and endotoxin level <0.25 EU/ml [74]. The types of water recommended for pharmaceutical applications and operations are given in Table 3.9 [82].

Traditionally, the pharmaceutical plants used distillation - multieffect or vapour compression - to obtain water free of organisms and pyrogens. Currently, when large amounts of USP purified water and small amounts of WFI are required, a RO-EDI membrane system is used for the production of the USP purified water, and a small distiller for the production of the WFI, as shown in Figure 3.46 [83]. The European Agency for the Evaluation of Medicinal Products (EMEA) has designated a new grade of water called Highly Purified Water "for the preparation of products where water of high biological quality is needed except where WFI is required" [82]. This type of water is generally produced using two-pass RO followed by mixed-bed deionisation and UF/MF as final particle barrier.

Case study. The case study describes a high-purity water plant similar to the one shown in Figure 3.46. The water treatment plant supplies 9 m^3/h USP grade water (conductivity = 0.1 μS/cm) to a drug manufacturing facility where it is used in the preparation of topical and oral medications. Raw (city) feed water is surface water of pH = 7.6 and

Table 3.9 USP water quality requirement by application

Application/operation	Water quality
Media preparation	USP purified
Seed and production bio-reactor batching	USP purified
Cell or mycelia separation	USP purified
Cell or mycelia washing	USP purified
Buffer preparation	USP purified
Diafiltration	USP purified
Column chromatography (pre-columns)	USP purified
Column chromatography (final column)	WFI
Viral clearance	USP purified
Final filtration	WFI
Lyophilisation	WFI

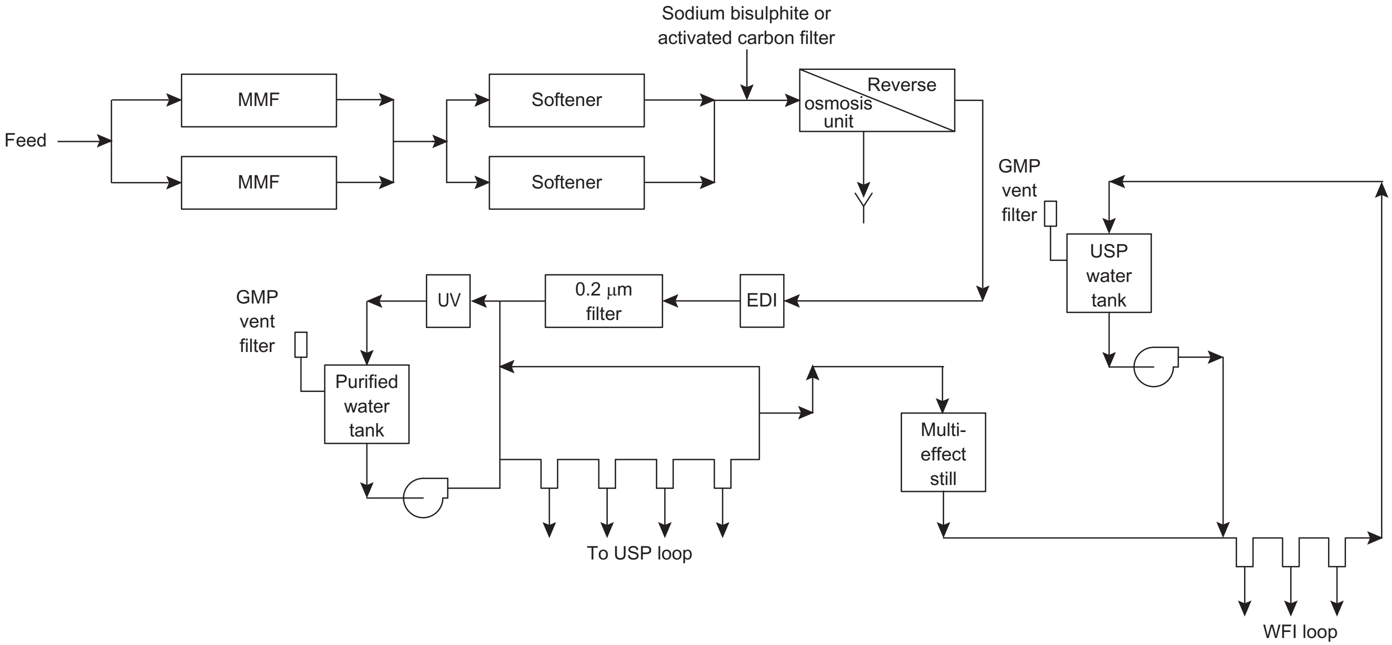


Figure 3.46 Process flow schematic of a typical high-purity water system for producing USP water and WFI in pharmaceutical manufacturing. *Source: Gsell.*

TDS = 140 mg/l with the following major constituents: bicarbonate = 19 mg/l; chloride = 19 mg/l; sulphate = 47 mg/l; silica = 7 mg/l; calcium = 9 mg/l; magnesium = 4 mg/l; sodium = 30 mg/l. The treatment steps follow the sequence given below:

$$\begin{aligned} &\textit{Duplex MMF} \Rightarrow \textit{Duplex IX softeners} \Rightarrow \textit{Carbon filter} \Rightarrow \textit{Holding tank} \\ &\quad \Rightarrow \textit{254 nm UV} \Rightarrow \textit{Single-pass RO} \Rightarrow \textit{EDI} \Rightarrow \textit{0.2}\,\mu\textit{m final filter} \\ &\quad \Rightarrow \textit{HPW to point-of-use} \end{aligned}$$

Pre-treated RO feed water combines with RO reject recycle water and flows to the RO skid through a 5.0 μm pore size (nominal) cartridge filter. During RO operation only a small portion of the RO feed water flows back to the holding tank continuously. When the RO system is not in operation the entire feed water by-passes the RO unit and recycles to the holding tank to keep the water in circulation and prevent stagnant water and biological contamination.

The single-pass RO unit is a three-stage (1:1:1) array designed to produce purified water at an overall recovery of ~75%. The TFC RO membrane average rejection is 98%. The permeate conductivity should be less than 10.0 μS/cm. When the ΔP across the membrane exceeds the maximum allowable value, the RO unit is taken out of service to clean the membranes. The frequency of cleaning the RO unit is typically 3–6 months for softened RO feed water.

The RO permeate flows to the EDI unit. The EDI system performance specifications are product water recovery = 90%; rejection > 99% with the product water conductivity <1.0 μS/cm, and TOC < 10 ppb. The EDI product water flows through a 0.2 μm cartridge final filter and the reject flows back to the holding tank. The high-purity water flows to the point-of-use at 9 m^3/h.

USP plant operation modifications

High-purity water production methods such as those discussed above are based on certain well-established rules such as RO product recovery of 70–80%, high fluid velocities in the HPW loop, hot water sanitisation, elimination of the chemical or hot water sanitisation of carbon filters, and use of stainless steel piping in USP water systems. Modifications to these design guidelines have been suggested [82]:

- Operate the RO units systems at 50% recovery instead of 70–80%. This reduces the frequency of membrane cleanings substantially, increases reliability, and results in consistent product water quality. In addition, the reject water is better suited for reuse applications such as for cooling tower make-up. It can also be used as feed for WFI vapour compression stills and clean steam-generators, provided the silica content is less than 15 mg/l.
- It is not necessary to operate the RO-EDI system in a USP water plant continuously. This wastes water and there is no benefit in microbiological control. Similarly, hot water sanitisable RO and EDI systems are no better at controlling bacteria.

- Frequent backwash of carbon media filters is more effective than hot water or steam sanitisation since the microbial load reduction by sanitisation is temporary due to the rapid recolonisation of the sanitised biofilm in the carbon bed.
- Minimum fluid velocities in the HPW recirculating loops are 2–3 m/s. Apparently, there is no single velocity based on which a loop system can be designed or operated to control the formation of biofilms.
- WFI operation is believed to be as effective at 60°C as it is at 80°C. Hence, hot water sanitisation of the RO-DI systems at 60°C instead of 80°C should be considered.
- As in the case of semiconductor plants, PVDF piping should be used in high-purity loops in USP plants. It is 30–35% cheaper than 316 L SS and reduces steps such as cleaning and passivation of SS components.

3.4 WATER RECLAMATION AND RECYCLING

Reclaimed and recycled water is an important and reliable resource of water for potable, non-potable, industrial and irrigation use, especially in water-stressed countries, to meet increasing water demands. In rapidly emerging countries such as India, water reclamation and recycling seems to be the only viable solution to the perpetual and worsening water crisis in urban areas. According to an Ernst & Young study, investment in the Indian water sector could reach $130B by 2030 [84]. In semiarid areas such as the US southwest reclaimed water is an indispensable water source for the petrochemical industry. In many refineries water consumption has increased because of special refining requirements. For example, to reduce sulphur in diesel and petrol a large number of hydrotreating units that consume water were installed. The switch to heavier, higher sulphur crudes also increased the number of processing units and, thus increased the water consumption. There are only two avenues for meeting these water demands: treatment of domestic/industrial wastewater effluent and seawater desalination. The former requires water reclamation and recycling. California promulgated the earliest wastewater quality guidelines for reuse applications (Title 22 Guidelines) during the 1970s. Today, more than half of reclaimed water in the US is for industrial processes, cooling, and public and private gardening. Only one-third is used for agricultural irrigation. In northern Europe, about 84% of the reclaimed wastewater is used for industrial and municipal applications, whereas in drier southern countries 44% is used for irrigation.

Water reclamation refers to the recovery of reusable high-grade water from municipal or industrial effluents by the removal of pathogens, dissolved organics and salts for applications in, for example, power plants and semiconductor fabs. The beneficial uses of reclaimed water besides agricultural, urban and industrial applications include restoration of ground water quality following industrial contamination and augmentation of traditional water sources such as groundwater or surface water [85]. In reuse applications, the feed water is usually biologically treated municipal wastewater. Generally speaking, it is required that municipal wastewater is either secondary or tertiary treated water before it

Table 3.10 Typical feed water and product water quality targets for high-grade industrial and potable water

Parameter	Feed water[a]	Product water[b]
Total suspended solids (TSS)	2–20 mg/l	<1 mg/l
Total coliforms	10^6–10^6 cfu/100 ml	<1 cfu/100 ml
Total organic carbon (TOC)[c]	8–12 mg/l	0.1–1 mg/l
Total nitrogen[d]	1–40 mg/l	1–10 mg/l
Total dissolved solids (TDS)[e]	350–1200 mg/l	50–200 mg/l

[a] Typical range of values for secondary effluent (post-activated sludge settling tank) used in municipal water reclamation projects.

[b] Indicative requirements for high-grade and potable reuse projects. Actual requirements determined by local conditions.

[c] Final TOC requirements and nature of TOC are very site-specific and determined by the needs of industry or regulatory agencies.

[d] Feed water nitrogen values vary depending on the level of nutrient removal. Final nitrogen concentration depends on industrial water requirements or the environmental protection regulations.

[e] Final TDS levels depend on the ultimate use of reclaimed water. Often, minerals are added to the water to stabilise and mitigate against the aggressive nature of the reclaimed water (typical of RO permeate).

Source: [85].

can be reclaimed for health reasons. The composition of commonly used wastewater and reclaimed water are given in Table 3.10. Examples of several major water reclamation projects are given in Table 3.11 [85]. Two well-known examples of advanced wastewater reclamation membrane-based plants are the Water Factory 21 in southern California and the NEWater Factory in Singapore [86]. UF/MF applications are shown in Figure 3.47.

3.4.1 Industrial water treatment

In the industrial sector, water is often recycled for generating high-purity water for power plants, oil refineries and semiconductor manufacturing plants. According to one survey, membrane filtration for recycling water has been beneficial in all cases with overall savings ranging between $102,000 for a 6-$m^3$/h water treatment plant and $640,000 for a 50-$m^3$/h plant [87]. For example, at a leading semiconductor manufacturing plant in the UK, financial savings are nearly 20% since 83% of the treatment cost is associated with bringing new raw water for the DI water treatment plant. Spent water from the manufacturing plant is passed through an activated carbon filter for removing hydrogen peroxide, which is present in some of the acid baths – the main difference between the reclaimed water and the raw water quality is the very low cation and bacterial content in the reclaimed water. Next, weak anion resin is used to remove free ions such as sulphate, phosphate and fluoride. The IX effluent flows through 10.0 μm filters and 254 nm UV lights before flowing to the RO unit. The RO product water mixes with the pre-treated potable water and the combined water has a conductivity of 3.0 μS/cm [88].

Case study I. Secondary treatment effluent from a sewage plant is processed by an integrated membrane system to supply reclaimed water for high-purity water production at a wafer manufacturing facility in Singapore [89]. Effluent from an activated sludge

Table 3.11 Examples of water reclamation projects

Application	Location	Purpose/benefit
I. Irrigation – Agriculture	Santa Rosa, California	Reclaimed water is used to irrigate food and non-food crops
II. Irrigation – Urban	Irvine Ranch, California; Rouse Hill, NSW, Australia	Uses include landscape irrigation and toilet flushing
III. Industrial	West Basin, Los Angeles	The West Basin recycling project was built to serve the "big 3" oil refineries in Los Angeles with reclaimed water in lieu of groundwater. Reclaimed water is used in cooling towers and as make-up for high-pressure boilers.
	Luggage Point, Brisbane	The Luggage Point reclamation project supplies potable water at a clear fuel refinery. The cost to supply potable water was significantly greater than the treatment and conveyance costs for the reclamation project.
	Wafer Fabrication Plants, Singapore	UPW produced from reclaimed water with consistent levels of TOC was substituted for surface water that had wide variations in the level of organic carbon that caused problems or the UPW system.
IV. Groundwater management	WF 210, Orange County, California	Reclaimed water is injected into a potable aquifer to prevent ingress of seawater into the groundwater basin. The reclaimed water is also used to recharge the ground water basin.
V. Augmenting surface waters	Republic of Singapore	Use reclaimed water to augment the island's drinking water reservoirs, thereby reducing the dependence on importation of fresh water.

Source: [85].

treatment facility is dosed with sodium hypochlorite, which combines with ammonia present in the feed to form chloroamines to control membrane fouling. The pre-treated water flows to a MF unit that clarifies the feed water by removing suspended solids, colloidal particles (partially) as well as bacteria and protozoa and lowers the turbidity to less than 0.1 NTU. The MF membranes are hollow fibres with nominal pore size of 0.2 μm. The MF permeate flows to the RO unit, which removes salts, very fine colloids, and any trace bacterial and viruses. The RO permeate is treated by a 254-nm UV light for disinfection.

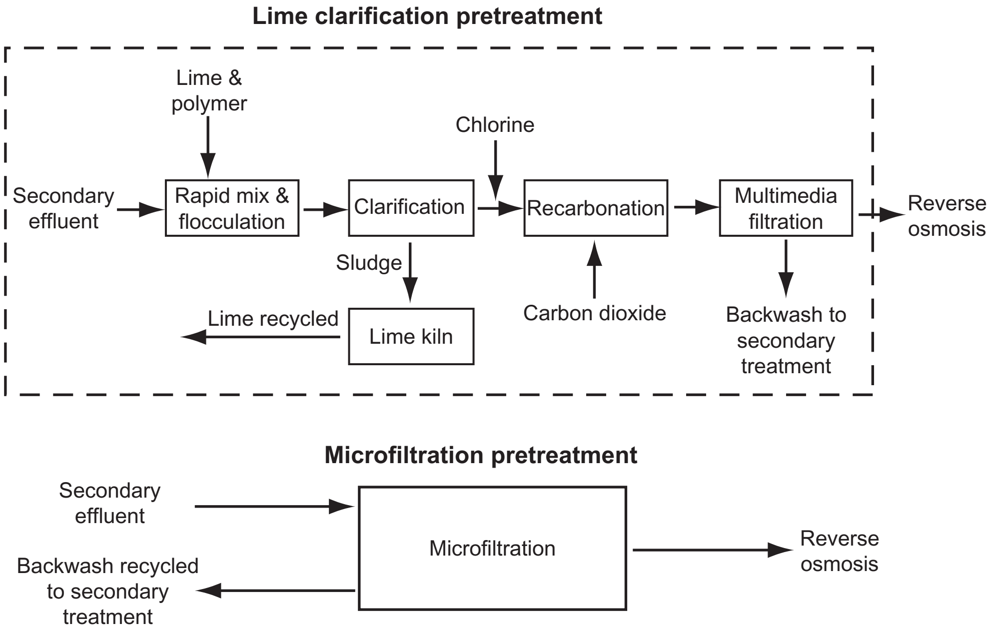


Figure 3.47 Process flow schematic of a MF-RO membrane system water reclamation plant. *Source: [87].*

The quality of reclaimed water from secondary treated sewage is comparable to the potable water supply from the data in Table 3.12. Although the type of RO membranes is not revealed, most likely it is low-fouling TFC membranes (spiral wound, 20 cm × 100 cm nominal element) with neutral or hydrophilic surface. These membranes are less prone to fouling due to their lower affinity to adsorption of dissolved organics and bacterial growth. The reclaimed water proved to be a reliable source of feed water for the UPW plant.

Case study II. Secondary treatment sewage effluent at a paper and fibreboard manufacturing plant is reclaimed to provide boiler feed water to a 2640 megawatt (MW) power plant in New South Wales, Australia [87,90]. The membrane system is of the dual-membrane type – MF and RO. The MF membranes are hollow fibre polypropylene (PP) with a nominal pore size of 0.2 μm. The RO membranes are spiral-wound cellulose acetate (CA) polymer based. Pre-treated wastewater free of oil and grit is pumped to the MF system at 210 m^3/h, as shown in Figure 3.48. The MF permeate is dosed with sodium hypochlorite to control biological growth. Sulphuric acid (4%) is added to reduce the pH and provide optimal operating conditions for the CA membranes (pH = 5–6 operating range). Next, an anti-scalant is added upstream of the 5.0 μm cartridge filter before water flows to the high-pressure RO pump. The RO permeate flows to a degasifier to remove dissolved carbon dioxide and raise the pH to seven. Degasified

Table 3.12 Water analyses of membrane-treated wastewater and potable water

Parameter	Membrane-treated water	Potable water
pH	7.0–7.5	8.0–8.75
Conductivity, μS/cm	100–180	120–160
TOC, ppm	0.05–0.15	1.0–1.5
Ions (mg/l)		
Calcium	0.01–0.02	10–15
Magnesium	<0.03	<0.1
Sodium	15–20[a]	2–3
Boron	0.02–0.08	0.02–0.05
Chloride	8–10	8–10
Sulphate	<0.045	15–20
Phosphate	<0.08	<0.08
Silica	0.6–0.7	3–4

[a] After caustic dosing.
Source: [89].

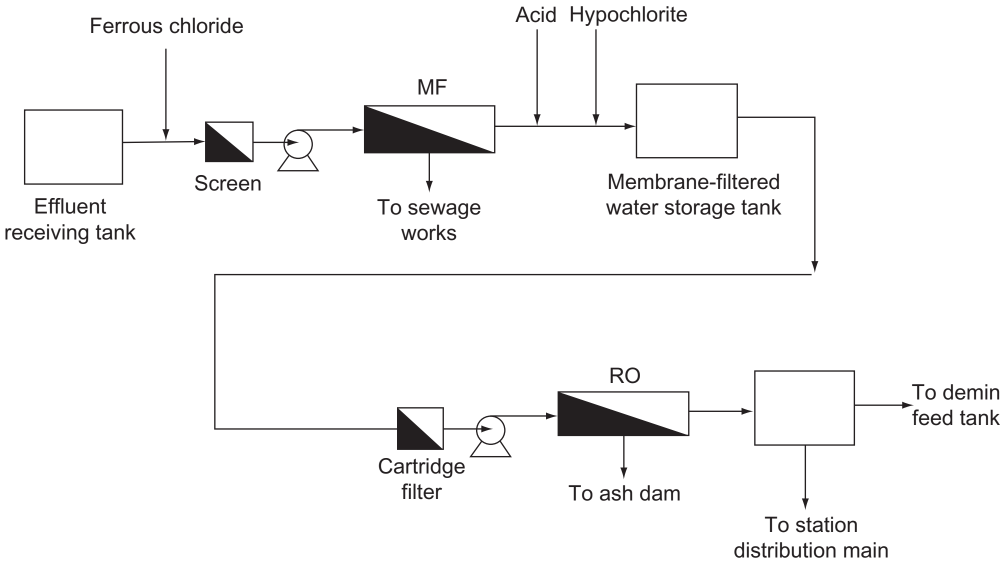


Figure 3.48 City of Los Angeles hybrid membrane water recycling plant flow schematic. *Source: [90].*

water flows to a MBIX deioniser, producing high-purity water for the power plant steam generators. The RO reject is dosed with ferrous chloride before it flows to a wastewater processing plant prior to disposal.

The MF unit consists of two parallel trains containing 90 modules per train with a total membrane area of 2700 m^2. The MF system operating conditions are 90% product water recovery, 212 m^3/h feed water supply and 4.5 bar g feed pressure. The average membrane flux is 72 lmh. Membrane fouling is controlled by backflushing the MF modules every 15–60 min. The MF membranes are cleaned with caustic soda (1%) every 200 h. Membrane integrity is monitored with the aid of an automatic pressure decay test every 24 h. The MF permeate SDI was routinely <2, surpassing the normal level of three for RO feed water.

The RO system consists of two single-pass parallel trains. Each train is a two-stage (10:6) array. The RO system is designed to supply 160 m^3/h permeate. The operating conditions are 80% product water recovery, 160 m^3/h product water supply and 15 to 35 bar g operating pressure. The average membrane flux is 22 lmh. The salt rejection was 98% with the permeate TDS equal to 50 mg/l, BOD less than 1 mg/l and turbidity less than 0.1 NTU. The main problems were manganese fouling of MF membranes and organic fouling of RO membranes. Manganese fouling was addressed by using citric acid and organic fouling was corrected by adjusting the chlorine level in feed water. Annual savings in operating costs were reported to be in the range of $800,000 [90].

Case study III. One of the water reclamation projects listed in Table 3.11 is located in the West Basin Municipal Water District (WBMWD) in southern California. The facility was built in 1995 to address acute water shortages in southern California. The El Segundo water recycling plant reclaims 4700 m^3/h of municipal wastewater from Los Angeles's Hyperion wastewater treatment plant, producing several different water qualities of water, as shown in Figure 3.48 [90]. The plant has gone through a series of modifications and expansions since it was completed in 1995; for example, prior to the first-phase expansion in 1996, the secondary effluent for ground water restoration was treated in a 790 m^3/h conventional pre-treatment system similar to the one shown in Figure 3.48. The treatment facility was expanded using hollow fibre MF membranes instead of conventional treatment. The 390 m^3/h MF-RO integrated membrane system is also shown in Figure 3.48. Thus, 1180 m^3/h combined purified water is injected into the ground to prevent seawater intrusion into the groundwater aquifer at 50% of the cost of conventional pre-treatment. The operating pressure is 15–35 bar g. The average membrane flux is 35 lmh. The filtered water turbidity is less than 0.1 NTU and SDI less than three, which exceed RO membrane feed water quality requirements. The pressurised MF membrane modules (Memcor® CMF) are backwashed every 18 min and chemically cleaned every 2–4 weeks.

The RO system consists of a single-stage array containing 108 pressure vessels with seven CA membrane spiral-wound elements (20 cm × 100 cm nominal) operating at an average flux of 17 lmh. One year after the plant came on-line, the CA membranes were replaced with polyamide TFC membranes, reducing the energy consumption by nearly 50%. The RO system product water recovery is quite high ~85%, and the TFC membranes reduce the TDS from 800 mg/l water to less than 20 mg/l. The membrane cleaning interval typically is 1–2 months.

In 1997, the plant was further expanded to purify the tertiary treated water for the boiler feed IX system at a local oil refinery, as shown in Figure 3.49. The MF-RO system treats tertiary effluent, producing 500 m^3/h re-purified water. Tertiary treatment includes ferric chloride, coagulation, flocculation, granular media filtration and chlorination. The RO system consists of four trains with 35 pressure vessels, and each vessel houses six TFC membrane, spiral-wound elements (20 cm × 100 cm nominal) in series. According to the WBMWD operating data, tertiary effluent reduces membrane fouling and increases the intervals between chemical cleanings significantly; the MF membrane cleaning interval increased to 3 months from 2 to 4 weeks, whereas the RO membrane cleaning interval increased sixfold in 6–9 months. The success of this plant resulted in similar MF-RO plants built at two more local refineries, as shown in Figure 3.49, using

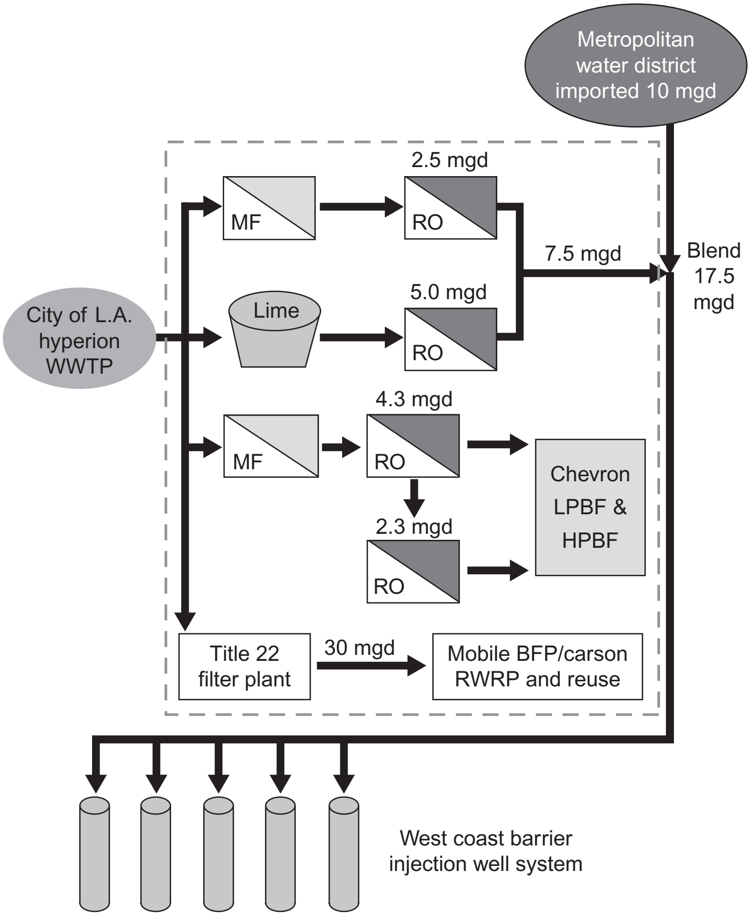


Figure 3.49 Simplified RO pre-treatment with MF instead of lime clarification. *Source: [90].*

submerged MF (Memcor® CMF-S) membrane modules. Total capacity using the MF-RO integrated system is to be expanded to 1.8×10^6 m^3/d by 2020.

Case study IV. In another application of membrane filtration for water reuse, a tubular cross-flow MF membrane system was installed to reclaim and reuse 70% of the RO reject from the make-up RO system that treats industrial wastewater at a General Motors plant in northeast Mexico [90]. The only source of water in this desert region is an aquifer, which is also the only source of drinking water for the local community. The need to conserve water was, therefore, paramount.

In this MF-RO integrated membrane system, the reject from the primary RO (PRO) system is mixed with media filter backwash and the IX system regeneration (backwash and rinse water) wastewater. The combined wastewater is treated with magnesium chloride in a contact reactor to precipitate silica. Soda ash and lime are added to precipitate calcium hardness as calcium carbonate and magnesium as magnesium hydroxide. The precipitates and particles are removed in a cross-flow tubular MF membrane unit, producing filtered water with a SDI of less than three. The 0.1 μm pore size (nominal) MF membranes are PVDF cast on the inner surface of a porous polyethylene tube. The operating conditions are 1.5–2.5 bar g feed pressure and 5100 lmh average flux. The MF membranes are backwashed periodically with plant air every 18–30 min, and the chemical cleaning frequency ranges from 2 to 4 weeks. Chemical cleaning is a two-step process; cleaning with sodium hypochlorite to remove bacteria followed by hydrochloric acid cleaning to remove hardness scale. The MF filtrate flows is desalinated by RO.

The secondary RO (SRO) system consists of two trains operating in parallel. Each unit is a three-stage (5:2:1) array operating at an average flux of 20 lmh. The high quality of the MF filtrate ($SDI < 3$) made it possible to operate the SRO units at 85–90% product water recovery. The SRO permeate is adjusted for pH with HCl and blended with the PRO feed water or used as potable water in the automotive plant.

3.4.2 Municipal water application

Low-pressure MF/UF membranes are very effective in removing microbiological parasites, *Giardia* and *Cryptosporidium* and are being increasingly used in many municipal water treatment plants. Membrane filtration is a highly effective barrier technology against suspended solids, colloidal particles, cysts and bacteria producing treated water with very low turbidity (0.1 NTU) and consistent quality irrespective of the feed source, as discussed in Chapters 1 and 2.

Design data of six select MF/UF drinking water plants are summarised in Table 3.13 [91]. The data is based on an exhaustive study covers treatment objectives, membranes, pressurised and submerged MF/UF units, dead-end and cross-flow MF membrane systems, operating conditions, membrane flux, required pre-treatment and post-treatment,

Table 3.13 Design data summary of select MF/UF municipal water treatment plants

Item	Bendigo – Australia	Ennerdale – UK	San Patricio, Texas	Minneapolis – USA	San Antonio, Texas	CCK – Singapore
Total capacity	126,000 m^3/d	59,000 m^3/d	30,000 m^3/d	265,000 m^3/d	34,000 m^3/d	182,000 m^3/d
Source water	Surface – aqueduct, reservoir	Surface – shallow lake	Surface – 60% river, 40% reservoir	Surface – Mississippi River	Surface – Medina River (> 2000 NTU)	Surface – reservoirs
Important issues	Organics	Algae bloom	High TOC, hardness, alkalinity & turbidity	Variable feed quality – alkalinity, organics	Pre-filter clogging	High TOC, turbidity, algae and colour
Treatment objective	Organics removal, pH control, low turbidity	*Cryptosporidium* 4-log removal	Removal of *Giardia* & *Cryptosporidium*	Drinking water	*Cryptosporidium* removal	Pathogen, algae & TOC removal
Membrane system/ type	Submerged – MF	External – MF	External – MF	External – UF	External – UF	Submerged – UF
Operating mode/ flow direction	Semi-continuous dead-end; O-I flow	Semicontinuous dead-end; O-I flow	Cross-flow w/ 10% recycle; O-I flow	Semicontinuous dead-end; I-O flow	Cross-flow or dead-end; I-O flow	Semicontinuous dead-end; O-I flow
Design flux	60 l/m^2/h	160 l/m^2/h at 16°C	99 l/m^2/h at 20°C	97 l/m^2/h	115 l/m^2/h at 20°C	68 l/m^2/h
Feed pressure	<1 bar g	2 bar g	2–3 bar g	2–3 bar g	2–3 bar g	<1 bar g
TMP	–	<1 bar	~1 bar	–	<1.5 bar	5–18 in Hg
Filtrate recovery	95%	~90%	94–96%	~90%	90–95%	>95%
Membrane pore size	0.2 μm	0.2 μm	0.1 μm	0.02 μm	0.01 μm	0.04 μm
Membrane polymer	PVDF; hydrophobic	PVDF; hydrophobic	PVDF; hydrophobic	PES-PVP blend; hydrophilic	CA – hydrophilic	PVDF; hydrophobic
No. of modules; module dimensions	8 cells, 576 modules/cell	17 primary units	6 trains, 50 modules/ train; Module 15 cm × 200 cm, 50 m^2 area	28 PVs, 4 modules/ PV; Module 20 cm × 150 cm, 35 m^2 area	7 trains, 48 modules/ train; Module 30 cm × 120 cm, 55 m^2 area	8 trains, cassettes/ train; 2790 m^2 total membrane area

Membrane supplier	Memcor (USFilter/ Siemens)	Memcor (USFilter/ Siemens)	Pall	Norit	Aquasource	Zenon
Integrity testing	Daily PDT	Weekly PDT	Daily PDT	Daily water displacement test	Weekly PDT	Daily PDT
Pre-treatment	ACH coagulation, lime, CO_2	30 μm drum screen	ClO_2, coagulation-flocculation w/ alum	PAC, $KMnO_4$, alum, lime, $FeCl_3$, Cl_2, NH_3	PAC, H_2SO_4, $FeSO_4$	Cl_2, alum coagulation, polymer, sand filter
Post treatment	Ozone, GAC	NaOCl; pH adjust w/NaOH; o-phosphate	Cl_2, NH_3, F, orthophosphate Zn	Cl_2, NH_3, F, polyphosphate	NaOCl, NH_3, F	Cl_2, NH_3, F, lime, CO_2
Product quality	<0.1 NTU	No *Cryptosporidium*	3-log virus inactivation	4-log removal	Drinking water	<0.1 NTU
Year commissioned	2002	1999	2000	2005	2000	2007
Costs	–	–	Memb. Equip.: \$2.8 M Opex: \$0.678 M/yr	Plant Capex: \$58 M Opex: \$3.1 M/yr	Memb. Equip.: \$3.8 M Water cost: \$0.334/m^3	Plant Capex: \$19.5 M
Special features	–	Secondary MF treats primary MF backwash	Cl_2 tolerant membrane (5000 ppm Cl_2)	500 ppm Cl_2 tolerance	200 ppm/d Cl_2 tolerance	–

ACH: aluminium chlorohydrate; GAC: granulated activated carbon; PAC: powdered activated carbon; PDT: pressure decay test; TMP: trans-membrane pressure; PV: pressure vessel; O-I: outside-inside; I-O: inside-out; CA: cellulose acetate; PES: polyether sulphone; PVP: polyvinylpyrrolidone; PVDF: polyvinylidene fluoride. *Source:* Based on [91].

plant capacities, and costs. For specifications of major commercial MF/UF products, refer to Table 6.14.

Case study I. The NEWater Factory in Kranji, Singapore, built by USFilter/Siemens WT in 2002, is perhaps the most famous wastewater recycling plant in the world, known for producing "new" water for drinking from treated sewage wastewater [86]. The plant was built to meet Singapore's critical water demands. The wastewater is purified in three steps:

- First, the treated wastewater is pumped through hollow fibre MF membranes (pore size 0.2 μm) in pressurised Memcor® CMF modules. Every 25–30 min the microfilters are cleaned backwashed; the residue or cake formed on the membrane surface is first loosened by air scouring and then flushed away during backwash.
- Second, the MF filtrate is purified by low-pressure RO membranes to remove salts, any traces of pesticides and other chemical compounds.
- Third, the desalted water is disinfected by 254 nm UV lamps to destroy any bacteria and biological compounds.

The plant produced 18,200 m^3/d potable water in 2003. The process was so successful that plant capacity was expanded to 273,000 m^3/d in 2013 with submerged membranes (Memcor® CMF-S). The product water meets the drinking water standards of the World Health Organisation (WHO) and the US Environmental Protection Agency (EPA). About 1% of the NEWater flows to the drinking water reservoir and the rest is used for manufacturing plants, e.g., semiconductors. Previously, the sewage plant used conventional treatment and transferred the wastewater to sea. Currently, NEWater meets 30% of Singapore's water demand. The current NEWater capacity will eventually be tripled to meet 55% of Singapore's future water demand. Given the limitation of used water catchment and water reclamation in the small island nation, it is exploring the possibility of increasing the rate of recovery in the RO process in order to boost NEWater production [86].

Case study II. The desert community of Scottsdale, Arizona does not have natural surface water sources and the groundwater supply is decreasing. Historically, the community treated and disposed of its wastewater. As the city grew, disposal of wastewater became uneconomical for several reasons: (i) the sewerage system would require upgrading, (ii) water lost from the city would have to be replaced at a further treatment cost, and (iii) the city was spending money for disposing treated wastewater. To overcome these concerns, the city selected a MF-RO treatment system to treat tertiary effluent and use it for groundwater recharge, which earns credits from the state for withdrawing water from the aquifer. Reclaimed tertiary effluent not used for irrigation is treated by MF and RO and then recharged to the aquifer. Colorado River water treated by MF alone is also recharged. The advanced water treatment facility is described below [92]:

- The MF system consists of 24 units containing 90 pressurised Memcor® CMF modules (membrane pore size = 0.2 μm), each with a capacity of 70,000 m^3/d filtrate.

There are four MF trains of six units each: two/three trains treat tertiary filtered water, which has been nitrified/denitrified, and one/two trains treat the river water. The wastewater effluent is chlorinated upstream of the tertiary filters for algae control. Ammonia is injected upstream of the MF units to ensure the water has a residual. The MF filtrate turbidity is 0.1 NTU and SDI is 1.2. Since the MF filtrate is virtually free of particles, it can be directly recharged to the aquifer. The product water recovery is ~90%.

The design flux is 70 lmh when treating Colorado River water and 95 lmh when treating tertiary effluent. The flux is higher when treating effluent for several reasons: (i) effluent stream is up to 10°C warmer than surface (river) water, (ii) turbidity is lower than river water, and (iii) effluent has a chloramine residual that minimises biological fouling. Backwash is every 15–30 min with chemical clean-in-place (CIP) every 2–4 weeks depending on the feed water; for example, the MF units treating river water and operating at the effluent water flux are cleaned monthly. The MF units operate at a Pressure Decay Test of <1.4 kPa/min and LRV ~ 4.5.

The integrity of the membrane system is normally tested by a pressure decay test (PDT), as discussed in Chapter 1. The results of PDT are needed for the plant operator to know the actual log reduction value (LRV) of the plant. The calculation is generally based on the ASTM D6908-6906 method; the air flow in an integrity test is compared to the air flow through a complete membrane breakage. The PDT is sensitive enough to be able to detect a single broken membrane in even the largest membrane racks and that a 4-LRV can be guaranteed as long as the pressure decay rate is within the specified range.

The RO system consists of 14 trains with each train rated for a flow rate of 5300 m^3/d at 85% recovery. Each train is a three-stage (24:10:5) array containing 156 8832-HR TFC Magnums (Fluid Systems), i.e., four 20 cm × 100 cm spiral-wound membrane elements per pressure vessel. The flux is 17.7 lmh (nominal). Since RO feed water is hard and alkaline, it is treated with sulphuric acid and anti-scalant to prevent scaling.

Case study III. The Western Corridor Recycled Water (WCRW) project in Queensland, Australia was completed in 2009–2010 – one of the largest advanced water recycling projects in the world, it provides up to 232,000 m^3/d of high quality recycled water for industry, irrigation and indirect potable reuse [93]. It includes three advanced water treatment plants (AWTPs), which reclaim wastewater from six existing wastewater treatment plants: Bundamba plant, the largest (100,000 m^3/d), treats effluent from four wastewater treatment plants at Bundamba, Goodna, Wacol and Oxley; the other three plants treat secondary effluent from the Luggage Point and Gibson Island wastewater treatment plants. The Bundamba AWT plant was the first large facility designed to meet stringent nitrogen, disinfection and emerging contaminant quality parameters.

The wastewater constituents of all the waters fall in the range of TSS = 2–20 mg/l, Turbidity = 2.3–14 NTU, BOD = 2–12 mg/l, TOC = 11–40 mg/l, TDS = 490–1200 mg/l, Total nitrate as N = 3.3–26.4 mg/l, Ammonia as N = 0.6–13.7 mg/l, Total phosphorous as P = 1.9–12.4, Manganese = 0.02–0.5 mg/l, and Alkalinity as $CaCO_3$ = 140–240 mg/l. The main treatment steps are UF and RO, followed by advanced oxidation using UV and hydrogen peroxide.

- Preliminary treatment comprises chloramination, coagulation and pH adjustment. A chloramine residual of 1 ppm minimises bio-fouling of the MF membranes. Mono-chloramine is formed by controlled addition of chlorine and ammonia. Ferric chloride is added to expedite flocculation and allow materials to be removed by the UF membranes. The pH is controlled to remove phosphates to minimise RO fouling.
- Membrane filters are Memcor® CMF. Trans-membrane pressure (TMP) and flux are maintained by regular – every 30 min – air-scour "backwash." Eventually, TMP increases over time (normally about 30–35 days) due to particulate and biological fouling. When the TMP reaches 1.5 bar, the membranes are cleaned with chemicals using solutions of sodium hypochlorite and/or citric acid sequentially. The membrane flux is 44 lmh and the MF filtrate has a SDI value of 3 to 4 and turbidity 0.1 to 0.2.
- The RO membrane modules are 45 cm (18 in.) in diameter (Koch). The RO system is a three-stage array (7:4:2). Each RO skid is rated for 7500 m^3/d permeate. The treated water quality guarantee for nitrogen is 1.2 mg/l, which was specified so as not to add nitrogen to the receiving lake. Hence, high rejection membranes were chosen, with nitrate reduction of about 85% along with ammonia rejection of about 90%. The RO feed pressure is, therefore, higher as compared to other BWRO applications. Since the RO permeate is aggressive, it is remineralised with calcium carbonate and CO_2.
- Advanced oxidation – 254 nm bacteria destruct UV and H_2O_2 – is done when the reclaimed water is discharged to lakes and other surface water bodies. Hence, it must contain minimal levels of pathogens and trace organics and be protected against emerging contaminants. Guidelines for water recycled to a drinking water source area 1-log reduction in nitroso dimethyl amine and a 0.5-log reduction of 1,4 dioxane.
- RO reject (concentrate) contains nutrients and solids: nitrate = 27 mg/l, phosphorous (as P) = 7 mg/l, TDS = 6400 mg/l and TSS = 30 mg/l. In order that the instantaneous nutrient and suspended solids loads in the receiving rivers do not exceed the stringent environmental limits, RO reject water undergoes biological treatment to achieve the following nutrient and suspended levels on a 50 percentile basis: nitrate as N = 1 mg/l, phosphorous as P = 4 mg/l, and TSS = 10 mg/l.

3.4.3 Submerged membrane filtration

In submerged membrane filtration, UF/MF membrane modules are immersed in water in an open tank [94,95]. Water permeates the membranes under a small trans-membrane pressure (TMP), typically <1 bar, and is withdrawn from the fibre bore by the permeate pump. Polarisation control is by backwash and/or two-phase air bubbles, depending on the module geometry and type of feed. The membranes are either flat-sheet or hollow fibres. The membrane pore varies between 0.01–0.1 μm for hollow fibres to 0.2–0.4 μm for flat-sheet membranes. Membrane properties and module design specifications are given in Table 6.13.

Submerged membrane filtration (sMF) is an extension of the pressurised MF/UF (pMF) filtration, as discussed in Chapters 1 and 2. It has evolved rapidly since the early 1990s. Examples of submerged membrane units are shown in Figure 3.50. Submerged MF is designed for large wastewater treatment plants. For example, long-term testing of the pMF and sMF technologies at Orange County Water District Water Factory 21 (OCWD WF21) demonstrated the cost-saving benefits of sMF for large water treatment plants. The sMF process has several advantages over pMF based on field experience [94]:

- Reduced footprint – Space requirement for sMF is 50% less than the pMF
- Reduced complexity – 80% reduction in peripheral equipment
- Reduced costs – 10–15% reduction in operating costs and 20% reduction in capital costs

Submerged membrane modules became prominent in the water industry because [95]:

- Dead-end filtration was suited for low solids feeds, whereas bubbled cross-flow was suited for more fouling feeds
- Acceptance of modest fluxes and low TMPs

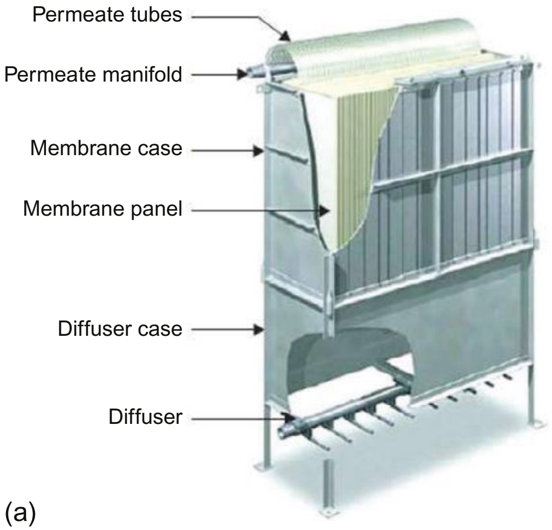


Figure 3.50 (a) Kuboto submerged flat-sheet membrane unit. *Source: Ultrapure Water.*

(Continued)

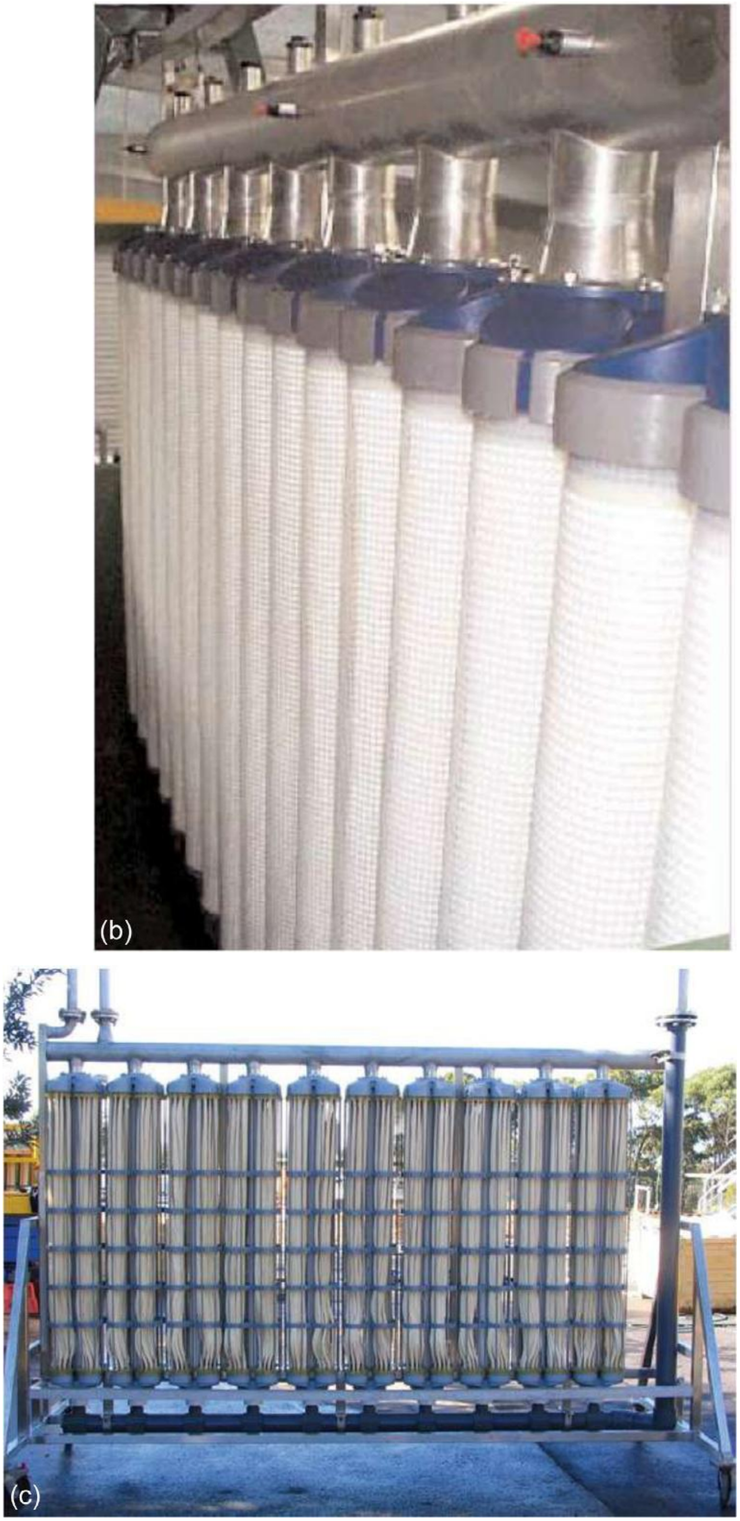


Figure 3.50—cont'd (b) Memcor® submerged hollow-fibre membranes modules. *Source: USFilter*. (c) Memcor® submerged hollow-fibre MBR unit. *Source: USFilter*.

- Energy consumption is a fraction of that in cross-flow systems: 0.05–0.1 kWh/m^3 for sMF, 0.1–0.2 kW/m^3 for pMF, and 2.5–3.0 for x-flow MF (see Table 5.2).
- sMF membranes can achieve a superficial velocity (m/h) 10 times higher than in sand filters and produce a far superior quality water

A typical sMF system consists of one or more membrane module cells and the peripheral equipment including filtrate pumps, blowers, air supply system, a clean-in-place (CIP) system and a control system. Multiple cells are grouped in "trains," typically up to ten cells per train. Each cell in a train shares peripheral equipment and communications system for monitoring and control. Larger systems are split into multiple parallel trains. The submerged membrane modules are attached to a filtrate (clean water) manifold, as shown in Figure 3.50 [94]. A process flow sheet of a sMF system is shown in Figure 3.51. During the normal filtration cycle, the feed enters the bottom of each cell via a central feed channel and passes over and around the membrane. The feed water surrounds the multiple membrane modules and the hundreds of thousands of individual hollow membrane fibres within the modules. The flow is drawn through the walls of the membrane fibres (outside-in flow) by vacuum to the inside of the fibre (lumen). Filtered water then exits via the top of the module through the clean water manifold.

The PLC (programmable logic control) controlled membrane unit is cleaned periodically by permeate backwashing based on TMP to maximise the interval of chemical cleanings. At the end of the liquid backwash cycle, air is introduced at the base of the modules to scour the membranes to loosen the dirt and debris from the surface of the membrane fibres. To facilitate scouring and debris removal of the fibres inside the modules, air is introduced within the base of the modules through a series of air connections in the bottom manifold. As the air continues to loosen the dirt on the surface of the

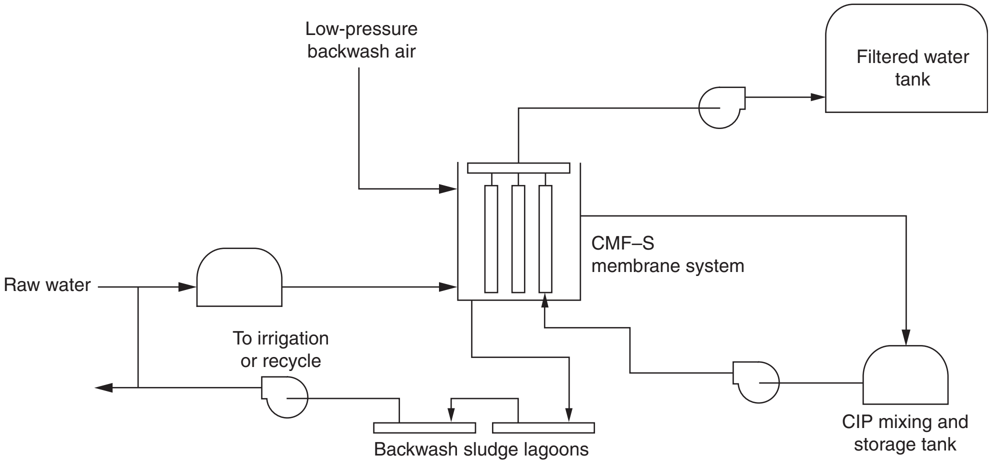


Figure 3.51 Submerged membrane system process flow sheet. *Source: USFilter.*

membrane fibres, clean, filtered water is back-fed from the inside of the fibres. This operation assists in the flushing of debris from the membrane outside surface. The entire backwash sequence takes 2–3 min.

Case study I. The Bendigo water treatment plant (WTP) (Table 3.13) in central Victoria, Australia produces drinking water for nearly 110,000 people. Drought conditions had severely impacted Coliban Water's catchments and, therefore, an alternative secure water supply was needed. When commissioned in mid-2002, the Bendigo WTP was the largest submerged membrane (Memcor® CMF-S) plant in the world with a maximum capacity of 126,000 m^3/d [96]. Larger plants have been built since then including the 273,000 m^3/d sMF Zenon plant at Chestnut in Singapore [95]. The minimum requirements were removal of 2.0–5.0 μm particles, 4-log reduction for *Cryptosporidum*, and reliable removal of organics including algal toxins, colour, taste and odour compounds. Thus, the main objectives of the plant are clarification and disinfection.

Raw surface water has variable colour, turbidity, alkalinity and metals concentration. The plant combines sMF, ozonation and biological activated carbon (BAC). Raw (surface) water is pre-screened and dosed with lime and carbon dioxide in a contact reactor to control alkalinity and corrosion. Next, water is dosed with a coagulant, liquid aluminium chlorohydrate (ACH), upstream of the membrane plant to remove colour, some organic content and dissolved metals. The coagulant dosage is typically 5–6 mg/l (ACH dosage of up to 20 mg/l did not affect performance). The coagulant precipitate is removed by MF. The coagulant/sMF process removes up to 15% of the dissolved organic carbon [96]. The MF filtrate is pumped to the ozone/biologically active (BAC) system for disinfection and to reduce the original carbon level in water, eliminating taste and odour compounds. The ozonated water flows to an ozone contactor that allows 5 min detention time at maximum plant flow. Ozone, an oxidant, disinfects and destroys algal toxins and breaks down the complex organic material to simpler forms for downstream biological treatment. Post-treatment is required since the membranes remove only about 20% of the natural organic matter.

The sMF system consists of eight cells (six on-line and two on standby), each containing 576 submerged membrane modules (Memcor® CMF-S). Water enters at the bottom of the cell and is drawn through the membranes (pore size = 0.2 μm) by a filtrate pump (one filtrate pump per cell). The cells are backwashed every 20–45 min using the filtrate and air to scrub the fibre surface. Chemical cleaning is done when the maximum TMP is reached. Membrane performance is monitored for turbidity and particle count. A daily pressure decay test is performed to check the integrity of the hollow fibres. All three plants achieved levels >7-log removal/inactivation of pathogens [96].

Case study II. Orange County Water District (OCWD) is located between Los Angeles and San Diego counties in southern California and manages the groundwater basin that supplies about 3.0×10^8 m^3 per year potable water to a population of more than 2 million. One of OCWD's best known projects is Water Factory 21 (WF21), which protects groundwater from seawater intrusion by injecting up to 56,800 m^3/d of highly treated reclaimed water blended with deep-well water into four coastal aquifers. More than half of the injected water flows inland and augments potable water supplies [97]. The injected water quality must exceed potable water quality to prevent plugging of the aquifer and prevent degradation of groundwater quality.

WF21 is an advanced wastewater treatment (AWT) facility that reclaims secondary treatment effluent. In the beginning of 1975, the AWT plant consisted of lime clarification, ammonia stripping, recarbonation, multimedia filtration, granular-activated carbon (GAC) filtration and chlorination. RO treatment was added in 1977 to reduce salts and organics in one-third of the flow stream. The 19,000 m^3/d RO plant consisted of 252 spiral-wound cellulose acetate membranes (20 cm diameter) in a three-stage array (24:12:6). The percentage of organic carbon by RO was greater than by GAC, and in 1985, ammonia-stripping towers were removed since RO reduced ammonia and nitrate concentrations by 80%. The WF21 treatment process flow schematic is shown in Figure 3.52.

In 1992, evaluation of MF for replacing conventional pre-treatment was initiated with a small pilot unit. The positive results of pilot testing with pMF (Memcor® CMF) led to the installation of a 2700 m^3/d pMF demonstration plant. The plant, consisting of MF, RO and UV disinfection was started in 1997. The RO system uses thin-film composite PA membranes, producing RO permeate that meets all the requirements of the US National Primary Drinking Water Regulations, and reduces the concentration of TOC to less than 0.1 mg/l.

Based on the success of the pMF demonstration unit, a four-module sMF (Memcor® CMF-S) pilot unit was commissioned in 1998. After 1 year of operation, the sMF demonstrated increased cleaning intervals while operating at flux equivalent to the pMF pilot and demonstration systems. In early 2000, the sMF pilot was scaled-up to a 32-module 900 m^3/d demonstration system. Both the pMF and sMF systems were operated simultaneously for a year to compare the data. The data were used to design a 23,000 m^3/d sMF system, which was installed in 2004. This system provided injection water during the construction of the 265,000 m^3/d sMF plant using Memcor® CMF-S membranes.

Case study III. In 1997, the first MF-RO plant was commissioned to reclaim secondary treatment effluent at the El Segundo recycling plant of the West Basin Municipal Water District (WBMWD) in southern California for injecting RO purified water into a seawater barrier to control seawater intrusion into groundwater. The injected water quality must exceed potable water quality to prevent plugging of the aquifer and prevent degradation of ground water quality. The original membrane filtration systems were pressurised MF (Memcor® CMF), as discussed in Section 3.4.1. As a part of Phase IV expansion, a submerged MF system (Memcor® CMF-S) was installed in 2005 for treating 44,000 m^3/d secondary treatment effluent [94].

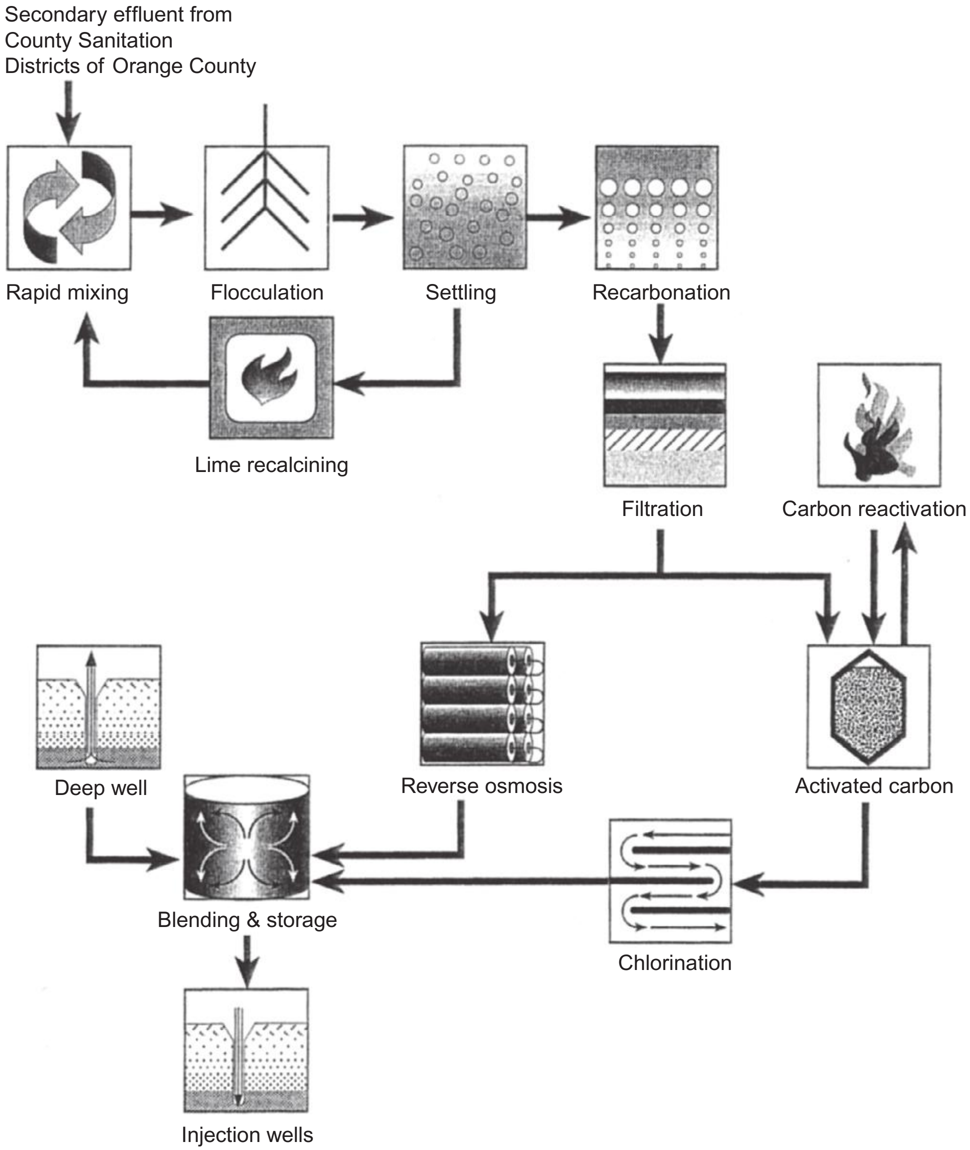


Figure 3.52 RO membrane-based water treatment system at Water Factory 21.

Similarly, a 4600 m^3/d Memcor® CMF-S system was installed at a 1200 MW coal-fired power plant in the UK when the well water source that provided feed water to the RO-IX high-purity water system was shut down. The sMF system treats surface water and cooling tower blowdown, providing filtered water to the RO-IX deionisation system with turbidity <0.1 NTU, suspended solids at the detection limit of 1 ppm and SDI <3. The MF membranes were oxidant-resistant PVDF with a pore size of 0.1 μm.

Case study IV. A 182,000 m^3/d sMF system in Choa Chu Kang, Singapore treats surface water from three reservoirs – Kranji, Pandan, and Tengeh. The feed water is high in TOC (8–15 mg/l), turbidity (up to 200 NTU), algal count (45×10^8 cells/m^3) and colour. The treatment objectives are: turbidity <0.1 NTU, removal of pathogens and algae, and TOC reduction. The potable water is designed to meet WHO Guidelines for Drinking Water Quality. The sMF system uses Zenon 1000 hollow fibre UF membranes with a pore size of ~ 0.04 μm. The filtration system consists of eight trains with a total membrane area of 2790 m^2. The operating conditions are feed pressure <1 bar g, flux ~ 68 lmh and product water recovery $\sim 95\%$ (see Table 3.13). Pre-treatment includes chlorination, coagulation and sand filtration. Post-treatment consists of chlorination, ammonia, fluoride dosage, lime and CO_2.

3.5 MBR SEWAGE AND WASTEWATER TREATMENT

3.5.1 Membrane bioreactor systems

Membrane bioreactors (MBR) are used to treat sewage and wastewaters and achieve purification with respect to biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), ammonia (NH_4^+-N), total nitrogen (N) and total phosphorous (P). The MBR technology combines an activated sludge process with biomass separation by membrane filtration. Thus, the MBR process combines a bioreactor with a membrane module each with a specific function; biological degradation of organic pollution is carried out in the bioreactor by adapted microorganisms, and separation of microorganisms in the treated wastewater is done with a membrane module [7,98–100]. The principal microsolute in the liquor is extracellular polymeric substances produced by bacteria. The primary role of the membrane is to provide a barrier against suspended solids in the mixed liquor.

There are two system configurations, as discussed in Chapter 2, immersed membranes in the bioreactor or external membranes placed outside the bioreactor. Submerged systems (sMBR) are more economical than external (eMBR) systems based on energy consumption [98]; a recycle pump is not required since aeration generates a tangential liquid flow in the vicinity of the membranes, and the operating conditions are milder than in external MBR systems because of lower values of TMP and tangential velocities at the membrane surface. Estimates for energy consumption are ~ 0.5 kWh/m^3 for sMBR and ~ 3.0 kWh/m^3 for eMBR (see Table 5.2). The membranes can be flat sheet of hollow fibres, as shown in Figure 3.50. A process flow schematic of a submerged MBR system is shown in Figure 3.53.

The MBR concept came about in the late 1960s from the conventional activated sludge system by installing MF membrane elements in the aerated tank stage. The first successful plants were installed in the mid-1990s. By decoupling the activated sludge process from the settling characteristics in conventional plants, the footprint of a wastewater

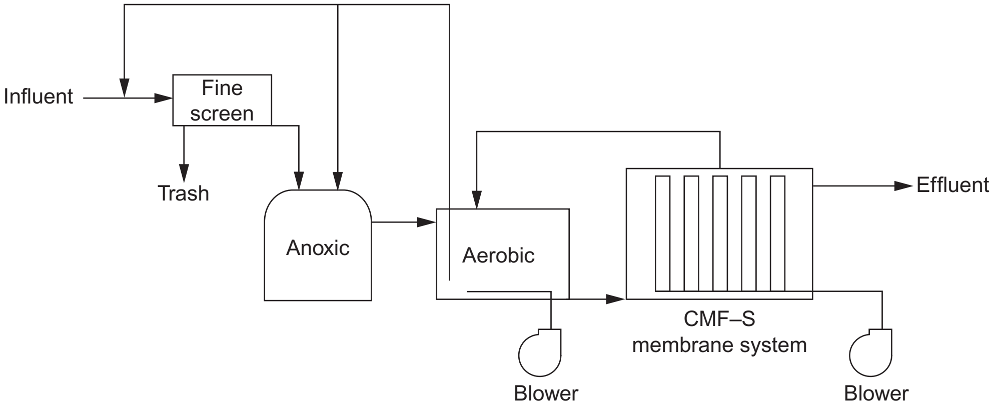


Figure 3.53 Membrane bioreactor (MBR) system process flow schematic. MBR combines biological degradation with membrane separation. Raw municipal water flows to an aerated bioreactor where the organic components are oxidised by the activated sludge. The aqueous sludge then passes through a MF or UF membrane filtration unit, separating water from the sludge. The sludge flows back to the bioreactor while the membrane permeate is discharged or reused. *Source: USFilter.*

treatment system is reduced by more than 50%. Submerged membranes prevent passage of contaminants while allowing the free passage of biologically treated water, thus eliminating the need for secondary clarification and tertiary filtration. Since the particulate solids content in the wastewaters treated by sMBR systems is relatively high (e.g. TSS = 10–15 mg/l) with additional colloids and macrosolutes, bubbled cross-flow is used to minimise concentration polarisation and subsequent fouling [95]. Aerators mounted below the membrane modules or cells release air bubbles, which rise around the membranes, creating water circulation and scouring the membrane surface, as shown in Figure 3.54.

Since membrane filtration is unaffected by sludge settleability, the activated sludge process can be optimised for biological activity by operating at very high mixed-liquor suspended solids (MLSS) concentrations (10,000 to 15,000 mg/l suspended solids), allowing the activated sludge process to treat a higher flow and load in the same tank, resulting in more complete biological oxidation [101]. Very high mean cell residence times result in higher removals of difficult-to-treat compounds such as endocrine disrupters.

Application of an integrated MBR–RO process is not uncommon [7,102]; for example, desalting of mixed tannery effluents for irrigation purposes. RO membrane reduces the salt content of tannery effluents significantly. Unfortunately, the high organic content of the tannery effluents – high COD and BOD – results in rapid scaling and biofouling of RO membranes. The MBR pre-treatment reduces biofouling and scaling of RO membranes, resulting in much improved overall performance. MBR using polyether sulphone

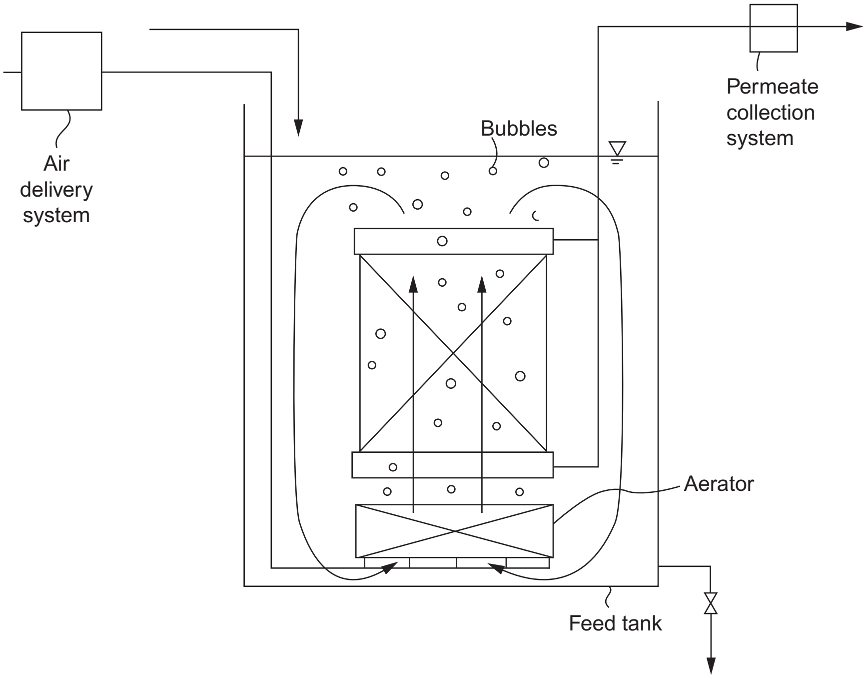


Figure 3.54 Schematic of the aeration process in a submerged MBR.

UF membranes with a MWCO of 100,000 Da was highly effective in removing organic pollutants and suspended solids prior to RO desalination [102].

3.5.2 Applications of MBRs

Since the first commercial plants were installed in the mid-1990s there has been a rapid growth in the application of MBRs. By 2008, more than 2000 units had been installed for treatment of sewage and wastewater [91,95]. At the same time the capacity of the MBR plants has grown. One of the largest MBR plants in the world, capable of treating up to 100,000 m^3/d of sewage per day, was built in Muscat, Oman in 2013–2014. The plant deployed flat-sheet Kuboto submerged MBR units to degrade organic matter and remove solids, including harmful bacteria, and use reclaimed water for irrigation. Because of acute water scarcity in the region, countries are increasingly deploying MBRs to reclaim water for non-potable applications such as irrigation instead of energy intensive seawater desalination [103].

Case study I. In 2007, two of the largest MBR plants in the world for treating landfill leachates were built in Istanbul, Turkey. The capacities are 1200 m^3/d (Plant A) and 2000 m^3/d (Plant E) [104]. The plants use external MBR systems (Norit X-flow UF) to treat waters with high COD (20,000 mg/l), BOD (13,000 mg/l), TSS (1500 mg/l) and nitrogen (3000 mg/l). The leachate is also high in TDS (25,000 mg/l), alkalinity (13,000 mg/l as $CaCO_3$) and hardness (2500 mg/l as $CaCO_3$). The hydraulic retention time of plants A and E is 16.7 and 9 days, respectively. The MLSS values are 8–15 g/l. The eMBR effluent constituents are:

- Plant A: COD = 125 mg/l, BOD = 50 mg/l, Total N = 400, TSS = 35
- Plant E: COD = 800 mg/l, Total N = 100, TSS = 350

The MBR effluent is treated with NF membranes to remove residual COD and heavy metals, thus making it possible to discharge the treated water into the Black Sea. The NF system water recovery is 90%.

Case study II. A milk processing MBR effluent plant (Kuboto, sMBR, flat-sheet, Model ES150) in Ballyragget, Ireland was commissioned in 1999. The MBR system was used to upgrade the existing industrial effluent treatment plant. The plant consists of 80 × 150 membrane units with a flow of 7100 m^3/d and membrane surface area = 9600 m^2. Due to the nature of the incoming effluent, chemical cleaning is more frequent than municipal effluent treatment plants [105]. The MBR effluent quality is Total N < 15 mg N/l; P < 0.6 mg P/l; and BOD < 10 mg/l. The feed wastewater quality is BOD load = 16,000 kg BOD/d; COD load = 24,850 kg COD/d; Total ammonia load = 185 kgN/d; and MLSS = 12,000–18,000 mg/l. The membrane units are in a modular arrangement of eight steel aeration tanks, operated in two groups of four tanks. The plant control is achieved by allowing the level to vary within the aeration tanks in proportion to the incoming flow. The units are housed outdoors in open aeration tanks. There is no odour.

Case study III. The food processing plant in St Mary's, Ontario discharges to a municipal wastewater treatment works and must meet the limits for BOD (300 mg/l) and TSS (350 mg/l). The mean influent COD and BOD concentrations are 400 and 5500 mg/l, respectively. The wastewater also includes oil and grease [98].

Wastewater is pumped to a dissolved air flotation (DAF) unit to remove free oil, grease and solids. The DAF effluent is pumped to the bioreactor tank. A coarse bubble diffuser grid distributes air in the bioreactor. Caustic soda and phosphorous are added to the biological process if needed. The bioreactor mixed liquor flows to a tank that houses the sMBR (Zenon, ZeeWeed® membranes). The ZeeWeed® tank contains two ZeeWeed® 500c cassettes with 12 modules in each cassette, providing a total membrane area of 557 m^2. The membranes are air-scoured. A centrifugal pump extracts the permeate from the sMBR by applying a slight vacuum. Mixed liquor in the membrane tank is returned to the bioreactor at 5 × the feed flow rate to ensure a uniform concentration between the two tanks (~10–15 g/l). Citric acid and NaOCl are used for cleaning the membranes. Waste-activated sludge is discharged to a filter press for dewatering. The design capacity of the system is 150 m^3/d. The membranes operate at a flux of ~12 lmh. Backpulsing is for 30 s every 10 min. The TMP is maintained between 0.14 and 0.44 bar with an average of 0.17 bar. CIP cleaning is twice weekly, with injection of a 200 mg/l NaOCl hypochlorite solution during backpulsing for a duration of

1 h. The MBR effluent quality is COD < 145 mg/l, BOD < 20 mg/l, and TSS < 1 mg/l. Waste sludge is dewatered in a filter press and then transported to a landfill.

Case study IV. The MBR plant in St. Austell, Cornwall, UK treats up to 40 m^3 of effluent per day [98]. The effluent is composed of sewage, biocompostor effluent and storm water. The MBR system is eMBR (Millenniumpore, MT). The wastewater COD is 120–780 mg/l. The eMBR unit is a cylindrical bioreactor tank fitted with two vertically oriented PVC-housed MBR modules, 22.5 cm diameter × 1.2 m long. The reactor capacity is 4 m^3 and the membrane area is 8.6 m^2 per module. The membrane pore size is 0.05 μm. The flow rate is ~70 m^3/h, yielding a mean cross-flow velocity of 2 m/s at a TMP of ~0.8 bar. The average operating flux is 16.5 lmh (30 lmh max). The specific energy consumption is 1.8 kWh/m^3 for the membrane unit. The MLSS is maintained at 12–15 g/l.

Case study V. The photographic paper production plant in Tilburg, Holland discharges wastewater, which is high in dissolved organic matter; COD = 1800 mg/l, BOD = 850 mg/l, and TSS = 48 mg/l [98]. The plant is a hybrid sMBR-RO plant. The sMBR unit is Toray UNIBRANE®, flat sheet UF membranes. The biological treatment in the MBR consists of an aeration basin with separate denitrification. Aeration is achieved using disc aerators to achieve the desired dissolved oxygen level in the reactor. A third basin contains the membrane modules: 12 stacks of 135 m^2 area, each fitted with 100 flat-sheet membrane panels, and a total membrane area of 1620 m^2. The membranes are air-scoured continuously. The supernatant flows back to the denitrification basin. Residual sludge (~18 g/l) is transferred to the decanter to produce a dewatered product of 20–24% solids for recovering the silver (300–400 ton annually).

The UF unit is designed for a flow rate of 45 m^3/h with a flux of 21.6 lmh (27.8 lmh max). The membrane TMP is 15 mbar with the mean permeability ~1500 lmh/bar at 20°C. The MBR operating cycle is 8 m "on"/2 m "relaxation." CIP is with NaOCl (6 g/l solution) annually. The UF permeate is pumped to the RO system at 20–25°C. The RO unit is a three-stage (4:2:1) array with six elements per pressure vessel. The RO elements are spiral-wound 20 cm diameter (Toray SU-720). The membranes are brackish water polyamide membrane thin-film composite. The feed pressure is 11–14 bar g and the product water recovery is ~85%. The RO permeate is polished by mixed-bed ion-exchange to provide boiler feed water. The plant meets the effluent concentration limits: COD <51 mg/l, (>97% removal), undetectable TSS and <5 mg/l Total nitrogen.

REFERENCES

[1] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Holland, 1997.
[2] H. Strathmann, Membrane separation processes: current relevance and future opportunities, AIChE J. 47 (5) (2001) 1077–1087.

[3] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[4] S.K. Sikdar, J. Burckle, J. Rogut, Separation methods for environmental technologies, Environ. Progress 20 (1) (2001) 1–11.

[5] T.M. Harten, L.M. Vane, D. Szlag, Separations research in the U.S. Environmental Protection Agency, ACS Symp. Ser. 766 (2001) 222–235.

[6] J. Tanninen, L. Kamppinen, M. Nystrom, Pretreatment and hybrid processes, in: A.I. Schafer, A. G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 241–262.

[7] M. Nystrom, J.M.K. Nuortila, M.J. Manttari, Nanofiltration in the pulp and paper industry, in: A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 363–393.

[8] S.A. Holditch, Getting the gas out of the ground, CEP 108 (8) (2012) 41–48.

[9] F.-R. Ahmadun, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, J. Hazard. Mat. 170 (2009) 530–551.

[10] M. Kyburz, G.W. Meindersma, Nanofiltration in the chemical processing industry, in: A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 329–361.

[11] C. Cagle, Sustainable solutions for flowback/produced water challenges in oil and gas fields. Paper presented at the AIChE 2012 Annual Meeting, Pittsburgh, USA, November 2012.

[12] Water Desalination Report 28 (3) (2012).

[13] R. Bond, S. Veerapaneni, I. Rackley, A. Ventimiglia, W. Pack, Reverse osmosis and vapour compression brine distillation to treat a shallow brackish groundwater in Las Vegas valley, in: W.C. Lauer (Ed.), Desalination of Seawater and Brackish Water, AWWA, Denver, 2006, pp. 151–167.

[14] IDE Thermal Desalination Solutions, Mechanical Vapour Compression brochure. www.ide-tech.com.

[15] M. Bradford, I. Buchanan, I. Moore, Refinery and heavy oil production wastewater recycle and reuse, Proceedings 70th International Water Conference, Orlando, USA, October 2009.

[16] P. Eriksson, M. Kyburz, W. Pergande, NF membrane characteristics and evaluation for seawater processing applications, Desalination 184 (2005) 281–294.

[17] T. Melin, J. Meier, T. Wintgens, Nanofiltration in the leachate industry, in: A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 395–413.

[18] P.M. Gallagher, D.L. St. Germain, Arsenic in dinking water: regulations and treatment options. Paper presented at the Third NSF International Symposium on Small Drinking Water and Wastewater Systems, Washington, D.C., USA, April 22–25, 2001.

[19] L.D. Nghiem, A.I. Schafer, Trace contaminant removal with nanofiltration, in: A.I. Schafer, A.-G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 480–520.

[20] J.D. Chwirka, C. Colvin, J.D. Gomez, P.A. Mueller, Arsenic removal from drinking water using the coagulation/microfiltration process, J. AWWA 96 (3) (2004) 106–114.

[21] K. Soldenhoff, J. McCulloch, A. Manis, P. Macintosh, Nanofiltration in metal and acid recovery, in: A. I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 459–477.

[22] G. Bargemann, M. Timmer, C. van der Horst, Nanofiltration in the food industry, in: A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 305–328.

[23] M. Cheryan, Ultrafiltration and Microfiltration Handbook, CRC Press, Boca Raton, FL, 1998.

[24] S.S. Koseglu, G.J. Guzman, Applications of reverse osmosis technology in the food industry, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 300–333.

[25] G.T. Austin, Schreve's Chemical Process Industries, McGraw-Hill, New York, 1984.

[26] US Patent, # 6,406,546; # 6,406,547; # 6,406,548.

[27] N.W. Pirie, Leaf Protein, Cambridge University Press, London, 1978.

[28] H.T. Ostrowski-Meissner, Protein concentrates from pasture herbage and their fractionation into feed- and food-grade products, in: L. Telek, H.D. Graham (Eds.), Leaf Protein Concentrates, AVI Publishing Co., Westport, CT, 1983 (Chapter 15).

[29] O. Kohler, R.H. Edwards, D. de Fremery, LPC for feeds and foods: the Pro-Xan process, in: L. Telek, H.D. Graham (Eds.), Leaf Protein Concentrates, AVI Publishing Co., Westport, CT, 1983 (Chapter 18).

[30] R. Singh, L.F. Whitney, C.S. Chen, Recovery of alfalfa protein by membrane ultrafiltration, in: Proceedings of the American Society of Agricultural Engineers Annual Meeting, Oklahoma City, OK, 1974, June, Paper No. 74-6003.
[31] J.E. Flinn, Green plants as biofactories for drugs, BioPharm Intern. 17 (8) (2004) 42–49.
[32] S.S. Koseglu, J.T. Lawhon, E.W. Lusas, Membrane processing of crude vegetable oils: pilot plant scale removal of solvent from oil miscellas, J. Amer. Oil. Chem. Soc. 67 (5) (1990) 281–289.
[33] A.K.S. Gupta, Process for refining crude glyceride oils by membrane filtration. U.S. Patent # 4,062,882, December 13, 1977.
[34] US Patent # 6,833,149.
[35] P. Hogan, R.P. Canning, P.A. Peterson, R.A. Johnson, A.S. Michaels, Osmotic distillation, A new option. Chem. Eng. Progress 94 (7) (1998) 49–61.
[36] W. Eykamp, Alternative separation processes, in: D.H. Perry, D. Green (Eds.), Perry's Chemical Engineers' Handbook, seventh ed., McGraw-Hill, New York, NY, 1999 (Sec. 22).
[37] L.R. Weatherely, Engineering Processes for Bioseparations, Butterworth-Heinemann, Oxford, UK, 1994.
[38] T. Matsuura, Synthetic Membranes and Membrane Separation Processes, CRC Press, Boca Raton, FL, USA, 1994.
[39] R. Klassen, A.E. Jansen, Achieving flue gas desulphurisation with membrane gas absorption, Filt. Sep. (2003) 26–28, September.
[40] R. Singh, Sustainable fuel cell integrated membrane desalination systems, Desalination 227 (2008) 14–33.
[41] S.J. Kim, S.H. Ko, K.H. Kang, J. Han, Direct seawater desalination by ion concentration polarisation, Nat. Nanotechnol. 5 (2010) 297–301.
[42] J. Kiernan, Electrochemical desalination challenge reaps results, World Water Water Reuse Desal, Autumn (2001) 26–28.
[43] Y. Tanaka, Ion Exchange Membrane Electrodialysis: Fundamentals, Desalination, Separation, Nova, New York, NY, 2010.
[44] R. McIlvaine, Desalination and reverse osmosis markets, Desalination (Filt. + Sep.) 3 (2) (2008) 16–18.
[45] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301–310.
[46] M. Elimelech, W.A. Philip, The future of seawater desalination: energy, technology, and the environment, Science 333 (2011) 712–717.
[47] B.V. der Bruggen, C. Vandecasteele, Distillation vs. membrane filtration: overview of process evolutions in seawater desalination, Desalination 143 (2002) 207–218.
[48] National Research Council, Review of the Desalination and Water Purification Technology Roadmap, National Academic Press, Washington, DC, USA, 2004.
[49] A. von Gottberg, J. McArdie, B. Antrim, D. Halperm, Hollow fiber UF pretreatment for RO brackish water and sweater desalination systems, Ultrapure Water 22 (3) (2005) 23–29.
[50] T. Prato, E. Schoepke, L. Etchison, T. O'Brien, B. Hernon, K. Perry, M. Peterson, Production of high purity water from seawater, Ultrapure Water 20 (8) (2003) 20–25.
[51] M. Wilf, C. Bartels, Optimisation of seawater RO systems design, Desalination 173 (2005) 1–12.
[52] N. Voutchkov, R. Semiat, Seawater desalination, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 47–86.
[53] I.D.A. Desalination Yearbook, Media Analytics Ltd, UK, Oxford, 2010–2011, 2011.
[54] I.D.A. Desalination Yearbook, Media Analytics Ltd, UK, Oxford, 2013–2014, 2014.
[55] B. Alspach, I. Watson, And every drop to drink, in: W.C. Lauer (Ed.), Desalination of Seawater and Brackish Water, AWWA, Denver, 2006, pp. 3–18.
[56] R. Singh, S.V. Cabibbo, Hydraulic turbine energy recovery – R.O. system, Desalination 32 (1980) 281–296.
[57] V. Veerapaneni, B. Long, S. Freeman, R. Bond, Reducing energy consumption for seawater desalination, J. AWWA 99 (2007) 95–106.

[58] R.L. Truby, Seawater desalination by ultralow-energy reverse osmosis, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 87–100.

[59] A. Kumano, N. Fujiwara, Cellulose triacetate membranes for reverse osmosis, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 21–46.

[60] R. Burch, Gold Coast desalination project, Desal. Water Reuse 18 (2) (2008) 22–28.

[61] Yuma BWRO plant retrofit, Desal, Water Reuse 16 (4) (2007) 26–30 (accessed 4 May, 2010). http://www.desalination.biz/news/news_story.asp?id=5317.

[62] C.A. Buckley, C.J. Brouckaert, C.A. Kerr, RO applications in brackish water desalination and in the treatment of industrial effluents, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 275–299.

[63] S.V. Cabibbo, D.B. Guy, A.C. Ammerlaan, A. Ko, R. Singh, RO Technical Manual, NTIS Publications, Springfield, Virginia, USA, 1979.

[64] S.V. Cabibbo, D.B. Guy, A.C. Ammerlaan, A. Ko, R. Singh, Parametric study on brackish water desalting plants, NWSIA J (1979) 17–36, July.

[65] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination 264 (3) (2010) 268–288.

[66] R.P. Allison, C. Touchstone, Modernizing a 28-year old surface water desalination plant, in: W. C. Lauer (Ed.), Desalination of Seawater and Brackish Water, AWWA, Denver, 2006, pp. 515–524.

[67] J. Kincl, A. Cernin, L. Novak, Electrodialysis treatment of wastewaters, MemBrain-MEGA technical paper, 2010.

[68] A. Sharbat, N.E. Moe, J. Loya, J. Barber, A. Ghassemi, Reducing cost of inland desalination. Pushing the conventional design limits in EDR and EDR/RO/NF hybridisation efforts. Paper presented at the AIChE 2012 Annual Meeting, November 2012, Pittsburgh, USA.

[69] R. Singh, Brine recovery at industrial RO plants – conceptual process design studies. Paper presented at the 2nd Oxford Water and Membranes Research Event, Oxford, UK, June 2008.

[70] T. Davis, B. Biagini, M.A. Capelle, B. Mack, H. Johnson, E. Gilbert, L. Jessup, Collaborative development of zero discharge technology. Paper presented at the AIChE 2012 Annual Meeting, Pittsburgh, USA, November 2012.

[71] Y. Oren, E. Korngold, N. Daltrophe, R. Messalem, Y. Volkman, L. Aronov, et al., Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach, Desalination 261 (2010) 321–330.

[72] C.J. Gabelich, M.D. Williams, A. Rahardianto, J.C. Franklin, Y. Cohen, High-recovery reverse osmosis desalination using intermediate chemical demineralization, Desalination 301 (2007) 131–141.

[73] G.A. Pittner, High purity water production using reverse osmosis, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 334–363.

[74] A. Dey, Ultrapure water by membranes, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 371–405.

[75] G.A. Pittner, The economics of desalination processes, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 76–103.

[76] J. Wood, Continuous electrodeionisation for power plants, Filt. Sep. 45 (5) (2008) 17–19.

[77] S. Siverns, C. Wilson, J. d'Ailly, Process water treatment: navigating the options, Chem. Eng (6) (2000) 64–71.

[78] T. Witham, Reusing nature's most precious resource, WAVE/USFilter 2 (1) (2003) 34–36.

[79] B. Parekh, A. Xia, M.E. Clarke, J. Smith, Process to purify water for immersion lithography, Ultrapure Water 24 (7) (2007) 31–36.

[80] B. Parekh, Emerging applications of high purity water: meeting challenges of advanced semiconductor manufacturing, Ultrapure Water 25 (4) (2008) 38–43.

[81] W.V. Collentro, Pharmaceutical Water, CRC Press, Boca Raton, FL, USA, 1999.

[82] H. Moes, R.C. Livingston, Producing affordable high-purity water, BioPharm Intern. 17 (8) (2004) 28–40.

[83] G. Gsell, Water systems utilizing multiple-effect and vapour compression technologies compared, Pharm. Eng. March/April (2004) 48.
[84] A. Modi, Liquid gains, Business Today 22 (24) (2013) 92–96.
[85] T. Fane, P. Macintosh, G. Leslie, Water reclamation, remediation and cleaner production with nanofiltration, in: A.I. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 287–304.
[86] R.L. Stover, Close circuit desalination achieves high recovery at Kranji, World Water Water Reuse Desal. 4 (4) (2013) 12–13.
[87] S. Judd, B. Jefferson, Industrial effluent recycling in the power industry, Ultrapure Water 21 (4) (2004) 37–42.
[88] S. Judd, B. Jefferson, Industrial wastewater recovery and re-use with membranes, Filt. Sep. Sept. (2003) 38–40.
[89] B. Vishwanath, K. Kekre, G.H. Tao, Reclaimed water: an alternate source for high-purity water production in the semiconductor industry, Ultrapure Water 20 (5) (2003) 41–46.
[90] M. Mierzejewski, D. Guendert, Industrial applications using microfiltration as RO pretreatment, Ultrapure Water 21 (7) (2004) 29–35.
[91] J.R. Pressdee, S. Veeraapaneni, H.L. Shorney-Darby, J.A. Clement, J.P. Van der Hoek, Integration of Membrane Filtration into Water Treatment Systems, AWWA, Denver, USA, 2006.
[92] Scottsdale – Arizona Water Treatment Facility, Siemens Water Technologies brochure, 2009.
[93] G. O'Toole, Drought-busting down under, Desal. Water Reuse 17 (3) (2007) 46–51.
[94] Memcor® CMF-S Microfiltration Technical Data. USFilter, 2003.
[95] A.G. Fane, Submerged membranes, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 239–270.
[96] Coliban-Victoria Water Treatment Facility, Siemens Water Technologies brochure, 2008.
[97] Using Reclaimed Water to Augment Potable Water Resources, Chapter 7, Am. Water Works Assoc., Special Publication: Denver, USA, 1998, pp. 252–260.
[98] S. Judd, The MBR Book, Elsevier, Oxford, UK, 2006.
[99] P. Cornel, S. Krause, Membranes bioreactors for wastewater treatment, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 217–238.
[100] B. Marrot, A.P. Barrios-Martinez, N. Roche, Industrial water treatment in a membrane bioreactor: a review, Environ. Progress 23 (1) (2004) 59–68.
[101] G.T. Daigger, B.E. Rittman, S. Adham, G. Andreottola, Are membrane bioreactors ready for widespread application? Env. Sci. Tech. 39 (19) (2005) 399A–406A.
[102] W.G. Scholz, P. Rouge, A. Bodalo, U. Leitz, Desalination of mixed tannery effluent with membrane bioreactor and reverse osmosis treatment, Env. Sci. Tech. 39 (21) (2005) 8505–8511.
[103] P. Riley, Oman's submerged membrane bioreactor proves itself, Desal. Water Reuse 20 (3) (2010) 42–43.
[104] B. van Es, Y. Balahorli, Giant Turkish landfill leachate plants use UF and MBR, Desal. Water Reuse 20 (3) (2010) 39–41.
[105] R. Severn, Long term operating experience with submerged plate MBRs, Filt. Sep. Sept. 40 (7) (2003) 28–31.

CHAPTER 4

Hybrid Membrane Plant Design and Operation

> *"We can't solve problems by using the same kind of thinking we used when we created them."*
>
> ***— Albert Einstein***

A membrane plant encompasses several technologies and processes since a standalone membrane system cannot produce a highly purified product because of physical and chemical constraints of synthetic membranes, and because membranes can foul prematurely in the case of liquid separations if the pre-treatment is not well-designed or is not working effectively. Hence, integrated plants are the rule as detailed in Chapter 3. Some of the earliest hybrid membrane plants were designed for dairy processing [1] and brackish water desalination [2]. The optimal success of a well-designed plant depends on the ability to operate various systems achieving highest possible output using minimum energy and generating as little waste as possible with maximum safety for employees and environment. Plant operation requires a diversity of problem-solving activities, which must occur in an information-rich environment. Current and historic plant data and characteristics of equipment and information obtained from troubleshooting the failure spots must be available and integrated at points of decision.

The design, equipment specification and operation of process plants depend on the quality and quantity of feed and product streams. The first step is a conceptual design – a process flow diagram (PFD) with mass and energy balances – followed by the design of each unit operation (UOP) and culminating in well-defined operating conditions [3]. The design of the hybrid membrane plant depicted in Figure 4.1 is based on the raw feed water analysis given in Table 4.1; the key aspect is the integration of various UOPs to produce the specified product under optimal conditions. For membrane systems used in water purification, the feed water quality is almost always unique and poses design and operation challenges.

In the first part of this chapter, we describe the engineering process and operation of a typical hybrid membrane plant for producing high purity water (HPW). In the second part of the chapter (Section 4.6), the design and operation of a low pressure membrane filtration plant for treating seawater prior to desalination by reverse osmosis is described. UOPs, system controls, plant operation, troubleshooting and maintenance, process design and equipment are discussed. These should familiarise the student of membrane technology about the intricacies of complex and hybrid membrane systems.

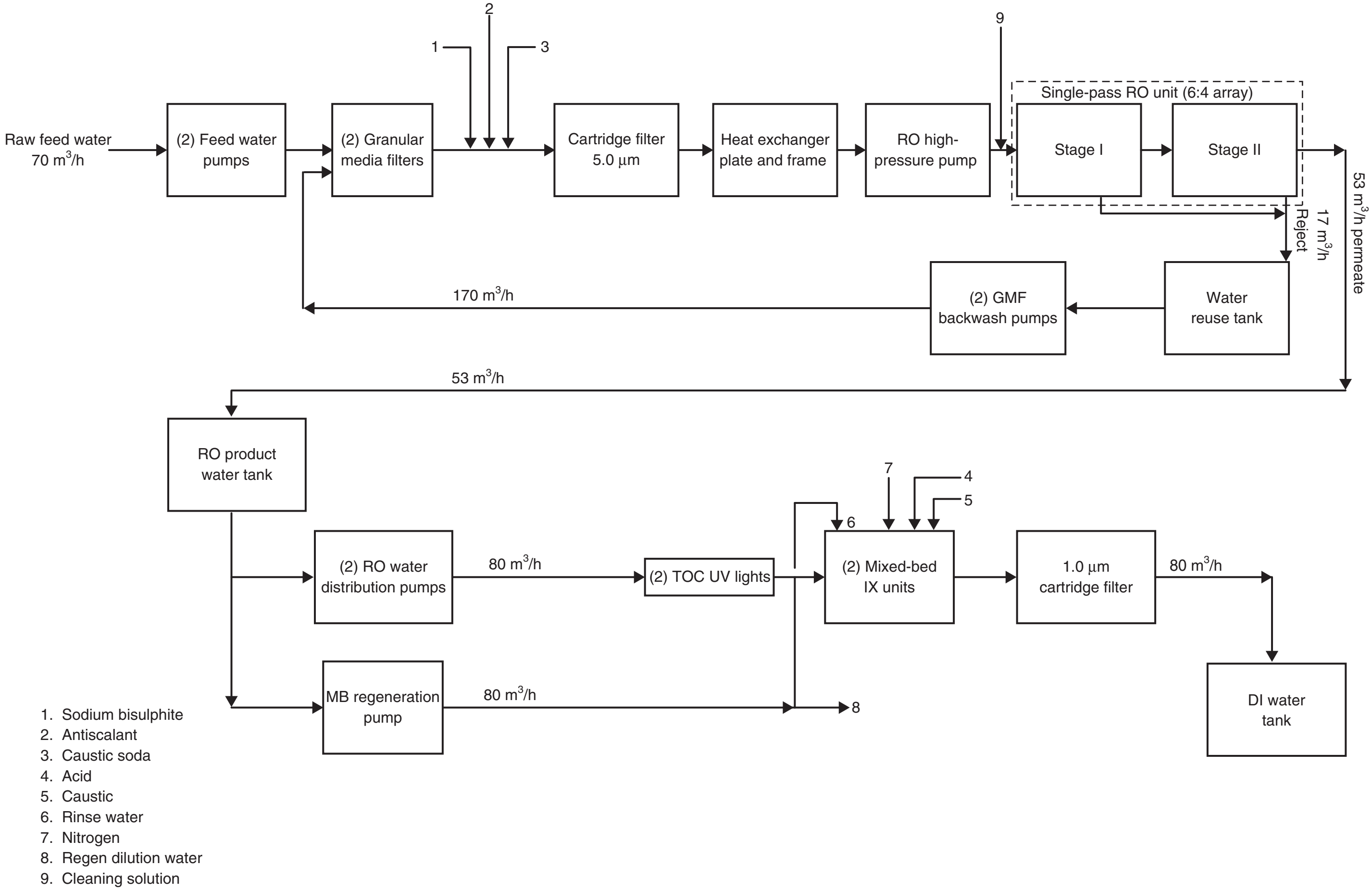


Figure 4.1 Process flow schematic of a hybrid plant.

Table 4.1 RO membrane (Hydranautics) performance projections

Project name	DI Water RO system	Permeate flow	53.00 m^3/h
HP pump flow	70.7 m^3/h	Raw water flow	70.7 m^3/h
Recommended pump pressure	8.0 bar		
Feed pressure	6.0 bar	Permeate recovery ratio	75.0%
Feed water temperature	25.0°C (77°F)		
Feed water pH	7.60	Element age	0.0 years
Acid dosage, ppm (100%)	0.0 H_2SO_4	Flux decline % per year	7.0
Acidified feed CO_2	4.2	Salt passage increase, % per year	10.0
Average flux rate	21.6 1/m^2 h	Feed type	Surface water

Stage	**Perm. flaw (m^3/h)**	**Flow/vessel**								
		Feed (m^3/h)	**Conc. (m^3/h)**	**Flux (l/m^2/h)**	**Beta**	**Conc, and throt. pressure**		**Element type**	**Elem. no.**	**Array**
						bar	**bar**			
1-1	37.5	11.8	5.5	25.5	1.14	4.2	0.0	ESPA2+	36	6 × 6
1-2	15.5	8.3	4.4	15.8	1.11	2.9	0.0	ESPA2+	24	4 × 6

Ion	**Raw water**		**Feed water**		**Permeate**		**Concentrate**	
	mg/l	**meq/l**	**mg/l**	**meq/l**	**mg/l**	**meq/l**	**mg/l**	**meq/l**
Ca	7.6	0.4	7.6	0.4	0.03	0.0	30.3	1.5
Mg	3.5	0.3	3.5	0.3	0.01	0.0	14.0	1.1
Na	50.0	2.2	50.0	2.2	0.82	0.0	197.5	8.6
K	0.5	0.0	0.5	0.0	0.01	0.0	2.0	0.1
NH_4	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0
Ba	0.100	0.0	0.100	0.0	0.000	0.0	0.399	0.0
Sr	0.000	0.0	0.000	0.0	0.000	0.0	0.000	0.0
CO_3	1.0	0.0	1.0	0.0	0.00	0.0	4.0	0.1
HCO_3	104.0	1.7	104.0	1.7	1.80	0.0	410.6	6.7
SO_4	34.0	0.7	34.0	0.7	0.08	0.0	135.8	2.8
Cl	12.2	0.3	12.2	0.3	0.12	0.0	48.4	1.4
F	0.5	0.0	0.5	0.0	0.01	0.0	2.0	0.1
NO_3	2.8	0.0	2.8	0.0	0.20	0.0	10.6	0.2
B	0.00		0.00		0.00		0.00	
SiO_2	26.0		26.0		0.24		103.3	
TDS	242.2		242.2		3.3		958.8	
pH	7.6		7.6		5.9		8.2	

Continued

Table 4.1 RO membrane (Hydranautics) performance projections—cont'd

	Raw water	Feed water	Concentrate
$CaSO_4/K_{sp} \times 100$	0%	0%	1%
$SrSO_4/K_{sp} \times 100$	0%	0%	0%
$BaSO_4/K_{sp} \times 100$	304%	304	1631%
SiO_2 saturation	19%	19%	74%
Langelier Saturation Index	−1.05	−1.05	0.67
Stiff and Davis Saturation Index	−0.99	−0.99	0.72
Ionic strength	0.00	0.00	0.01
Osmotic pressure	0.1 bar	0.1 bar	0.5 bar

4.1 RO MEMBRANE PLANT DESCRIPTION

Hybrid membrane plants for water purification consist of membrane (MF/UF/NF) or conventional pre-treatment systems, a single-pass or double-pass RO system, and, if required, a polishing system using either electrodeionisers or mixed-bed (MB) ion exchangers and UF/MF [4–6]. Purified water encompasses a wide range of pure grade waters varying in quality: potable (drinking) water, deionised (DI) water for power plants, HPW for beverage and pharmaceuticals manufacturing, and ultrapure water (UPW) for semiconductor plants, as discussed in Section 3.3 in Chapter 3. The UOPs shown in Figure 4.1 were discussed in Chapter 2. The plant is designed to supply up to 80 m^3/h HPW to the point-of-use (POU) with a resistivity of 16.0 MΩ-cm or higher.

The RO unit is the pivotal process since water production by membrane separation declines with time mainly due to fouling and other factors discussed in Chapter 2. The RO system must be run under conditions that minimise decline in flux while maintaining high product water quality. The pre-treatment system must be stable and reliable to ensure the RO unit operates continuously without frequent shutdowns for cleaning to restore flux and rejection. A stable RO membrane performance, in turn, is required to ensure the polishing system produces water that meets the product water specifications without frequent shutdowns for regeneration of ion-exchange resins.

4.1.1 Pre-treatment system

Raw feed water is pumped to the packed bed granulated media filters (GMF) by the feed water pump at 70 m^3/h and 4 bar g, as shown in Figure 4.1. The feed water quality is given in Table 4.1. Water flows through the media filter (one GMF is on standby) downwards through the media bed and out from the bottom at 70 m^3/h. All operating conditions – service and wash – and pneumatic valves are controlled by the programmable logic controller (PLC), as discussed in Section 4.2. A typical GMF is shown in Figure 2.4. The pressure drop across the GMF system is monitored by a differential pressure (ΔP) switch. When ΔP exceeds 1 bar (typically every 4 weeks), the filters are washed to clean the media bed. The media filters should be washed based on differential pressure and not run time. The unit to be washed is taken off-line, and the standby unit is brought on-line manually. The wash cycle is initiated manually at the main control panel (MCP), and consists of three steps: backwash, bed settle and rinse. Once initiated, the PLC controls the wash cycle progressing through each step sequentially – opening or closing the pneumatic valves and starting or shutting down the appropriate pumps, as given in Table 4.2. Only one GMF can be washed at a time.

During the backwash phase, water is transferred from the water reuse tank to the GMF by the backwash pump at 170 m^3/h and 3 bar g. Water flows from the bottom upwards through the bed. A high superficial velocity of 25–35 m/h is required to fluidise the media bed and remove dirt from the bed. The backwash phase lasts 15 min and is followed by a 2-min bed settle phase when no water flows to the filter. This allows the bed media to recover or "rest" before it is rinsed. During the rinse phase, the standby feed water pump transfers water to the media filter at 70 m^3/h and 3 bar g. Water flows downwards through the media bed and out from the bottom to drain. The rinse phase lasts 5 min. Once the GMF has been washed, it is placed in standby mode until the on-line unit needs to be washed.

The filtered water is monitored for turbidity continuously by a turbidity analyzer. The turbidity must be less than 1.0 NTU to prevent fouling of RO membranes by particulate matter. A higher NTU value means the GMF must be washed. The filtered water is injected with chemicals as it flows to the RO system to prevent scaling of membranes by sparingly soluble salts.

Table 4.2 Granular media filter valve operation

Process cycle	Open valves[a]	Prime mover
GMF-061		
Normal service:		
Service water in/out	OV-061-1/ OV-061-3	Feed water pump
Standby	All closed	Off
Washing:		
Backwash in/out	OV-061-2/ OV-061-4	GMF backwash pump
Bed settle	All closed	Off
Fast rinse	OV-061-1/ OV-061-5	Feed water pump
GMF-062		
Normal service:		
Service water in/out	OV-062-1/ OV-062-3	Feed water pump
Standby	All closed	Off
Washing:		
Backwash in/out	OV-062-2/ OV-062-4	GMF backwash pump
Bed settle	All closed	Off
Fast rinse	OV-062-1/ OV-062-5	Feed water pump

[a] See Figure 4.4 for valve location. OV-xxx... valves are pneumatic with manual over-ride.

Chemical treatment consists of three well-known treatment processes for ensuring reliable operation of RO membranes. First, a 20% sodium bisulphite (SBS) solution is injected by the chemical dosing pump (one pump is on standby). The injection rate is proportional to the RO feed water flow rate and is controlled by the PLC based on the chlorine concentration monitored by a chlorine analyser downstream of the in-line mixer. SBS like sodium sulphite and sodium metabisulphite is a reducing agent commonly used to dechlorinate RO feed or lower the chlorine concentration to less than 0.05 mg/l in RO plants that use polyamide aromatic membranes. It takes 7.33 mg/l of 20% $NaHSO_3$ solution to remove 1 ppm of residual chlorine in water on a stoichiometric basis.

A negatively charged anti-scalant (A/S) is injected by the chemical dosing pump (one pump is on standby) into the pressurised RO feed water line downstream of the SBS injection point. The injection rate or dosage is proportional to the RO feed water flow rate, and is controlled automatically. The A/S prevents sparingly soluble salts of calcium and magnesium from precipitating out and scaling the membrane surface, as discussed in Chapter 2.

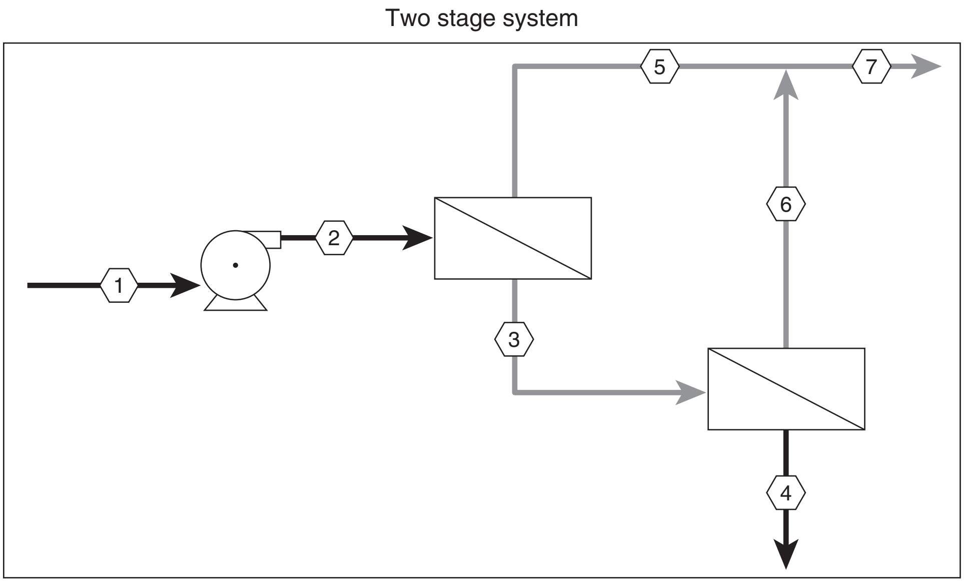
Caustic soda (50% NaOH solution) may be injected into the RO feed water line by the chemical dosing pump (one pump is on standby) to maintain the pH of RO feed water between 7.5 and 8.5 if there is no likelihood of carbonate scaling. The injection rate is controlled by the PLC based on the pH value measured downstream of the in-line mixer. At alkaline pH conditions, dissolved CO_2 gas is converted to bicarbonate ions, thereby enhancing membrane rejection (lower permeate conductivity).

The pre-treated water flows to the cartridge filter (nominal pore size of 5.0 μm) at 70 m^3/h. The pressure drop (ΔP) across the filter is monitored by a local ΔP indicator/switch. When ΔP exceeds 1 bar or every 3 months, the plugged cartridges are replaced. The pleated depth filter cartridges are sized based on flow rate and pressure drop, e.g. the rating is 30 l/m per 25 cm long cartridge with a pore size of 5.0 μm.

The RO feed water flows through a parallel plate-and-frame heat exchanger. The PLC maintains the water temperature at 25 ± 1°C by controlling the heat exchanger steam flow. A rule of thumb is that RO membrane flux increases 3% per °C rise in temperature as a result of reduced viscosity. A constant water temperature is necessary to compare RO flux data. Otherwise, the flux data must be normalised to evaluate flux with time. Heat exchanger sizing is based on the maximum anticipated flow rate and temperature rise. The heat transfer area is a function of heat load (ΔH), overall heat transfer coefficient (U), log mean temperature difference (ΔT_{lm}) and heat exchange interface material.

4.1.2 RO membrane system

The RO membrane separation process reduces the total dissolved solids concentration from 242 mg/l in feed water to less than 4 mg/l in product water corresponding to an


Two stage system

		1	2	3	4	5	6	7
Flow	(m^3/h)	70.7	70.7	33.2	17.7	37.5	15.5	53.0
Pressure	(bar)	0.0	6.0	4.2	2.9	0.0	0.0	0.0
TDS	(ppm)	242.2	242.2	513.2	958.8	2.2	6.1	3.3

Figure 4.2 RO membrane projection process flow schematic.

average salt rejection of 98%, as shown in Table 4.1. The RO unit uses thin-film composite (TFC) polyamide membranes in spiral-wound configuration. The single-pass RO system is a two-stage (6:4) membrane array designed to achieve a product water recovery (PWR) of 75% (53 m^3/h permeate–70 m^3/h feed), as shown in Figure 4.2. The RO high-pressure pump transfers water to the RO membrane array at 70 m^3/h and 14 bar g (total delivery head or TDH). The permeate flows to the RO product water tank at 53 m^3/h, and the reject flows to the water reuse tank at 17 m^3/h. (See Section 4.2.)

During start-up, the RO skid inlet pneumatic valve opens automatically, and RO pretreated water starts flowing to the RO high-pressure pump. The membranes are flushed for 60 s at line pressure, and the permeate is diverted to the water reuse tank. When the RO pump inlet pressure exceeds the minimum permissible value (see Table 4.5), the pump starts. Initially, the permeate is diverted to the water reuse tank for a few minutes to allow the product water conductivity to drop below the maximum permissible value. At the end of the “quality rinse” phase, the RO permeate is diverted to the RO product water storage tank via the service manual valve. The permeate service and divert valves are controlled manually (automatic valves are also used). RO membrane post-shutdown flushing is recommended by membrane manufacturers to prevent scaling.

The inlet pressure to the membrane array is adjusted manually by a globe valve (when the RO pump speed is controlled by a variable frequency drive (VFD); the membrane inlet pressure control valve does not require adjustment). The reject water flow rate is controlled manually by adjusting the reject flow control globe valve. Both valves are adjusted to achieve the desired PWR (%). The pressure required to achieve the permeate and reject flow rates is set during the initial run. As the membrane performance deteriorates with time, these valves require adjustments.

Product water flow rate higher than the maximum allowable limit is indicative of higher than design recovery. Similarly, reject flow rate lower than the allowable reject flow rate is reflective of higher than design recovery. Both these performance conditions can result in premature scaling by the precipitation of sparingly soluble salts and must be avoided. Hence, RO pump operation must be adjusted when the permeate flow rate exceeds the maximum design value or the reject flow rate drops below the minimum design value. Similarly, when ΔP across the RO unit exceeds the maximum recommended value, the RO system should be shut down for cleaning the membranes. The RO membranes are cleaned according to the procedure recommended by the membrane manufacturer, as discussed in Chapter 2.

RO permeate flows to the RO product water storage tank at 53 m^3/h. If the tank is full or if the permeate conductivity exceeds the maximum permissible value (see Table 4.5) for an extended period of time (minutes), the RO system should be shut down. The feed water and permeate flow rate date is used by the PLC to calculate % recovery. Similarly, RO feed water and permeate conductivity is monitored continuously, and the data are used by the PLC to calculate salt rejection or simply %rejection.

The RO product water storage tank has a capacity of 76 m^3. The tank is positioned directly downstream of the RO unit, so that the downstream equipment such as MB ion exchangers and ultraviolet (UV) units can be operated continuously. With storage, fluctuations and demand for the finished water can be addressed economically. The RO unit can be designed for the average demand and storage designed to fill the gap between average and maximum [5]. The tank is also provided with level switches, a level transmitter, a low pressure nitrogen blanket and a high efficiency particulate air (HEPA) filter to prevent atmospheric contamination and increase in conductivity due to absorption of CO_2.

Water is transferred from the RO product water storage tank to the TOC destruct UV lamps by the RO water distribution pump (one pump is on stand-by) at 80 m^3/h. Irradiation with 185 nm ultraviolet light is very effective in destroying residual organic matter (TOC) not removed by the RO membrane. The 185 nm rated UV light also reduces the organic load on anion resins in the MB ion exchangers (deionisers) downstream. The UV units also render more than 90% bacteria ineffective. This is especially important because the MB units operate at neutral pH and are thus capable of supporting rapid bacterial proliferation [6].

4.1.3 MB ion-exchange polishing

Water flows through the UV lights to the top of the MB deioniser (one deioniser is on standby) down through the resin bed and out from the bottom of the vessel to the final microfilter skid. Each packed-bed MB vessel contains a mixture of 3.26 m^3 strong base anion resin (OH^- form) and 2.18 m^3 strong acid cation resin (H^+ form) in a 60:40 ratio, as shown in Figures 2.9 and 2.11. The bed also contains 0.54 m^3 of inert resin, which forms a separate layer between the two IX resin layers when backwashing, thus ensuring there is no mixing of acid and caustic solutions during resins regeneration. The ion-exchange process is discussed in Chapter 2.

The MB deionisers are designed to produce demineralised water with resistivity >16.0 MΩ-cm (conductivity <0.063 μS/cm). All operating modes – service, standby, and regeneration – are controlled by the PLC, which opens and closes the pneumatic valves and the corresponding solenoid valves. The process operating conditions are given in Section 4.2. Valve operations are detailed in Table 4.4.

The deionised product water flows through two 1.0 μm cartridge filters operating in parallel to the DI water storage tank. The cartridge filters operate as resin traps removing particles such as resin fines. When ΔP exceeds 0.7 bar, the cartridges are replaced. When the water tank is full or the product water resistivity is less than 15.0 MΩ-cm, water gets diverted to the RO product water storage tank via an automatic valve. This ensures the RO system is in operation continuously without frequent shutdowns and start-ups. It is preferable to replace the final filter cartridges based on time and not differential pressure to ensure there is no bacterial growth in DI water since ΔP may not increase substantially unless there is a catastrophic failure of MB internal laterals and distributors.

When the MB product water resistivity drops below 15.0 MΩ-cm and silica level exceeds 30 ppb (μg/l), the MB resins are considered to be exhausted for the purpose of producing HPW. The exhausted MB unit is shutdown for regeneration, and the standby MB unit is switched to service mode.

The MB regeneration cycle summarised [4,7,8] below was discussed in Chapter 2:

1. Fill the MB vessel with RO product water slowly through the bottom distributor until the level is 15 cm above the top of the resin bed.
2. Backwash to remove resin fragments and debris (and to separate the resins) for 10–15 min or until no fines are visible in wastewater.
3. After the backwash, allow the resins to settle into three layers – anion, inert, cation – from top to bottom based on density for 5 min.
4. The regeneration efficiency can be improved by warming the bed to 45°C for 30 min for removing silica. Warm water is passed through the anion resin bed and ambient temperature water is passed through the cation resin bed.

5. Commence simultaneous acid and caustic regeneration; 6% HCl solution upflow through the cation bed for 30 min and 4% NaOH solution at 43–49°C downflow through the anion bed for 60 min. The two streams flow out to wastewater neutralisation tank through the interface collector imbedded in the inert resin layer.
6. Start the slow rinse cycle to displace the caustic and acid solutions from their respective beds with dilution water for 20 min.
7. Repeat the above rinse cycle at a much higher flow rate for 45 min to purge the respective beds of any traces of acid and caustic.
8. Use high-pressure nitrogen to push water in the bed out to drain until the water is at bed level.
9. Mix the resin with nitrogen for 10 min in two steps. In Step I, pressurised N_2 enters the bottom of the MB vessel, mixes the resin and exits through the top vent.
10. Repeat nitrogen mix. In Step II, N_2 enters the centre of the resin bed through the interface distributor/collector. After 5 min of mixing, water is drained to bed level by opening the vessel drain valve and closing the vent valve. This ensures that the bottom of the bed is well mixed and compacted.
11. After the nitrogen mixing steps, refill the MB vessel with water. Water flows down through the bed from the normal service inlet forcing N_2 through the top of the vessel.
12. Final rinse of the MB resin bed for 5–10 min or until the product water resistivity achieves the specified value.

The regeneration cycle is initiated manually at the MCP. Once initiated, the PLC controls the regeneration cycle progressing through each step sequentially. Only one MB can be regenerated at a time. During acid regeneration, concentrated HCl (35% wt.) is educted from the acid tank and mixed with dilution water transferred from the RO product water tank to make a 6% acid solution before it flows to the MB deioniser. Similarly, during caustic regeneration concentrated NaOH (25% wt.) is educted from the caustic tank and mixed with water pumped from the RO product water storage tank to make a 4% caustic soda solution before it flows to the MB deioniser. The dilution water is heated to 43–49°C before it flows to the eductor. The water temperature is controlled by the PLC, which modulates the steam temperature control valve to adjust the steam flow rate. The acid and caustic concentrations (% wt.) of the regenerating solutions are measured downstream of the eductors by their respective conductivity sensors. The PLC adjusts each chemical flow control valve based on the measured concentration value.

Mixing of anion and cation resins is critical for achieving the design resistivity and silica during quality rinse. Cross-contamination during regeneration can also affect the rinse time when the separation is poor. Under such circumstances, the IX resins are exhausted to achieve complete separation.

4.2 PLANT DESIGN AND CONTROLS

Whether designing a new system or plant, modifying an existing one, or operating the plant, understanding the interface between process engineering and system controls is important. The PFD in Figure 4.1 and the operating conditions given in this section form the basis for designing the UOPs. While system operation and performance are determined by the specifications of components, the automated control system is required to run the plant at system design conditions. Process specifications are discussed below. Equipment requirements are discussed in Section 4.5.

4.2.1 Granulated media filter

GMF design criteria

The design of media filters is based on three criteria: (a) linear velocity, (b) freeboard for backwashing, and (c) operating pressure [4,9]. During normal service, linear velocity should be 12–21 $m^3/h\ m^2$ cross-sectional area. Higher velocity affects filtration adversely and can result in channelling in the media bed. The vessel diameter is based on the normal service feed flow rate to achieve the recommended linear velocity. The media bed consists of 0.6–0.8 mm anthracite (45 cm deep); 0.45 mm filter sand (35 cm deep); and 0.25 garnet (5 cm deep) from top (coarser) to bottom (finer) with a depth of 0.9–1 m, as shown in Figure 2.4. The media bed depth is typically based on a maximum pressure drop of 1 bar. The vessel straight shell height (SSH), in turn, is based on bed depth and a bed expansion of 50–60% during backwashing. The backwash linear velocity should be 29–36 $m^3/h\ m^2$ at 15–27°C. The design of vessel internal distributors and laterals is based on a minimum backpressure of 0.3 bar to achieve a uniform distribution of water across the bed cross-section during the service run.

GMF operating conditions

Service flow rate	70 m^3/h
Operating pressure	4 bar g
Operating temperature	12 °C
Bed pressure drop	<1 bar
Backwash flow rate	170 m^3/h
Rinse flow rate	70 m^3/h
Valve sequencing	See Table 4.2

4.2.2 RO membrane system

RO design criteria

The RO unit design is based on meeting the specified product water quality and flux. RO unit service run is based on permeate conductivity (% rejection), productivity

(%recovery), time and feed pressure, which are affected by membrane scaling and fouling. The performance criteria for cleaning the membranes are discussed in Section 4.3.

The computer-generated design of the single-pass, two-stage RO membrane array (6:4) is shown in Figure 4.2 based on standard design parameters. The stream numbers in the figure are 1 is raw feed water, 2 is first stage feed, 3 is first stage reject/second stage feed, 4 is system reject, 5 is first stage permeate, 6 is second stage permeate, and 7 is system permeate. The RO membranes are TFC polyamide wrapped in spiral-wound modules, 20 cm diameter × 100 cm long. Additional information is provided in Table 4.1. The β factor is within range, and the LSI is negative as required.

RO operating conditions

Product water recovery	~75%
Product water flow rate	53 m^3/h
Product water conductivity	<10.0 μS/cm
Average salt rejection	~99.0%
Feed water flow rate	70 m^3/h
Operating pressure	14 bar g
Operating temperature	25°C
RO array ΔP	<4 bar
Cleaning solution flow rate/vessel	>0.2 m^3/h
Cleaning solution pressure	3 bar g
Cleaning solution temperature	<30°C
Cleaning solution pH	4.0–9.0
RO feed water SDI	<3.0
RO feed water LSI	<1
Valve sequencing	See Table 4.3

Typically, RO systems are designed with the following general conditions for safe and reliable operation [2,9]:

Table 4.3 RO unit valve operation

Process condition	Open valves[a]	Prime mover
Service feed/product/reject	OV-161-1/ MV-161-3/MV-160-2	RO high-pressure pump
Membrane array feed pressure control	MV-161-1 (open 30%)	N/A
Reject flow control	MV-161-2 (open 50%)	N/A

[a] See Figure 4.7 for valve location. OV-161-1 is a pneumatic valve with manual over-ride.

- The initial minimum %rejection is based on chloride ions and applies to each membrane element. Further, membrane deterioration may cause individual element salt passage to double within 3 years.
- Always operate the RO unit at the lowest system pressure that produces the design flow rate and %rejection.
- Product water back-pressure greater than the system pressure at any time will damage the RO membranes.

4.2.3 MB ion-exchange system

MB design criteria

The deioniser vessels are 2.1 m D × 3 m SSH. Each MB vessel contains 3.26 m^3 strong base anion resin (OH^- form), 2.18 m^3 strong acid cation resin (H^+ form) and 0.54 m^3 inert resin. This translates into a freeboard of 72% for bed expansion when the bed depth is 1.7 m. The service linear velocity of 25 $m^3/h/m^2$ (10 gpm/ft^2) is within the resin manufacturer's range of 25–35 $m^3/h/m^2$ (10–15 gpm/ft^2). The backwash linear velocity is 13 $m^3/h/m^2$ (5.5 gpm/ft^2). Based on resin manufacturer's hydraulic expansion curves, the bed expansion is about 60% when the water temperature is 16°C. The available freeboard is >70%. A general procedure for designing ion exchangers is given in Section 6.7.

MB operating conditions

Product water flow rate	80 m^3/h
DI water resistivity	$\geq$16.0 MΩ-cm
Operating pressure	5 bar g
Operating temperature	Ambient
Service run time	250 h
Maximum bed ΔP	1 bar
Backwash flow rate	45 m^3/h
HCl flow rate	5 m^3/h at 6% conc.
NaOH flow rate	7 m^3/h at 4% conc.
NaOH temperature	43–49°C
Slow rinse flow rate:	
Cation bed	4 m^3/h
Anion bed	6 m^3/h
Fast rinse flow rate:	
Cation bed	24 m^3/h
Anion bed	24 m^3/h
Final rinse flow rate	80 m^3/h
Nitrogen supply	425 N m^3/h at 2 bar g
Valve sequencing	See Table 4.4

Table 4.4 Mixed-beds valve operation

Process cycle	Open valves[a]	Prime mover
MB-281		
Normal service:		
Service water (in/out)	OV-281-19; OV-281-11/OV-281-13	P-231 or P-232
Standby	All closed	Off
Regeneration:		
Backwash (in/out)	OV-281-18; OV-281-12/OV-281-14	P-233
Acid regeneration (in/out)	OV-330-2; OV-281-16/OV-281-23	P-233 and eductor
Caustic regeneration (in/out)	OV-340-2; OV-281-17/OV-281-23	P-233 and eductor
Nitrogen mixing (in/out)	OV-281-20; OV-281-12/OV-281-22; OV-281-15	In-house nitrogen supply
Rinse (in/out)	OV-281-18; OV-281-11/OV-281-15	P-233
MB-282		
Normal service:		
Service water (in/out)	OV-282-19; OV-282-11/OV-282-13	P-231 or P-232
Standby	All closed	Off
Regeneration:		
Backwash (in/out)	OV-282-18; OV-282-12/OV-282-14	P-233
Acid regeneration (in/out)	OV-330-2; OV-282-16/OV-282-23	P-233 and eductor
Caustic regeneration (in/out)	OV-340-2; OV-282-17/OV-282-23	P-233 and eductor
Nitrogen mixing (in/out)	OV-282-20; OV-282-12/OV-282-22; OV-282-15	In-house nitrogen supply
Rinse (in/out)	OV-282-18; OV-282-11/OV-282-15	P-233

[a] See Figures 4.11–4.13. OV-xxx… valves are pneumatic with manual over-ride.

4.2.4 System controls

Generally speaking, the purpose of a control system is to supervise, control, monitor, schedule, document and record process parameters that are vital to plant operation. The control system of any plant or system is related to the process design of the plant and ultimately its operation, and must be able to cope with various uncertainties. In other words, the control system is closely tied to process operability. Process operability, in turn, involves the coordinated effort of both the operator and the automatic control system. The automatic controls system is PLC-based and includes the MCP and local control panels (LCP). PLC systems are preferred to discrete control systems because of the flexibility in establishing set-points and providing multiple functions.

Instrumentation and control systems are provided for monitoring and controlling the major process variables related to each equipment and UOP, as shown in the process flow

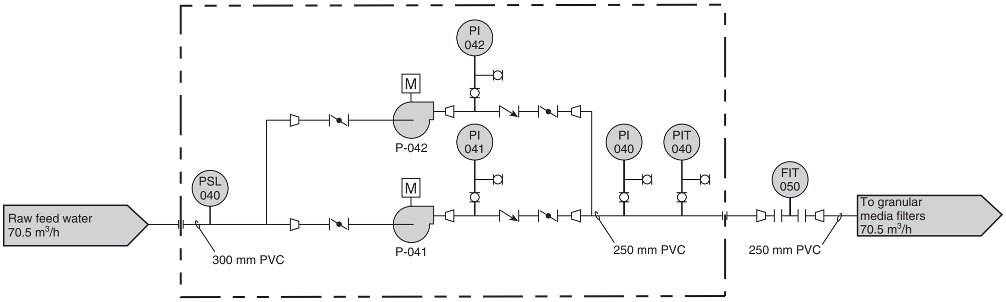


Figure 4.3 Feed water pumps process and instrumentation diagram (P&ID).

sheets (PFSs) in Figures 4.3–4.13. Instrumentation includes for example the primary element or sensor monitoring a controlled variable to a modulating control valve performing the throttling action. The pumps, media filters and the MB deionisers can be controlled automatically or manually, for example to control pressure, flow rate, or storage tanks water level. The RO feed pressure and reject flow control valves are typically controlled manually. All pump motors are controlled at either the LCP or the MCP. The pneumatic valves can be controlled manually by opening the override button for each corresponding solenoid valve in the local panel.

Analogue data signals (4–20 mA) from the instruments are sent to the PLC input module located in the MCP and to a digital display. These displays provide operators with the necessary data. All analogue signals for control such as pressure and flow for process water temperature control are obtained from the PLC. Alarms are produced by data received by the PLC from the instruments. Alarms are only produced when the process the instrument is monitoring is active. Most alarms often have several seconds delay associated with them to ensure the process has stabilised before activating the alarm.

The PLC responds to uncertainties and typical alarm conditions for each equipment or UOP, as defined in Table 4.5. The process description in Section 4.1 and process conditions defined in Section 4.2 provide the basis for operating the membrane plant equipment shown in Figures 4.3–4.13.

4.3 SYSTEM OPERATION

Initial start-up is the key to operating any plant or system efficiently and successfully because start-ups are often plagued with problems. Hence, strict criteria must be adhered to, defined either by the customer specifications or the plant manufacturer's standards. During start-up, the field engineers ensure all equipment is installed correctly, the vessels and the piping are hydro-tested, chemical tanks are full and the chemical pumps are calibrated, wiring is complete, the centrifugal pumps have been checked for rotation, all instruments are calibrated, the UV lamps and microfilter cartridges have been loaded,

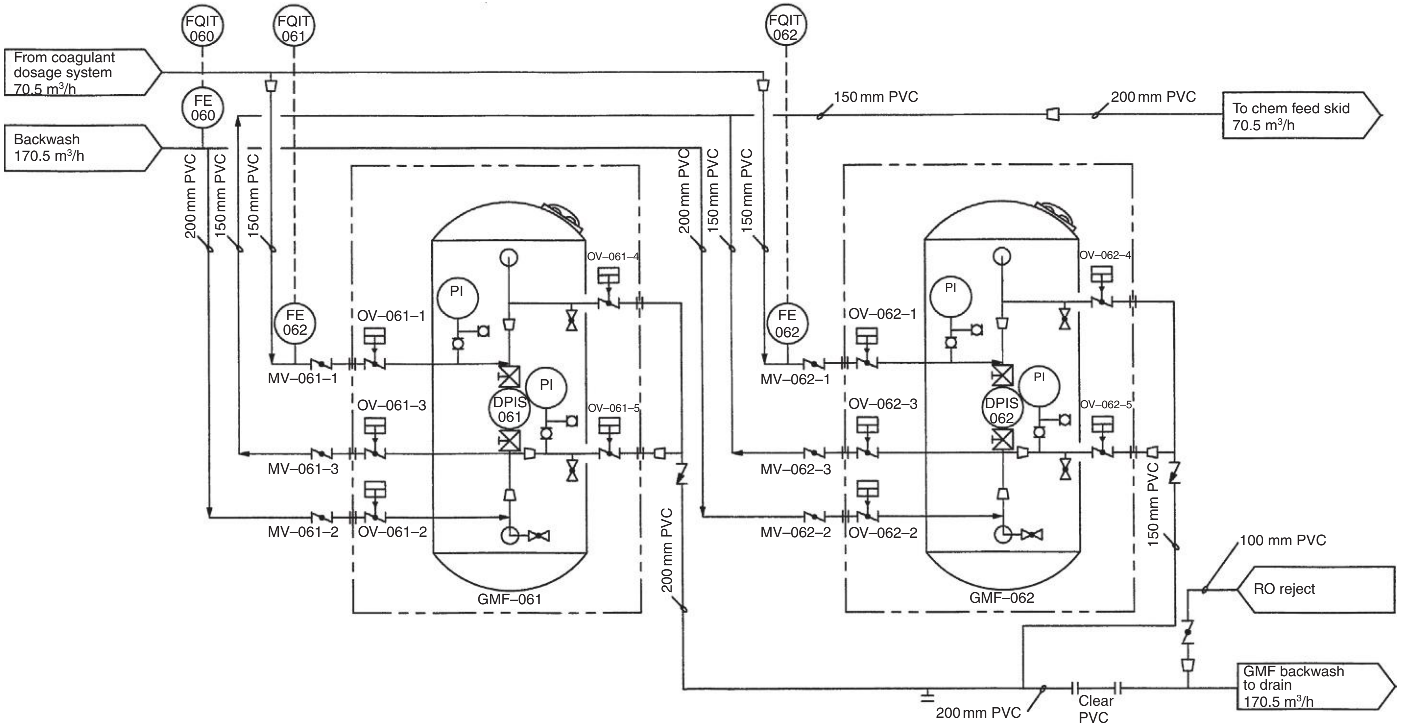


Figure 4.4 Granular media filters P&ID.

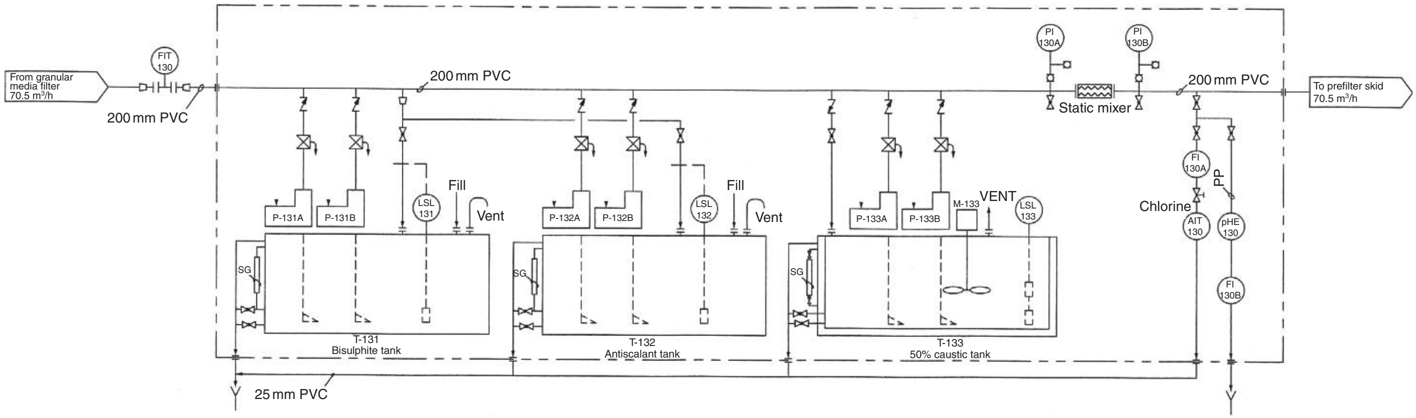


Figure 4.5 Chemical feed systems P&ID.

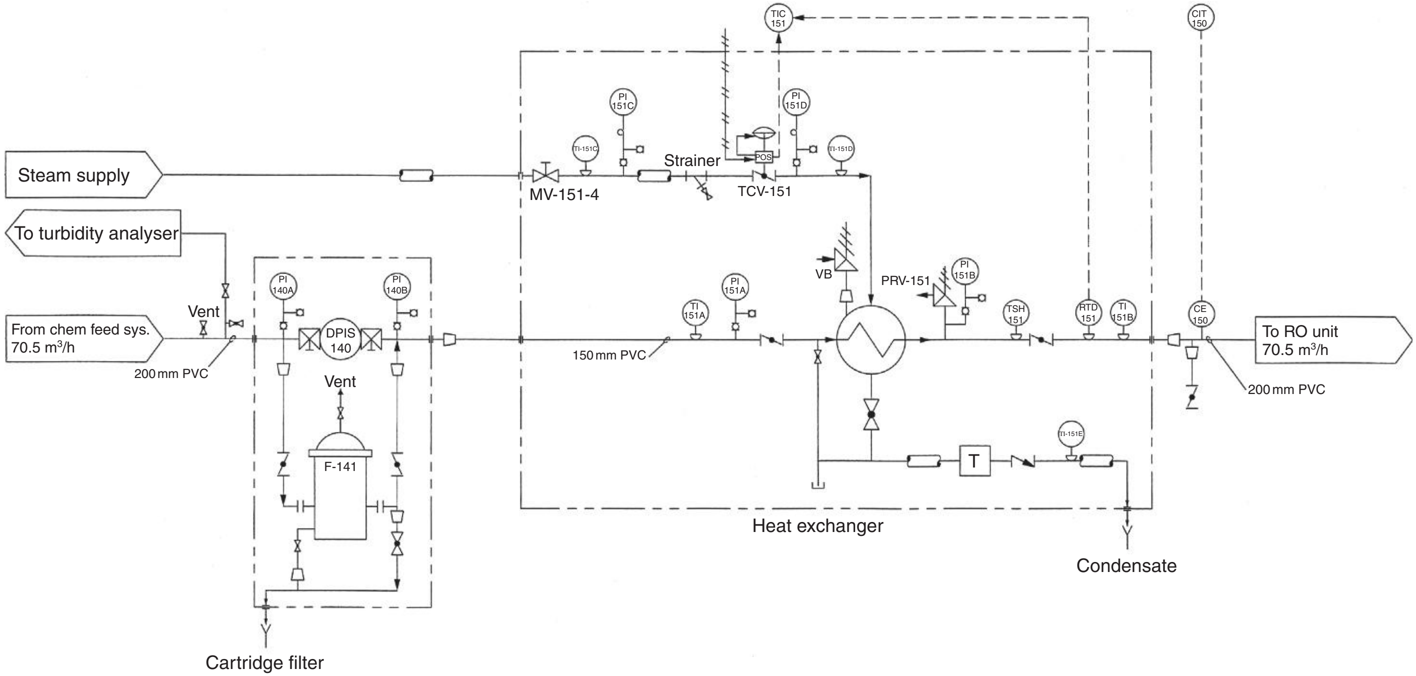


Figure 4.6 5.0 μm cartridge filter and heat exchanger system P&ID.

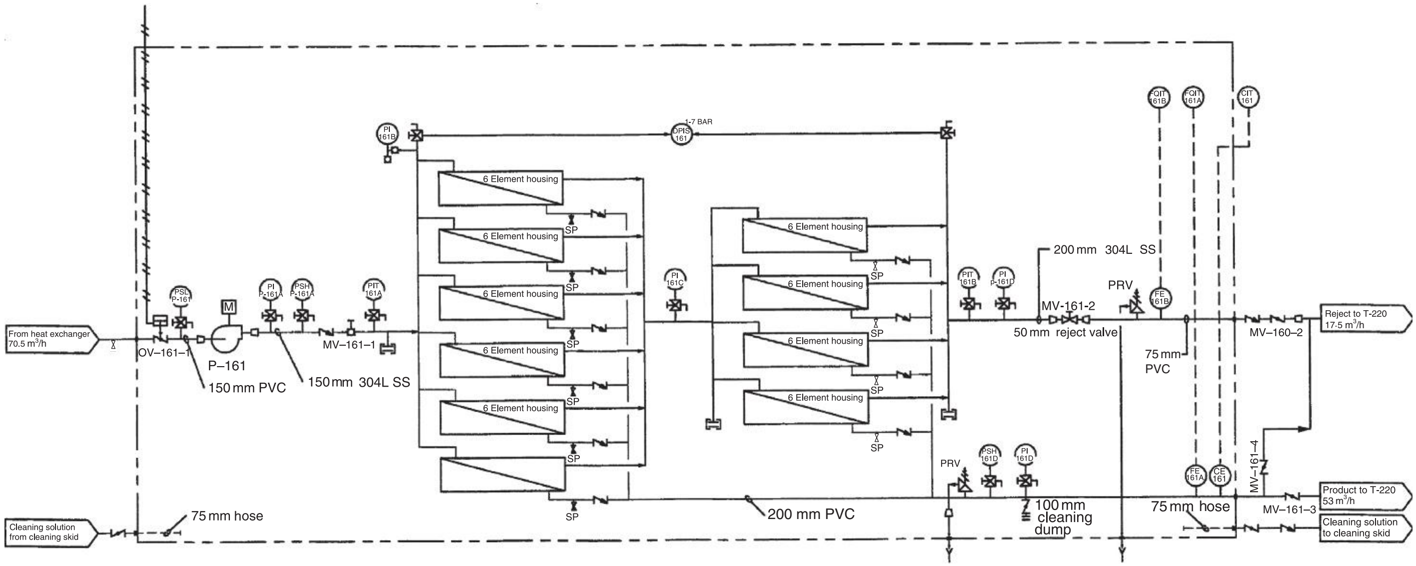


Figure 4.7 Single-pass, two-stage RO system P&ID.

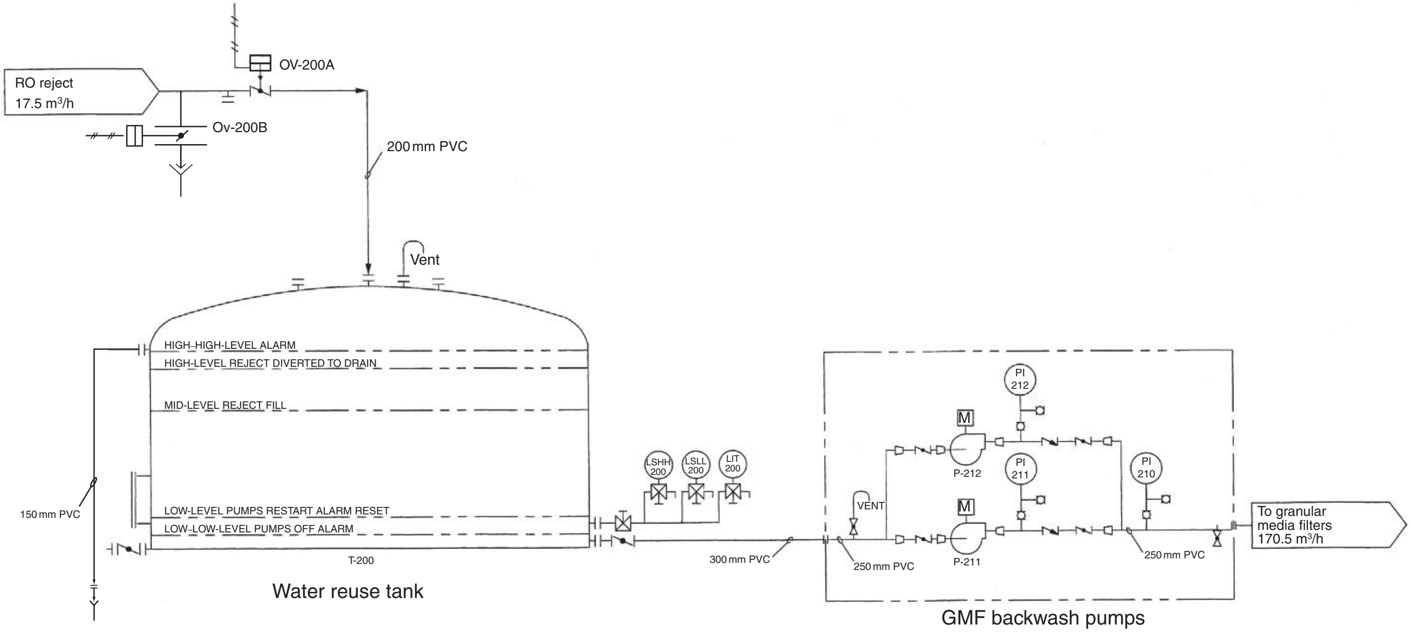


Figure 4.8 Water reuse tank system P&ID.

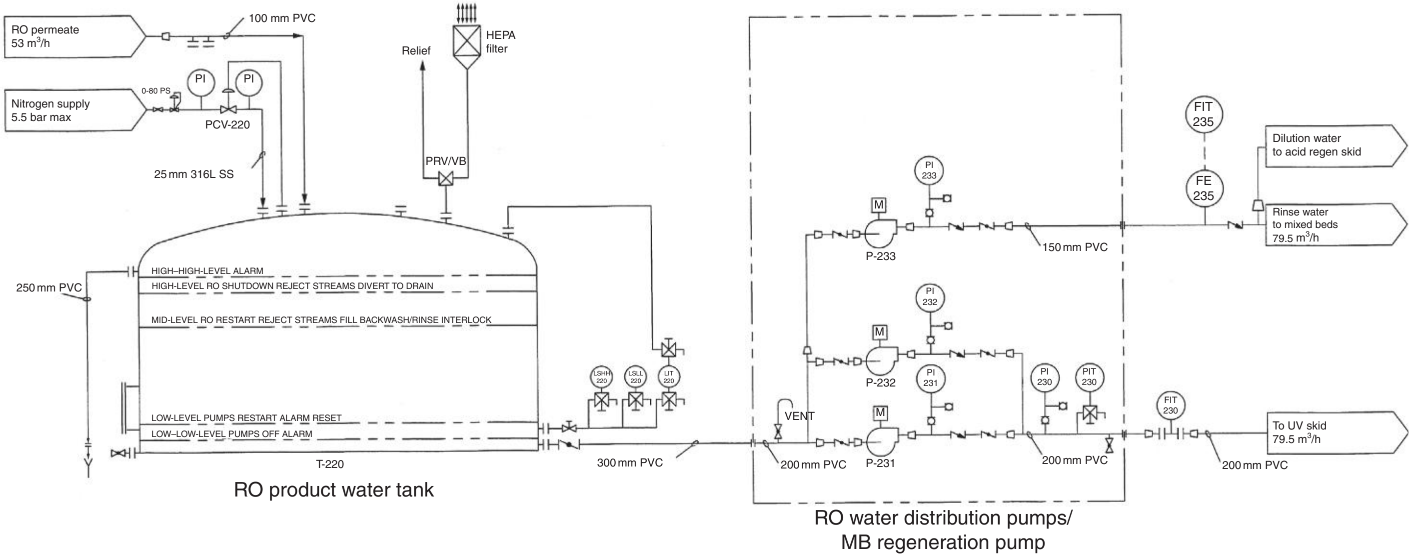


Figure 4.9 RO product water tank system P&ID.

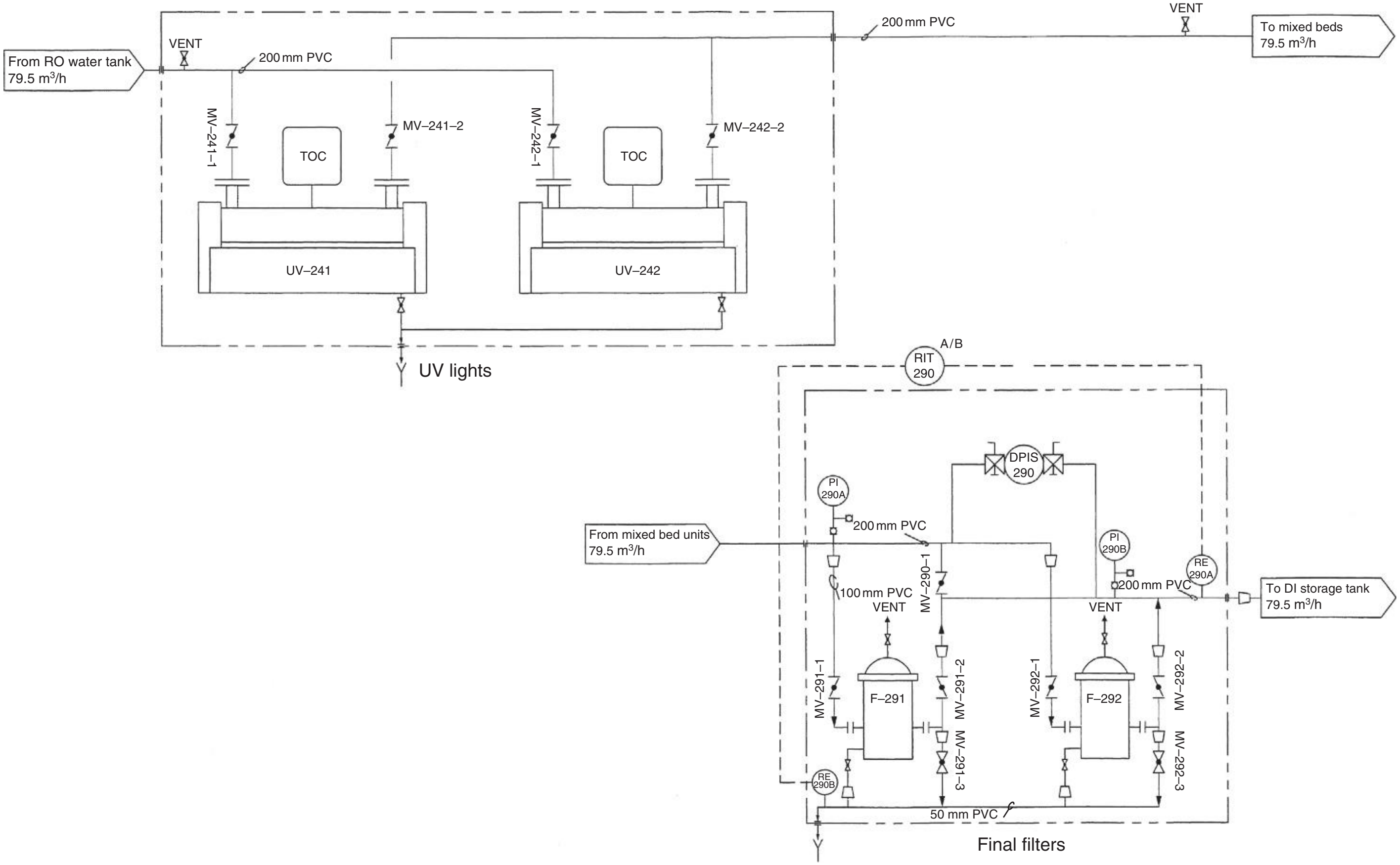


Figure 4.10 TOC UV light (185 nm) and 1.0 μm cartridge filter system P&ID.

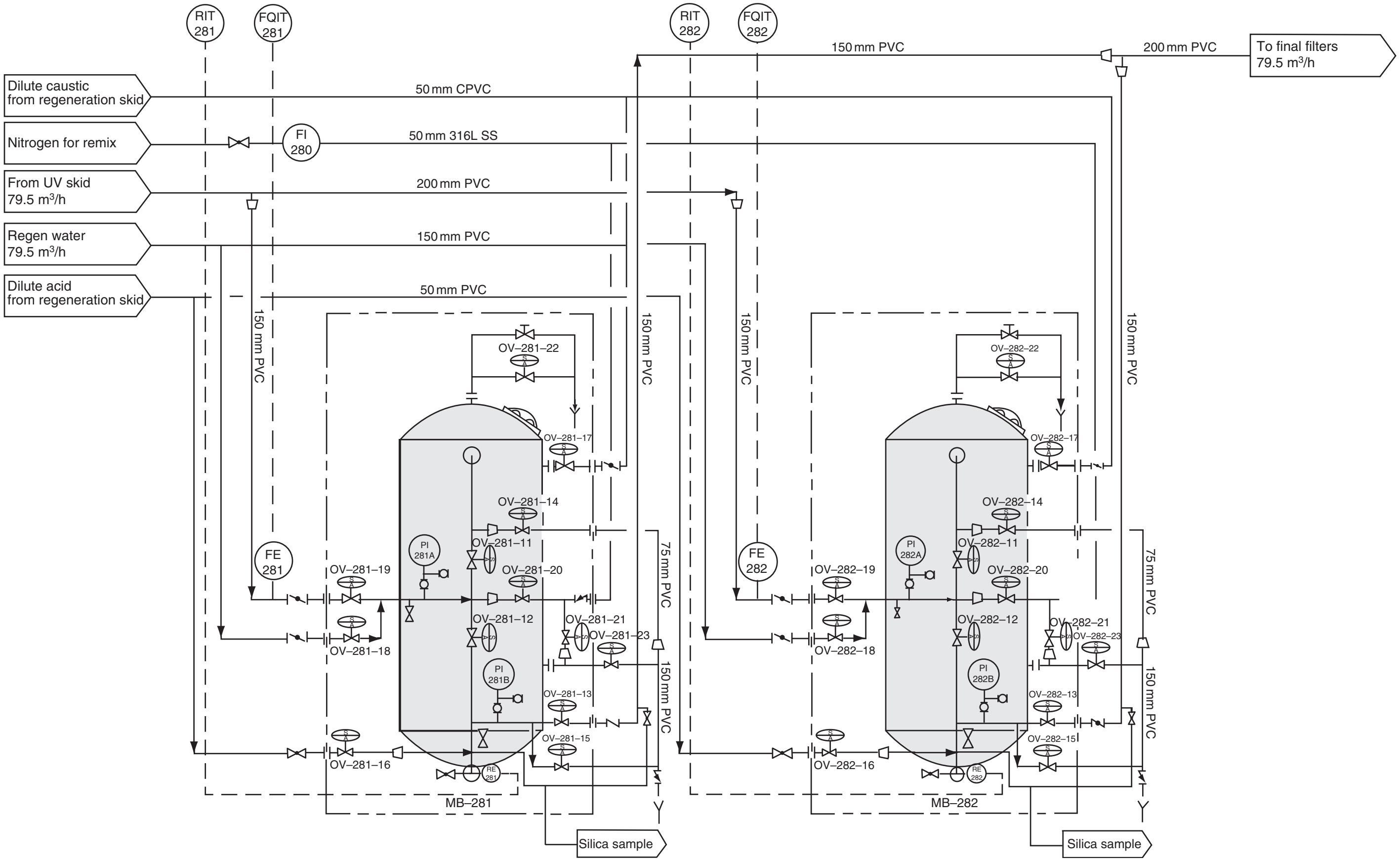


Figure 4.11 Mixed-bed ion-exchangers P&ID.

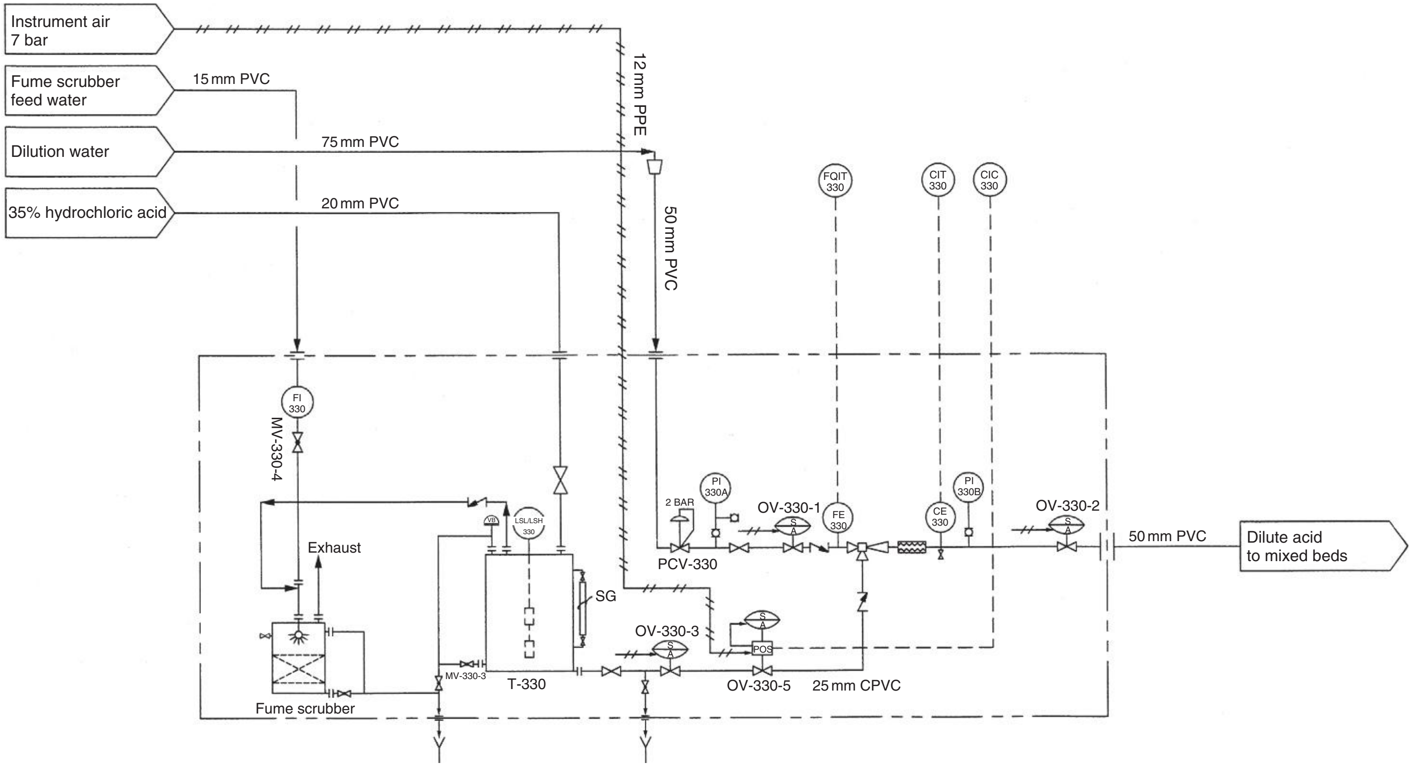


Figure 4.12 Acid regeneration system P&ID.

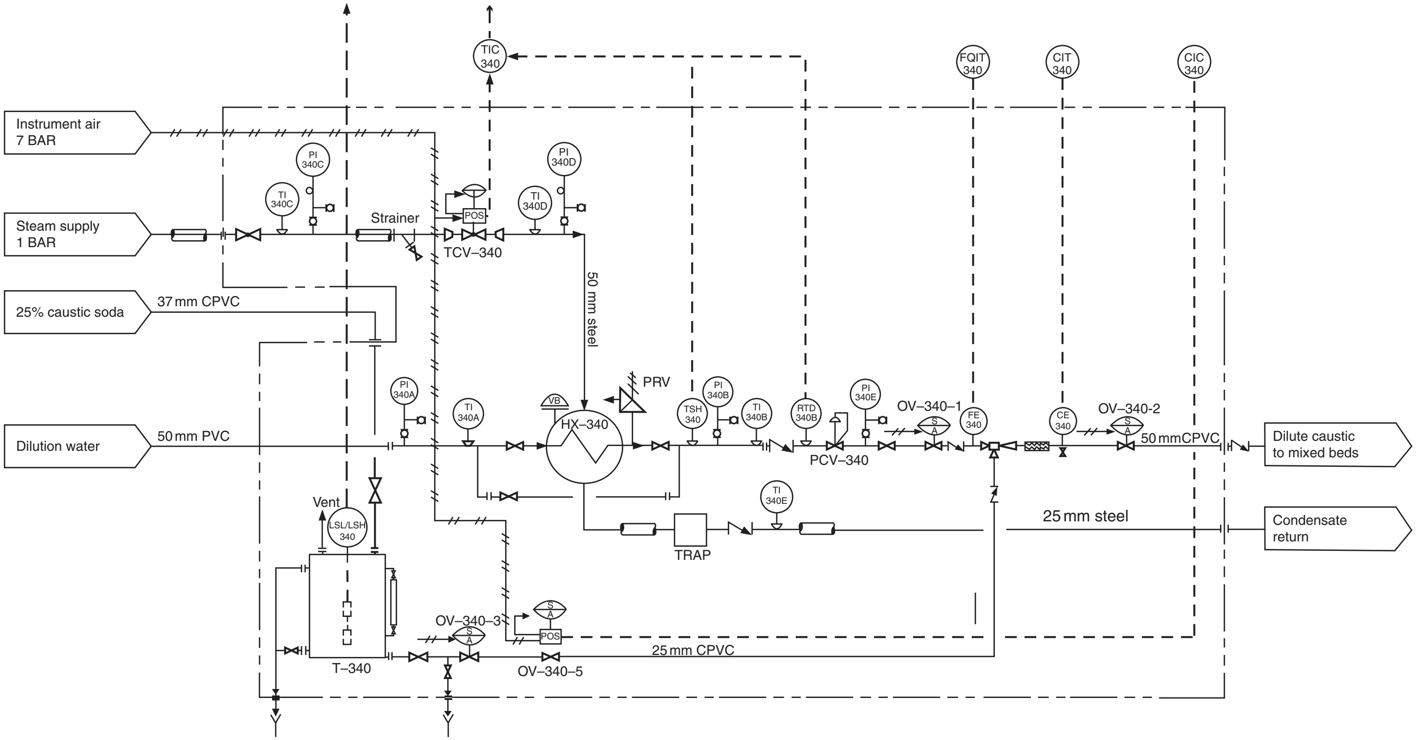


Figure 4.13 Caustic soda regeneration system P&ID.

Table 4.5 Typical process alarms

Process condition	Controller action	Set-point
Raw water high turbidity	Alarm	>1.0 NTU
Raw water pump low pressure	Alarm; pump off	0.7 bar g
Raw water pH range	Alarm	6.0–9.0
Granular media filters high Δ/P	Alarm	1 bar
Bisulphite tank low level	Alarm; bisulphite pump off	15%
Anti-scalant tank low level	Alarm; anti-scalant pump off	15%
NaOH tank low level	Alarm; NaOH pump off	15%
RO feed water high pH	Alarm	9
RO feed water low pH	Alarm	6
RO feed water high chlorine	Alarm	0.1
Cartridge filter high Δ/P	Alarm	1 bar
RO feed water high temperature	Alarm: temp. control valve closed	29°C
RO feed water low temperature	Alarm; temp. control valve open	18°C
RO pump low inlet pressure	Alarm; RO pump off	0.7 bar g
RO pump high outlet pressure	Alarm; RO pump off	18 bar g
RO low feed pressure	Alarm;	12 bar g
RO low reject pressure	Alarm;	6.9 bar g
RO high feed pressure	Alarm; RO pump off	19 bar g
RO high reject pressure	Alarm	18 bar g
RO high product pressure	Alarm	3.5 bar g
RO array high Δ/P	Alarm	5.5 bar
Tank T-200, low level	Alarm; transfer pumps off	15%
Tank T-200, high level	Alarm;	95%
Tank T-220, low level	Alarm; transfer pumps off	15%
Tank T-220, high level	Alarm; RO pump off	95%
RO permeate high conductivity	Alarm	10.0 μS/cm
RO permeate low rejection	Alarm	<92%
RO permeate high recovery	Alarm	>80%
MB product low resistivity	Alarm; DI tank divert valve open	≤15.0 MΩ-cm
MB product high silica	Alarm; DI tank divert valve open	20 ppb
Cartridge filter high ΔP	Alarm	0.7 bar
DI water low resistivity	Alarm	≤15.0 MΩ-cm
Acid tank low level	Alarm	15%
Caustic tank low level	Alarm	15%
Regen. HCl low concen.	Alarm	6%
Regen. HCl high concen.	Alarm	8%
Regen. NaOH soln. low concen.	Alarm	3%
Regen. NaOH soln. high concen.	Alarm	5%
Regen. NaOH soln. high temp.	Alarm; temp. control valve closed	29°C

the RO membrane elements have been installed in the pressure vessels, and the packed bed vessels have been filled with the specified media. In addition, during initial start-up the filter media is washed, the RO membranes are flushed of all preservatives, and the MB resins are regenerated and thoroughly mixed [5,6,8,9].

4.3.1 Start-up requirements

Criteria for acceptance of equipment should be reviewed first. After the equipment is installed, the standard preparation procedures listed below should be followed to ensure a safe and reliable operation:

1. Using the P&IDs, equipment and instrument lists check each system for piping, valves and inter-connecting piping.
2. Check all electrical connections.
3. Check all instruments and accessories.
4. Check all vents are operational.
5. Check lubrication on all pumps.
6. Check all centrifugal pumps for alignment and rotation.
7. Turn on instrument air and process nitrogen.
8. Check that steam is available for the heat exchangers.
9. Set pressure relief valves as required.
10. Check automatic valves operation.
11. Hydro-test the vessels and piping and check for leaks.
12. Drain vessels and visually inspect strainers and internals.
13. Rinse and drain all storage tanks.
14. Purchase all required chemicals.
15. Ensure the HEPA filters have been installed on the purified water storage tanks.
16. Load the filter media and ion-exchange resins.
17. Set and check temperature controller settings of the two heat exchangers.
18. Load RO membranes per the membrane manufacturer's instructions.
19. Check the Silt Density Index (SDI) of raw water. It must be <4. Check the turbidity of raw water. It should be <2.0 NTU.

Typically, each UOP shown in Figures 4.3–4.11 is started in sequence to ensure there are no bottlenecks during start-up. It also ensures any trouble spots are rectified before proceeding to the UOP, equipment, or instrument. The initial start-up procedure is often used as a hands-on-training exercise for the plant operators.

Granular media filters

The filters are washed to remove media fines prior to initial start-up as well as during the normal service run when required, as described in Section 4.1. The wash cycle consists of backwash, bed settle and rinse steps. The operating conditions and valve sequencing are given in Section 4.2. It is required that the system is shut down whenever there is a leakage.

RO membrane unit

All new RO elements are usually shipped with chemical preservatives to protect them from biological fouling. The RO membranes must be flushed to displace the preservative before using any RO product water per the membrane manufacturer's instructions for flushing the membranes. The membranes are flushed for 2–3 h at line pressure (RO high-pressure pump is off). The system operating conditions and valve sequencing are given in Section 4.2. It is required that the system be shut down whenever there is a leakage.

MB deionisers

The operating conditions and valve sequencing are given in Section 4.2. The ion-exchange resins are regenerated during initial start-up to wash the resin beds and to restore the resins to their desired operating conditions for normal service run as described in Section 4.1 and outlined in Table 4.6. The strong-based anion resins are regenerated to the hydroxyl form (OH^-), and the strong-based cation resins to the hydrogen (H^+) form. It is required that the system be shut down whenever there is a leakage.

If the IX resin is not fully exhausted prior to regeneration, it is difficult to separate the anion and cation resins completely. Complete separation is required to prevent cross-contamination and to produce ultra HPW with resistivity greater than 18.0 MΩ-cm. The procedure described below called "caustic kill" is employed to convert the heavier cation-exchange resin sites to the sodium form, resulting in even higher density than the lighter anion resins in the hydroxyl form. The procedure ensures complete separation of resins during backwashing [8]:

1. Flow a 4% NaOH solution through the entire bed for 15–20 min at the standard flow rate required for regeneration.
2. Monitor the resistivity of the water flowing to the drain. Continue until the MB effluent resistivity is 0.01 MΩ-cm, indicating cation resin exhaustion.
3. Mix the resins thoroughly to ensure further exhaustion.
4. Rinse the bed for 4–5 min.
5. Backwash the bed to separate the resins.
6. Regenerate the resins as described above.

Miscellaneous equipment

Other equipment including cartridge filters and ultraviolet (UV) lights must be rinsed before installing the specified cartridges and the UV lamps.

4.3.2 Operation

Once all the system components have been fine-tuned, the plant is ready for operating in its normal service mode. In modern integrated membrane plants, systems operation has become less dependent on the operator and more dependent on the automatic systems in place. However, human intervention is required during start-up. During normal operation, operators are required for starting the systems, for performance monitoring and

Table 4.6 A mixed-bed ion exchange unit regeneration procedure

Step	Cycle	Flow rate (m^3/h)	Duration (min)	Remarks
1	Pause for resin exhaustion	n/a	n/a	All valves closed
2	Caustic sol. for exhaustion	7.3	30	4% NaOH at 0.9 m^3/h
3	Bed rinse	65.5	155	P-233 is on
4	Pause for backwash	n/a	n/a	All valves closed
5	Backwash I	35	8	P-233 is on
6	Backwash II	26.1	20	P-233 is on
7	Settle the bed	n/a	10	All valves closed
8	Bed pre-heat	10.2	14	Water at 43°C
9	Caustic regeneration/ acid regeneration	7.3/4.8	54	4% NaOH downflow/6% HCI upflow
10	Caustic regeneration/ dilution water block	7.3/3.6	27	4% NaOH downflow/dilution water upflow
11	Slow hot rinse/anion bed and cation bed	6.4/3.6	43	Anion bed downflow/cation bed upflow. Dilution water at 43°C
12	Slow cold rinse/anion bed and cation bed	6.4/3.6	15	Anion bed downflow/cation bed upflow
13	Fast rinse I/anion bed and cation bed	24.3/ 24.3	1	Anion bed downflow/cation bed upflow, 50/50
14	Fast rinse II/anion bed and cation bed	24.3/ 24.3	38	Anion bed downflow/cation bed upflow, 50/50
15	Blowdown I	n/a	1	Bed drain
16	Blowdown II	n/a	4	Drain to 20 cm above bed level
17	Re-mix I	n/a	30	Nitrogen at 119 m^3/h
18	Re-mix II	n/a	1	Nitrogen at 425 m^3/h
19	Bed compaction	n/a	5	All valves closed
20	Vessel re-fill	18.2	4	Vent valve open
21	Pause for final rinse	n/a		
22	Final rinse	79.5	100	Rinse until resistivity is ≥ 16.0 MΩ-cm. P-233 is on
23	Quality rinse	79.5	50	P-233 is on, if necessary

data collection, for cleaning membranes, and for initiating media filters wash cycle and MBs regeneration cycle, replacing membranes and filter cartridges, routine maintenance of equipment and instruments as well as for correcting problems that may occur.

Service operation checklist

Follow the checklist given below perform the service run preparation process [5,6,10,11]. In addition, the equipment maintenance records provided in Section 4.4 should be reviewed prior to start-up.

1. Measure the SDI value of RO feed water. It should be ≤ 3. The turbidity must be less than 1.0 NTU.
2. Review the process operating parameters given in Section 4.2.
3. Activate all instruments including analysers, process monitors, level and pressure switches, and pressure and temperature transmitters.
4. Check that the anti-scalant (A/S), SBS and caustic soda (NaOH) tanks are full.
5. Ensure the regeneration skids HCl and NaOH tanks are full.
6. Verify the UV lamps have been installed.
7. Verify the microfilter cartridges have been installed.
8. Turn on the nitrogen supply for instruments, control valves, mixing resins and for blanketing RO product water storage tank.
9. Open the inlet and outlet valves of all the pumps as well as the storage tanks inlet and outlet valves.
10. Close the drain valves of all vessels. Open the vent valves of cartridge filter housings.
11. Also open all service manual valves on all skids including the media filters, cartridge filters, heat exchangers, UV lights, RO unit and MBs.
12. Set the RO water tank nitrogen blanket pressure at 3 in. w.c.
13. Turn the steam supply on for the RO feed water heat exchanger.
14. Review valve sequencing for the GMF given in Table 4.2.
15. Review valve sequencing for the RO unit given in Table 4.3.
16. Review valve sequencing for the MB given in Table 4.4.
17. Turn the MCP power switch on.
18. Verify the alarm set-points given in Table 4.5 have been entered in the PLC.
19. Power the following equipment in automatic mode at the MCP:
    - **a.** Feed water pump, P-041 or P-042
    - **b.** SBS pump, CP-131A or CP-131B
    - **c.** A/S pump, CP-132A or CP-132B
    - **d.** NaOH pump, CP-133A or CP-133B
    - **e.** RO high-pressure pump, P-161
    - **f.** RO water distribution pump, P-231 or P-232
    - **g.** UV lights, UV-231/UV-232

Use the PFSs in Figures 4.3–4.13 to guide you when operating each equipment.

Service run

1. Ensure the equipment has been screened for operation as defined above.
2. Prepare the daily data log such as Table 4.7 for data entry.
3. Press the service run pushbuttons for the GMF, RO and MB units at the MCP.
4. Water will start flowing to the media filter skid at 70 m^3/h and 4 bar g. Monitor the flow rate using FQIT-060. Monitor the pressure drop across the filter using DPIS-060. It should be less than 1 bar.

Table 4.7 A typical daily data collection form

Parameter	S	M	T	W	T	F	S
	(date)	(date)	(date)	(date)	(date)	(date)	(date)
Feed water data:							
Flow rate (m^3/h)							
Granular media filters ΔP (bar)							
Turbidity (NTU)							
Total hardness (mg/l)							
SiO_2 (ppm as SiO_2)							
Total dissolved solids (mg/l)							
pH							
RO unit data:							
Cartridge filter ΔP (bar)							
RO feed water SDI							
Feed temperature (°C)							
Feed pH							
Feed chlorine (ppm)/ORP (mV)							
Feed conductivity (μS/cm)							
Feed flow rate (m^3/h)							
RO pump inlet pressure (bar g)							
1st Stage operating pressure (bar g)							
2nd Stage operating pressure (bar g)							
Permeate pressure (bar g)							
Membrane array ΔP (bar)							
Permeate flow rate (m^3/h)							
Reject flow rate (m^3/h)							
Product water recovery (%)							
Normalised productivity (m^3/h)							
1st Stage permeate conductivity (μS/cm)							
2nd Stage permeate conductivity (μS/cm)							
Product water conductivity (μS/cm)							
Salt rejection (%)							
MB Deioniser Data:							
Product water resistivity (MΩ-cm)							
Product water silica (ppb)							
Mixed-bed ΔP (bar)							
Cartridge filter ΔP (bar)							
DI water resistivity (MΩ-cm)							

5. The PLC shuts down the media filter, GMF-061, when the differential pressure across the media bed exceeds 1 bar, and brings the standby filter, GMF-062, on-line simultaneously.
6. Turn the backwash pump switch to the auto position. Initiate the GMF-061 backwash cycle at the MCP. Once initiated, the PLC controls the cycle, as described in Section 4.2.
7. Monitor RO feed water chlorine using analyser AIT-130. It should be less than 0.1 ppm.
8. Monitor RO feed water pH using analyser pHIC-130.
9. Check the pressure drop across the cartridge filter, F-141, using DPIS-140. Replace the cartridges when ΔP is >1 bar or 3 months, whichever is sooner.
10. Monitor RO feed water temperature. It should be between 24 and 26°C.
11. The RO unit has several start-up conditions that must be specified:
    - a. During the 60-s pre-service flush cycle, the RO high-pressure pump is off while the RO membrane brine channels are flushed with water at line pressure (<2 bar g).
    - b. The pre-service flush cycle is followed by a 5-min quality rinse cycle when the RO permeate is diverted to the water reuse tank, T-200, via the divert valve, MV-161-4.
    - c. After 5 min, the RO high-pressure pump, P-161, starts provided the inlet pressure exceeds the minimum permissible value as monitored by PSL-161.
12. Monitor the RO product water conductivity using CIT-161. It should eventually drop below 10.0 μS/cm.
13. Adjust the reject flow control valve, MV-161-2, until the reject flow rate is 17 m^3/h when the RO permeate flow rate is 53 m^3/h as monitored by FQIT-161B and FQIT-161A, respectively.
14. It may be necessary to throttle the RO pump discharge valve, MV-161-1 (30% open nominal), while adjusting the reject flow control valve, MV-161-2 (50% open nominal), to achieve the desired flow rate. When making adjustments, be sure to avoid excessive pressure and flow.[1]
15. When the product water conductivity is ≤ 10.0 μS/cm, open the permeate service valve, MV-161-3, and close the divert valve, MV-161-4. Water will start flowing to the RO product water tank, T-220 at 53 m^3/h.
16. Enter RO performance data in Table 4.7 and use the data along with information given in Table 4.8 to evaluate the performance.

[1] The RO unit contains only one user controllable function, the control of the final reject flow rate. The reject flow control valve (50% open) is used in conjunction with the RO feed pressure control valve (25–30% open). The reject flow valve and the RO feed pressure valve are throttled to achieve the proper operating pressure necessary to achieve the desired product water recovery. These control valves may require fine tuning to achieve the desired productivity. In addition, as the membrane performance declines with time due to changes in the material properties of the polymer, the control valve settings will require adjustments, when higher feed pressures are required.

Table 4.8 RO unit performance analysis

Item	Diagnosis	Resolution
%Rejection – low	• Product water recovery higher than projected design recovery	• Reduce recovery and adjust flow rates to match RO projections
	• Inadequate operation pressure	• Increase RO operating pressure to match design projections
	• Change in feed water chemistry	• Check feed water chemistry. Run a new RO projection
	• Membranes may be fouled	• Determine the nature of the foulant(s) and clean the membranes
	• RO pre-treatment equipment malfunction	• Check feed water chemistry
	• Exposure to chlorine	• Check sodium bisulphite injection pump; replace damaged elements
	• Mechanical leaks in membrane elements	• Check product water conductivity at each housing to isolate the leaking seals
%Recovery – low	• RO operating pressure is too low	• Re-adjust membrane feed pressure
	• Permeate back-pressure high	• Ensure there are no restrictions in the permeate line
	• Membrane elements fouled by sparingly soluble salts; mineral scale	• Determine the nature of the foulant(s) and clean the membranes
	• RO feed temperature is colder	• Adjust the temperature to 25 ± 2°C
Permeate flux – high	• Chemical attack/chlorine exposure	• Replace damaged elements
	• Mechanical leaks in membrane elements	• Check the product conductivity at each housing to isolate the leaking seals

17. Clean the membranes as described in Chapter 2 to restore performance. Cleaning is implemented when any of the conditions discussed in Section 4.3.3 are true.
18. The RO water distribution pump, P-231 or P-232, transfers water to the MB polishing system at 80 m^3/h and 5 bar g.
19. Water flows through two TOC destruct ultraviolet (UV) lamps, UV-241/UV-242. The UV units switch on automatically when the RO water distribution pumps are turned on, and water starts flowing through the UV units. Monitor UV lamp intensity and temperature.
20. Water flows to MB-281 at 80 m^3/h. Monitor the pressure drop across the vessel. The ΔP should be <1 bar.
21. Monitor the product water resistivity. It should be $\geq$16.0 MΩ-cm.
22. Monitor the product water silica. It should be $\leq$20 ppb.
23. Monitor the pressure drop across the final filters, F-291/F-292. Replace the cartridges when ΔP is >0.7 bar.
24. Monitor the system product water resistivity, RIT-290. It should be $\geq$16.0 MΩ-cm.
25. Enter MB performance data in Table 4.7.
26. Evaluate the MB unit performance based on the criteria given in Table 4.9.
27. The PLC shuts down MB-281 when the product water quality deteriorates, and brings standby MB-282 on-line simultaneously.
28. Regenerate the MB polisher as discussed earlier in this chapter, and follow the procedure outlined in Table 4.6. Initiate the regeneration cycle at the MCP. Once initiated, the PLC controls the cycle.

4.3.3 Performance evaluation

Data collection and analysis is critical for monitoring system performance. As a minimum the data must be entered in Table 4.7. Mathematical relations for converting field data to performance data are given in Chapter 2. Normalised data must be plotted to study the performance trends, for example RO membrane rejection vs. time and RO productivity vs. time. The key performance parameters in Tables 4.8 and 4.9 should be used in conjunction with normalised data to evaluate system output. The data along with RO systems design guidelines provided in Chapter 2, and RO projections given in Table 4.1 should be used to monitor and troubleshoot the performance over time.

Most membrane problems occur due to a failure to record and analyse data. RO product flow data must be normalised to the same feed water temperature since RO membrane flux increases 3% per degree rise in temperature in °C, as discussed in Chapter 2. Data trending helps in diagnosing the system. Without data trending it is difficult to analyse when the membranes need to be cleaned, which should be cleaned when any of the following conditions are true:

- Permeate flow has dropped to 10–15% below the rated flow at normal pressure.
- Temperature-corrected feed pressure has increased 10–15% to maintain the rated permeate flow.

Table 4.9 Mixed-bed performance analysis

Item	Diagnosis	Resolution
Resin capacity – low	• Increase in total dissolved solids (TDS) concentration in feed water	• If no change, go to next step
	• Loss of resin	• Measure bed depth with resin in fully exhausted state. If no change, go to next step
	• Faulty regeneration conditions	• Verify (a) amount of regeneration solution used monthly is constant, (b) regeneration flow rates, and (c) regeneration concentrations
	• Inaccurate measurement of throughput	• Check integrator/totaliser flow meters
	• Faulty end-point measurement	• Check analytical instruments for measuring resistivity and silica
	• None of the above	• Analyse resins. Take a core sample from each quadrant of the resin bed. Combine the samples (1L) and send for analysis
Product water quality – inferior	• Higher than specified sodium leakage	• Check regeneration sequence at off-site regeneration facility
	• Silica leakage due to oxidative loss of functionality of anion resin	• Verify if there is chlorine in water
	• Silica leakage due to thermal loss of functionality of anion resin	• Check caustic solution temperature <54°C; verify the PLC controller set-point
	• Higher silica leakage due to incomplete NaOH regeneration	• Check NaOH regeneration solution concentration and flow rate
	• Fouled resins	• Check ΔP across the bed
Bed ΔP – High	• Inlet distributor blocked by finer resin beads due to a high backwash flow rate	• Reduce backwash flow rate. Verify water temperature is not colder than design temperature
		• Check resin bed is not compacted
	• Bed distributors/laterals blocked	• Check resin bed laterals distributors
	• Inaccurate flow meter readings	• Check flow meters regularly to ensure correct flow rates
		• flow rates
	• Vessel walls lining	• Check the quality of rubber lining by spark testing
	• Resin breakdown due to physical (osmotic and mechanical attrition) and thermal shock effects	• Remove fines by backwashing. Change operating conditions

- Permeate quality has decreased 10–15%; salt passage has increased 10–15%.
- Applied pressure has increased about 10–15%.
- The differential pressure across an RO unit has increased noticeably (>15%).

Once the membranes are cleaned, the operating conditions at the time of the new service run should be noted. This is the new starting base for comparing the performance before the next shutdown. Membrane flux is never restored 100% after cleaning due to aging of the membranes, and especially if the membranes are fouled, as shown in Figure 2.34. For a well-designed RO pre-treatment system, there is a gradual decline in flux with time. The slope of flux vs. time curve is a function of membrane compaction, restoration of flux after cleaning of mineral scales, and the severity of fouling. Cleaning may not restore the flux if fouling is irreversible [1,9].

4.4 SYSTEM DIAGNOSIS AND MAINTENANCE

4.4.1 Diagnostics

Considerable troubleshooting is often necessary during plant start-up. During normal service, troubleshooting is critical for understanding why a certain component is malfunctioning and what can be done to fix the problem by changing either the operating conditions or the equipment. Early detection of potential problems is possible through consistent recordkeeping and performance normalisation. Typical symptoms and recommended procedures recommended by equipment manufacturers are discussed. For alarm-related conditions, the information provided in the alarm chart in Table 4.5 can serve as a valuable guide. Once the problem has been detected, the cause of the problem must be identified and follow-up action taken according to the recommended remedial action.

According to the old adage, "prevention is better than cure," maintenance and calibration of instruments is important since accurate readings are required to detect a problem. Proper corrective action must be taken as soon as possible; otherwise, other equipment may be affected adversely. Preventive maintenance procedures are discussed in Section 4.4.12. In addition, the manufacturer's recommendations should be followed.

4.4.2 Process water pumps

General troubleshooting guidelines are provided for centrifugal pump equipment and process conditions. The pumps can be single-stage or multi-stage, horizontal, vertical, or submersible. Process-related problems depend on process design conditions for a particular system.

Problem (4.4.2)	**Solution**
I. Equipment related:	
Pump leaks at the pump head connection	• Inspect and replace the pump head seal
Pump leaks at the pump shaft	• Inspect and replace the pump shaft mechanical seal

Problem (4.4.2)	Solution
Excessive weep rate	• Examine the pump high-speed shaft assembly
Pump capacity is below design	• Check pump suction line for blockage, including valves • Check pump discharge line for blockage, including valves • Check pump impeller for damage
The performance has dropped below the pump curve	• Examine the pump high-speed shaft assembly
Pump performance is low or the pump is noisy	• Check pump suction and discharge lines for blockage, including closed valves • Check the system for entrapped air in the pump suction line • Check for damage to the pump impeller
II. Process-related:	
Pump does not run	• Verify that the pump is energised • Ensure the inlet valve is not closed • Check the low-pressure switch set-point. Increase the feed pressure • Ensure the feed water tank low-level set-point. Fill the tank
Pump shuts down	• The discharge pressure is too high. Check the high-pressure switch set-point • Process water receiving tank is full • Downstream equipment is not calling for water

4.4.3 Process water storage tanks

General troubleshooting guidelines are provided for process water storage tanks. The tanks act as equilibrium tanks for receiving water from upstream equipment and supplying water to downstream equipment or other equipment in the plant. The tanks are always supplied with level switches and/or level transmitters to start or shut off upstream/downstream equipment, e.g. shut down the process transfer pumps to protect the pumps from running dry and getting damaged or preventing tank overflow.

Problem (4.4.3)	Solution
Low-level alarm	• Check the status of tank water transfer pump to ensure that the pump was not in manual mode • Check the low-level alarm setting in the PLC • Check that the tank inlet water valves are open
High-level alarm	• Check that the high alarm set-point corresponds to the high-high tank level • Check that the tank inlet valves are closed, and the divert valves are open • Check that the tank feed water supply pumps/systems are not operating (should turn off automatically due to a process interlock) • Check that the supply pumps are not on

4.4.4 Chemical feed systems

General troubleshooting guidelines are provided for chemical dosage systems including tanks, pumps and tank mixers. Not all problems may be relevant to a particular system. Problems depend on system design and process conditions.

Problem (4.4.4)	Solution
Chemical pumps fail to operate	• Check that the start button is not in the auto position • See that the water flow rate exceeds the minimum permissible value • Check whether the solution level in the tank is below the low-level set-point value
Pump dosage rate is low	• Verify that the electronic pump controller is functioning at the desired rate. Verify pump speed and stroke length • Check the operation of the flow switch and the set-point value
Tank mixer fails to operate	• Check the start button is not in the auto position • Check whether the solution level in the tank is below the low-level set-point value
Low-level alarm	• Check the low-level alarm setting in the PLC • Check whether the solution level in the tank is below the low-level set-point value
Low-level switches fail to alarm or alarm prematurely	• Check the operation of the level switches
High chlorine (or ORP) alarm	• Verify chlorine (or ORP) analyser/controller set-point value • Check sodium bisulphite pump flow setting and calibration
High pH alarm	• Verify pH analyser/controller set-point value • Check NaOH pump flow setting and calibration

4.4.5 Granular media filters

General troubleshooting guidelines are provided for multi-media filters. These guidelines are also applicable to other filter systems such as activated carbon filters. Problems depend on system design and process conditions.

Problem (4.4.5)	Solution
No supply of water	• Check that the feed water pumps are operative, and the downstream equipment is calling for process water
The filter does not run in service mode	• Ensure the downstream equipment is calling for process water • Ensure the filter start switch is on • Verify the filter is not in the wash cycle
Process effluent turbidity is greater than 1.0 NTU	• Recalibrate turbidity analyser • Initiate the wash cycle • Verify wash cycle flow rates match the design condition

Problem (4.4.5)	Solution
Excessive ΔP across the media bed	• Check that the ΔP switch is not out of calibration • Initiate a two-step backwash sequence; start at one-half the flow rate gradually increasing to the design flow rate • Verify that the bed has not shrunk or compressed • Make provisions for air scouring (media filters only) to break loose the particles trapped in the upper layers of the bed

4.4.6 Cartridge filters

General troubleshooting guidelines are provided for cartridge filters. The filters vary in pore size rating, generally varying from 0.1 μm for final polishing filters to 5.0 μm filters for RO pre-filters. Sometimes cartridge filters with pore sizes of 10.0 μm are used in lieu of multimedia filters including backwashable cartridge filters. The pore size rating is nominal for 1.0 μm or higher cartridges and absolute for less than 1.0 μm cartridges. Absolute cartridges usually have a net negative charge to ensure >99% rejection of particles both by ionic repulsion and pore blockage.

Problem (4.4.6)	Solution
High ΔP alarm	• Check the differential pressure switch set-point • Change the filter elements
Cartridge filter elements foul prematurely	• Check the suspended solids removal performance (turbidity) of upstream media filter • Check the composition of raw water for any changes • Measure the SDI value of feed water • Media or resin fines in the cartridge filter indicates that a vessel distributor/lateral has failed

4.4.7 Heat exchangers

General troubleshooting guidelines are provided for heat exchanger performance. Process-related problems depend on operating and process design conditions and may not be unique to the system deployed, e.g. steam heated vs. chilled water heat exchangers. Procedures for cleaning heat exchangers are provided by manufacturers. Heat exchangers may be plate-and-frame or shell-and-tube type.

Problem (4.4.7)	Solution
Loss of temperature control	• Check the temperature set-point value in the PLC • Check the operation of temperature transmitter • Check the performance of steam pressure regulating valve • Check the performance of temperature control valve; check the operation of the positioner • Check for loss of instrument air pressure

Problem (4.4.7)	**Solution**
High-temperature alarm	• Verify that the controller set-point is below the high-temperature alarm value • Check the set-point of the temperature switch
Low-temperature alarm	• Verify that the controller set-point is above the low-temperature alarm value. Check the set-point of the temperature switch

4.4.8 RO membrane system

General troubleshooting guidelines are provided for troubleshooting RO system performance. Process-related problems depend on operating and process design conditions. Performance analysis information in Table 4.8 provides additional information for solving process and system problems.

Problem (4.4.8)	**Solution**
Feed/permeate high conductivity	• Check the conductivity cells. Check the conductivity analyser calibration • Check RO feed water composition
Low rejection alarm	• Check the conductivity cells. Check the calibration of conductivity analysers • Check the conductivity of permeate from each pressure vessel manually, and verify feed by-pass due to damaged O-rings or membranes
Product water recovery is high	• Verify the permeate and reject flow rates are within the design specifications • Check the calibration of flow monitors
Feed high-pressure alarm	• Check the alarm set-point of the high pressure switch • Check the ΔP across the RO unit; if it has increased significantly, higher feed pressure would be required to maintain normal productivity
Permeate high-pressure alarm	• Check the set-point of the high-pressure switch • Verify if there is any back-pressure in the permeate line
High ΔP alarm	• Check the historical performance data to ascertain if the increase is gradual or sudden. A gradual increase indicates fouling; a sudden increase indicates a faulty pressure indicator or a catastrophic membrane failure

4.4.9 MB ion exchangers

General troubleshooting guidelines are provided for troubleshooting MB ion-exchange systems. Process-related problems depend on operating and process design conditions. Performance analysis information in Table 4.9 provides additional information for solving process and system problems.

Problem (4.4.9)	Solution
Product water high silica concentration	• Re-mix the resin during start-up • Regenerate the resin bed. Check caustic regen. cycle temperature meets the design condition • Monitor quality rinse water quality
Low resistivity alarm	• Re-mix the resin during start-up • Regenerate the resin bed • Monitor quality rinse water quality
Mixed-bed fails to "rinse-up" after regeneration	• Verify the standard regeneration procedure, given in Table 4.6, and as follows: (a) Resin separation during the backwash step. Ensure there is a sharp resin separation as seen through the middle sight-glass. (b) Check caustic dilution water flow rate, concentration and duration. Also check the acid dilution water flow rate required for blocking the caustic flow. (c) Check the acid and caustic dilution water flow rates and solution concentrations during the caustic addition and acid addition steps. (d) Ensure that the water level after the bed drain-down is no more than 3–6 cm above the bed-level. (e) Confirm proper "air" mix flow rate and duration.
Resin bed high ΔP	• Re-mix the resins, as discussed in Table 4.9

4.4.10 MB regeneration systems

General troubleshooting guidelines are provided for troubleshooting MB ion-exchange systems. Use the guidelines in Section 4.4.9 when solving system problems. Process-related problems depend on operating and process design conditions and may not be unique to the system deployed.

Problem (4.4.10)	Solution
Chemical pumps/dilution water pumps do not operate in automatic mode	• Check the start button is not in the auto position • Check if the storage tank level reading at the local level indicator/controller is below the low-level set-point value
Chemical tank low-level alarm	• Check the low-level alarm setting in the PLC to ensure that it is set correctly
Chemical tank high-level alarm	• Check that the alarm set-point is set for the maximum operating capacity of the tank
Level switches fail to alarm or alarm prematurely	• Check the operation of level switches
High temperature alarm – caustic skid dilution water heat exchanger	• Check caustic tank heater temperature alarm set-point

Problem (4.4.10)	Solution
High or low concentration – regeneration solution concentration	• Take a sample and check the specific gravity of the dilute solution. Use specific gravity to check and re-calibrate the conductivity meter; readjust the set-point • Adjust the dilution water and acid (or caustic) flow rates tox obtain the desired concentration by adjusting the flow rate with valves on the skids

4.4.11 Ultraviolet units

General troubleshooting guidelines are provided for ultraviolet (UV) units. A low radiation intensity indicator is provided with all UV units. The lamp intensity should be greater than 80%.

Problem (4.4.11)	Solution
Low UV intensity	• Check if the UV lamp needs to be replaced • Check the operation of the UV intensity monitor and probe
Low-temperature alarm	• Verify that the set-point is above the low-temperature alarm value Check the set-point of the low-temperature switch
High-temperature alarm	• Verify that the set-point is below the high-temperature alarm value Check the set-point of the high-temperature switch

4.4.12 Preventive maintenance

Maintenance of equipment and components is critical for safe and efficient operation of a manufacturing plant. Equipment manufacturers usually supply maintenance procedures with the equipment. A recommended maintenance schedule is given in Tables 4.10 and 4.11. Adherence to the schedule and recording of information is necessary to satisfy potential warranty claims and for taking corrective action to protect the equipment from any potential damage. This schedule along with the equipment manufacturer's recommendations should be used to service or replace the components prior to component breakdown. It is important to maintain a log of regular maintenance service such as calibration of monitors, analysers, flow meters, switches, transmitters and gauges. A record of replacement of pump components, membrane cleaning, regeneration of ion-exchange resins as well as replacement of membrane elements and cartridge filters is especially important.

Table 4.10 Equipment maintenance schedule

Item	Frequency
1. *General*	
Inspect skids for alarm conditions, leaks, damages	D
Review operational data	D
Do control panel lamp tests	D
2. *Transfer pump*	
Replace mechanical seals	A
Replace head seals	A
3. *High-pressure RO pump*	
Lubricate the air motor located on pump suction	Q
Replace the pump lubricant and lubricant filter	Q
Replace seals and O-rings in the high-speed shaft assembly	A
4. *Chemical dosage pump*	
Inspect and clean the chemical containment area	W
Inspect and clean any chemical weeping from the pump injection heads	M
Replace the diaphragm	SA
5. *RO unit*	
Membrane cleaning	R
Inspect the operation and settings of the pressure and flow control valves	Q
6. *Mixed-bed deioniser*	
Check silica level for breakthrough	D
Check resistivity for breakthrough	D
Resin replacement	R
7. *Heat exchanger*	
Inspect the controller temperature set-point	M
Calibration of temperature transmitter	Q
Calibration of temperature switch	Q
Inspect the operation and setting of the nitrogen system temperature control valves	Q
8. *Water storage tank*	
Level transmitter and level switch calibration	Q
Inspect the tank ladder, railing and associated attachment hardware for loose nuts and bolts	Q
Inspect the tank tie-down hardware for loose bolts and nuts, or stress failure	Q
Inspect the operation and setting of the nitrogen system pressure control valve	Q
Inspect the operation and setting of the nitrogen system pressure relief valve	Q
Inspect and replace the HEPA filter	Q
Inspect the inside of the tank for damage and/or untimely surface wear or build-up of foreign matter on the tank bottom or walls	SA
9. *Chemical solution tank*	
Level transmitter and level switch calibration	Q
Clean the inside surface of tank	SA
Re-fill the tank	R
10. *Dead-end cartridge filter*	
Replace the cartridge filter housing head O-ring	A

Continued

Table 4.10 Equipment maintenance schedule—cont'd

Item	Frequency
Replace RO pre-filter cartridge elements	R
Replace final cartridge elements	SA/A
Autopsy the cartridge element	A
11. *UV lamp*	
Check the intensity and lamp indicator settings	D
Replace UV lamps	SA/R
Replace UV sleeves	SA/R
Calibrate the intensity meter	SA
12. *Switches*	
Temperature switches calibration check	Q
Pressure switches calibration check	Q
Check the operation of automatic level switch	Q
In the case of float switches, check their operation by manually depressing the level float	Q
Differential pressure switches calibration check	Q
13. *Pneumatic valve*	
Check the operation of solenoid valve	Q
Inspect the operation of automatic valve	Q
14. *Miscellaneous*	
Check pumps/motors for excessive vibration, noise and over-heating. Check lubrication level	W
Check equipment mounts especially pumps/motor	A
Backwash media filters to prevent biological build-up	W
Inspect ion-exchange vessel internals and lining	A
Repaint surfaces as necessary	A
Electrical relays; check and clean contacts	M

D, daily; W, weekly; M, monthly; Q, quarterly; SA, semiannually; A, annually; R, as required.

4.5 RO PLANT EQUIPMENT

Design, operation and maintenance of a system involve selection of process equipment based on sound and proven specifications. Specifications are the workhorse of any new plant. They provide the design and performance requirements discussed in Sections 4.1 and 4.2.

4.5.1 Equipment selection

Engineers select and evaluate process equipment. The selected equipment must be technically sound, reliable, safe and easy to operate, serviceable, economically attractive and environmentally sound, e.g. minimal noise pollution and no mechanical and fire hazards. For example, all pneumatic valves, except for the modulating valves, are air-to-open/spring-to-close valve type for safe shutdown unless the valve is a divert drain valve as

Table 4.11 Instrumentation maintenance schedule

Item	Frequency
1. *pH analyser*	
Check pH indicating transmitter controller set-point	M
Standardise pH controller	M
Replace pH element	SA
2. *Differential pressure monitor*	
Check the calibration of ΔP indicating transmitter	Q/SA
3. *Chlorine/ORP analyser*	
Check the consumable chemicals	M
Calibrate the analyser	M
4. *Flow indicator/totaliser*	
Calibrate flow indicators and transmitter	Q/SA
Check the calibration of flow controller	Q
5. *Temperature transmitter*	
Inspect the set-points of temperature controller	M
Inspect and check the calibration of	Q
6. *Pressure transmitter*	
Check the calibration of pressure indicating transmitter	Q
Check the calibration of pressure controller	Q
7. *Level indicator and transmitter*	
Calibrate level transmitter	Q
Calibrate ultrasonic level transmitter	Q
8. *Conductivity analyser*	
Check the calibration of the conductivity monitor	SA
Clean the sensor	Q
9. *Polishing analysers*	
Check the calibration of resistivity monitor	SA
Clean the sensors	Q
Calibrate silica analyser	M
Replace silica analyser reagent	M
Calibrate particle count analyser	
10. *Turbidity analyser*	
Clean the turbidity cell	M
Check the calibration of the analyser	Q

discussed in Chapter 2. Similarly, the heat exchanger should have enough surface area and the process water tank should have excess capacity to provide a margin for continuous operation. Some of the equipment used in RO plants operates under severe conditions, e.g. 30 bar g at 3000 rpm and 480 VAC/3 phase/50 Hz for operating the RO feed water pump. Specifications of major component are detailed in Section 4.5.2.

The process equipment should be designed with extra capacity, for example a pump must be sized large enough to overcome the pressure drop in the control valve or an orifice while delivering water or other fluid at peak flow and pressure. Some of the key features of centrifugal pumps and control valves are discussed in Chapter 6. The pump motor should be sized large enough for the pump's maximum impeller even when the pump comes with a smaller impeller initially; it is cheaper to replace the impeller than the motor in the future. The electric motor should have enough power to be non-overloading to ensure the motor would have enough power when the control valve is fully open with the pump following its pump curve.

RO high-pressure centrifugal pumps are typically multi-stage, vertical or horizontal, depending on the capacity. Increasingly, pump motors are using VFDs to maintain constant flow rate and pressure. VFDs allow the operation of pumps at pre-selected speeds, increasing or decreasing the flow and pressure characteristics for a given impeller size and motor power. Refer to Chapter 6 for additional information on centrifugal pumps.

Most RO systems are often designed for 70–75% PWR (corresponding to a feed/brine concentration factor of 4) to minimise the potential for scaling by sparingly soluble salts that get concentrated in the reject channel as permeate is removed from the membrane module. In the case of seawater desalination, PWR is held to less than 50% (concentration factor = 2) due to the very high osmotic pressure that in turn affects the size of the RO feed pump and membrane pressure vessel ratings. Operation at reduced recovery implies more membrane surface area resulting in higher initial capital cost, which is compensated by lower operation costs due to fewer shutdowns to clean the membranes and longer life. These aspects of RO design are discussed in detail in Chapter 2.

4.5.2 Equipment specifications

Major components of the integrated membrane plant are described below. Refer to the figure numbers to identify the equipment. A list of some of the leading process equipment manufacturers is given in Table 4.12 (detailed information is available on their websites).

Feed water pumps

The feed water pumps shown in Figure 4.3 are 316L stainless steel (SS) horizontal centrifugal pumps rated for a flow rate of 70.5 m^3/h at 2.8 bar g each. The totally enclosed fan cooled (TEFC) motors are rated for 18.7 kW, 3000 rpm, 460 V/3 Ph/50 Hz. The motor service factor is 1.15.

Granular media filters

The media filters shown in Figure 4.4 are rubber-lined (5 mm thick) carbon steel (ASME coded-stamped) vessels, 2.4 m diameter (D) × 1.83 m SSH and rated for a working pressure of 7 bar g. The hydraulic test pressure rating is 10 bar g. The internal distribution system consists of a PVC upper distribution system and a header and lateral bottom collection system. Each vessel is provided with two 8 cm × 30 cm sight glasses and a 40 cm × 50 cm elliptical man-way. All face piping is PVC, and accessories include pneumatic

Table 4.12 Partial list of equipment manufacturers

Component	Manufacturer
RO membranes (spiral – wound)	Desal, Dow/FilmTec, Fluid Systems, Hydranautics, IonPure, GE/Osmonics, Saehan, Toray, TriSep, Toyobo (hollow-fibre)
Cartridge filters	CUNO, Filterite, Gelman, Millipore, Optimum Filter, Pall, Pentec, Shelco, USFilter
MF/UF microfilters[a]	Pall, USFilter/Memcor, Zenon, Koch
Ion-exchange resins	Dow, Purolite, ResinTech, Rohm & Haas, Sybron, USFilter
Centrifugal pumps	Durco, Fristam, Fybroc, G&S, Goulds, Grundfos, Triclover, Worthington
Diaphragm pumps	LMI, Milton-Roy
Positive displacement pumps	Milton Roy, Pulsafeeder
Submersible pumps	Pumps Unlimited, Tonkaflo, T&T
Variable frequency drives	Allen-Bradley, Siemens, Yasakawa
Heat exchangers	Alfa-Laval, ITT, Trantor, Yula
Ultraviolet lamps	Aquafine, Trojan, Wedeco Ideal Horizon
Loop controllers	Foxboro
PLC	Allen Bradley, Honeywell, Siemens, Toyota
Pressure gauges/ switches	Ashcroft, United Electric
Process monitors/ transmitters	Endress-Hauser, Foxboro, GF Signet, Thornton, Yokogawa
Temp. gauges/ switches	Ashcroft
Chemical monitors	GLI, Orbisphere, Rosemount, Thornton
Chemical analysers	Anatel, HACH, Scientific Instruments
Plastic valves[b]	Asahi, George-Fisher, Hayward, Plastomatic
Ball valves	Apollo, Jamesbury, Swagelok
Butterfly valves	Bray, Keystone
Check valves	Apollo, Check-All, Hayward
Control valves	Fisher, Foxboro, Neles-Jamesbury, Stonel
Diaphragm valves	ITT
Needle valves	Marsh, Marquest, Nupro
Pressure regulating valves	Anderson Greenwood, Jordan Mark, Plasto-Matic, Protecto-Seal
Relief valves	Crosby, Kunkle, Protecto-Seal

[a] See Table 6.14.
[b] Ball, Butterfly, Check, Diaphragm, Relief, Others; CPVC, PVC PP, PVDF.

butterfly valves, isolation ball valves, pressure gauges, differential pressure gauges and paddle wheel flow elements. Each media filter contains 4.25 m^3 of granular media of varying porosity and density from top to bottom: anthracite (top), silica sand (centre), and garnet (bottom), i.e. the lightest and most coarsely graded material on top, the heaviest and the most finely graded material on the bottom, as shown in Figure 2.4.

Chemical feed systems

The chemical feed system consists of three systems, as shown in Figure 4.5. The SBS system consists of a 570-l feed tank and two injection pumps rated for 18.9 l/h at 5.5 bar g. The anti-scalant (A/S) system consists of a 570-l feed tank and injection pumps, rated for 18.9 l/h at 5.5 bar g. The caustic soda (NaOH) system consists a 570-l feed tank and injection pumps rated for 170 l/h at 5.5 bar g. The PVC injection pumps are positive displacement types with PVDF diaphragms. Each tank is provided with a mixer and a level switch. All motors are rated for 220 V/1 Ph/50 Hz.

Cartridge filter

The RO pre-filter shown in Figure 4.6 contains 24 polypropylene (PP) cartridges, 76 cm long (L), rated for 5.0 μm (nominal pore size). The cartridge separation efficiency is greater than 85% rejection for particles $\geq$5.0 μm in size. The filter vessel is 304 SS, ASME code construction, and rated for a design pressure of 10 bar g.

Feed water heat exchanger

The feed water heat exchanger system shown in Figure 4.6 is used for heating 70.5 m^3/h RO feed water to 25°C with low-pressure steam. The heat exchanger is a 304 SS plate-and-frame, counter current type, sized for 100% total flow. The rated design pressure is 6.9 bar g. The steam flow rate is 9103 lb/h at 1 bar g.

RO unit

The single-pass RO unit system shown in Figure 4.7 is a 6:4 staged array (10 pressure vessels) designed for a PWR of 75% using spiral-wound, TFC polyamide, full-fit RO membranes with an initial salt rejection greater than 99.0%. Each pressure vessel contains six elements connected in series for a total of 60 elements. The membrane elements are housed in FRP pressure vessels rated for 40 bar g. Each membrane element is 20 cm diameter × 100 cm long. The elements are rated for a nominal flow rate of 34 m^3/day with an average flux of 22 l/m^2/h based on well water. The membrane projections are given in Table 4.1. The RO high-pressure pump, P-161 is a 304L SS submersible, multi-stage centrifugal pump rated for 70.5 m^3/h at 17 bar g total delivery head (TDH). The TEFC motor is rated for 45 kW, 460 V/3 Ph/50 Hz, and 3000 rpm with a service factor of 1.15.

Water reuse tank

The water reuse tank shown in Figure 4.8 has a capacity of 76 m^3. The tank is 3.7 m D × 7.3 m SSH; FRP, flat-bottom, dome-top with 50 cm man-ways in the top dome and the side shell. It is provided with side mounted level switches and a level transmitter.

GMF backwash pumps

The backwash pumps shown in Figure 4.8 are 316L SS horizontal centrifugal pumps rated for 170 m^3/h at 3 bar g (TDH). The TEFC motors are rated for 30 kW, 460 V/ 3 Ph/50 Hz, and 1750 rpm. The motor service factor is 1.15.

RO product water tank

The RO product water tank system shown in Figure 4.9 has a capacity of 76 m^3. The tank is 3.7 m D × 7.3 m SSH; FRP, flat-bottom, dome-top with 50 cm man-ways in the top dome and the side shell. It is provided with side-mounted level switches and a level transmitter, a pressure relief valve/vacuum breaker, a nitrogen blanketing system, and a HEPA filter.

RO water-distribution pumps

The distribution pumps shown in Figure 4.9 are 316L SS vertical, multi-stage centrifugal pumps rated for 80 m^3/h at 5 bar g (TDH). The TEFC motors are rated for 33 kW, 460 V/3 Ph/50 Hz, and 3000 rpm. The motor service factor is 1.15.

MB regeneration pump

The dilution water pump shown in Figure 4.9 is 316L SS vertical, multistage centrifugal pump rated for 70 m^3/h at 5 bar g (TDH). The TEFC motor is rated for 33 kW, 460 V/3 Ph/50 Hz, and 3000 rpm. The motor service factor is 1.15.

Ultraviolet light units

The TOC destruct UV units shown in Figure 4.10 are rated for a dosage >120,000 μW s/cm^2 at 185-nm. The rated dosage is after 8000 h of operation. (Note: the bacteria destruct UV sterilisers are rated for a dosage >30,000 μW s/cm^2 at 254-nm.) The material of construction is 316L SS with passivated and electropolished wetted parts. The maximum operating pressure is 8 bar g. Each unit is provided with two light traps.

MB ion exchangers

The MB vessels in Figure 4.11 are ASME code stamped and rated for a working pressure of 7 bar g. The hydraulic test pressure rating is 10 bar g. The vessels are 2.1 m D × 3 m SSH and are lined with 5 mm thick unpigmented rubber. Each vessel is constructed of carbon steel with dished heads and a false-bottom. Each vessel is provided with a 60 cm man-way, three 8 cm × 30 cm sight glasses, and a 75 cm port for removing the resins. Each MB vessel contains 3.26 m^3 strong base anion resin (OH^- form), 2.18 m^3 strong acid cation resin (H^+ form), and 0.54 m^3 inert resin. The internal piping consists of a 316L SS upper distributor, a 316L SS bottom/acid distributor, and 316L SS interface and caustic distributors. All service water external piping and valves are PVDF. Acid and caustic solution piping is CPVC and polypropylene, respectively. The nitrogen line piping is 316L SS. The resin traps in each vessel product water line are 316L SS with wedge wire internals.

Cartridge filters

The filters in Figure 4.10 contain 19 polysulphone/nylon 66 cartridges, 76 cm long, rated for 1.0 μm (absolute) each. The cartridge separation efficiency is >99% rejection for particles ≥1.0 μm in size. The filter housing is 316L SS, ASME code construction, rated for a design pressure of 10 bar g. The cartridges are sized for 15 l/m per 25 cm length of the cartridge. The piping is PVC or PVDF.

MB regeneration skids

The MB regeneration skids shown in Figures 4.12 and 4.13 include hydrochloric acid dilution and caustic soda dilution systems, respectively. Each skid contains a 570-l FRP tank, a CPVC eductor for mixing water with the chemical, a conductivity (% concentration) analyser and pneumatic valves. Each tank is provided with an ultrasonic level switch. The acid skid is provided with a scrubber. The skid piping is CPVC. The caustic regeneration skid heat exchanger shown in Figure 4.13 is used for heating 9.5 m^3 dilution water to 43°C. The heat exchanger is a 304 SS plate-and-frame, counter-current type sized for 100% total flow. The rated design pressure is 6.9 bar g. The steam rate is 956 lb/h at 1 bar g.

Control panels

The MCP houses the entire system control package including the system PLC, graphic panel lights, enunciator, selector switches as well as monitors. The remote input/output (I/O) or LCP are provided on each skid for interacting with the MCP via the PLC. All panels are NEMA 4X enclosures.

4.6 MEMBRANE-FILTRATION SYSTEM

Traditional applications of UF and MF have been in the areas of biotechnology, dairy, colour removal from groundwater and industrial wastewater. Industrial wastewater treatment includes electroplating rinse water processing for paint recovery, treatment of oil/water emulsions, processing wastewater containing heavy metals, oil and grease prior to effluent discharge, textile wastewater, and pulp and paper wastewater, as discussed in Chapter 3 [1]. In the last 20 years, membrane filtration has emerged as a viable process for treating municipal waters and seawater prior to RO desalination.

The UF/MF market for municipal water treatment was worth $300 M in 2006 and is projected to double by 2014 [12]. This market is broadly divided into three categories: (i) drinking/potable water, (ii) seawater RO/NF pre-treatment, and (iii) wastewater reuse [12–16]. Increasingly, UF/MF systems are being used for RO/NF pre-treatment instead of conventional pre-treatment (coagulation, sedimentation, media filtration) (see Figure 3.47). Membrane filtration is a highly effective barrier to particles such as suspended solids, colloidal particles, cysts and bacteria, producing treated water with very low turbidity (0.1 NTU) and consistent quality irrespective of the feed source. High pressure membrane systems (RO/NF) operating on UF/MF-treated water are, therefore, less prone to fouling, require minimal chemical treatment and have higher on-stream time. The overall result is higher RO system throughput and longer RO membrane life.

Design of a membrane filtration plant requires a well-balanced selection of flux to optimise costs and minimise fouling. A low flux increases the capital cost (Capex) since high membrane area is required, whereas a high flux increases the operating costs (Opex) since fouling rates increase exponentially with flux, thus necessitating higher operating pressure and frequent chemical cleaning.

4.6.1 Principle of operation

Continuous cross-flow operation

Cross-flow UF and MF tubular and hollow-fibre membranes (asymmetric, phase inversion type, mostly cellulose acetate and polysulphone) have been used for processing industrial streams for more than 40 years, as discussed in earlier chapters, for treating wastewaters such as cooling tower blowdown with high concentrations of silica and hardness, treating RO concentrates and high salinity streams, and recovering heavy metals from laundromat wastewaters prior to discharge [1,17]. Schematic flow diagram of a typical cross-flow MF/UF system is shown in Figure 2.28. The treatment of such wastewaters requires addition of magnesium chloride and/or lime and soda ash to raise the pH to 11 to reduce silica and hardness to less than 50 mg/l (as $CaCO_3$) prior to demineralising with RO. Thus, MF replaces conventional lime softening clarifiers and multimedia filters and produces water of higher quality for discharge or RO feed water.

Cross-flow membrane filtration is a continuous process during the service cycle. The feed flow is inside out, i.e., the feed flows in the tube side and the permeate flows radially out of the tube wall. Ninety percent of the reject is typically recycled back to the feed tank at high velocities of 4–5 m/s. Because of the large i.d., as is the case with tubular membranes, the membrane elements can handle feeds with solid levels of up to 5%. The process is facilitated by operating in a turbulent regime to reduce the build-up of solute cake on the membrane surface. High turbulent cross-flow and large i.d. often eliminates the need for pre-filtration. The permeate flow rate is 10–15% of the cross-flow rate at a flux of ~300–500 $l/m^2/h$. Thus, a UF/MF system, designed for 20 m^3/h permeate flow rate, may require a feed/recirculation pump rated for 250 m^3/h at 3–4 bar g feed pressure. Back-pulsing with filtered water or permeate reduces the frequency of cleaning cycles. However, periodic chemical cleaning is required to remove or dissolve the strongly held accumulated particles that are not dislodged with backwashing. Overall, wastewater recoveries of up to 95% are achieved.

Low surface area and packing density (especially tubular membranes), large footprint and high power consumption – high cross-flow velocity required to prevent fouling results in increased head loss – makes cross-flow systems quite expensive (high Capex and Opex). They are, therefore, best suited for relatively small flows (up to 100 m^3/h) and special applications. Application of spiral-wound UF membranes is relatively new and limited to specific applications.

Semicontinuous dead-end filtration

The most commonly used membranes for municipal water treatment are hollow fibre modules that are supplied in three operating formats: (i) pressure-driven inside feed, (ii) pressure-driven outside feed, and (iii) submerged vacuum driven [12]. The UF/MF membrane (hollow fibre and capillary) technology for water treatment is relatively new and hence no single design has proved itself to be optimal. These membrane filtration systems operate in a semicontinuous dead-end mode with intermittent backwash often combined with air scour either during filtration and/or backwash cycles. The backwash controls the build-up of the foulants by removing particles from the membrane surface. Foulants that are not removed by backwash require chemical cleaning. A typical operating process is described below.

The flow regime is from outside of the fibre (shell side) through the pores in the membrane wall to the lumen side. As the water gets filtered, the solids rejected by the membrane form a cake layer on the membrane surface, as shown in Figure 1.12. The cake layer is removed by backwashing the membrane elements by air-scouring and air-assisted backwashing every 30–60 min to maintain the flux (constant flux operation). Backwashing also reduces the frequency of cleaning the membranes to 4–6 weeks and enables the membrane system to run on feed water with turbidity up to 500 NTU. The filtrate or product water turbidity is typically $\leq$0.1 NTU. Every 4–6 weeks the membranes are cleaned with acid followed by treatment with sodium hypochlorite.

UF and MF membranes alone do not remove total organic carbon (TOC) and trihalomethane (THM) precursors [13]. Hence, pre-treatment entails addition of chemicals such as coagulants ($FeCl_3$ or $FeSO_4$), alum or polyaluminium chloride to increase the size of suspended solids and colloidal particles and thus prevent or minimise colloidal, organic, and/or biological fouling. In the case of seawater desalination, membrane filtration has proven to be superior to multimedia filtration [14,15].

Constant flux vs. constant pressure and critical flux

Membrane systems operate in either constant flux (variable feed pressure) or constant pressure (variable water flux) mode. During constant flux operation, trans-membrane pressure (TMP) is increased to maintain the desired or design flux that otherwise continues to drop due to fouling. In constant pressure operation, the productivity decreases due to fouling. Constant flux operation is more common, especially in full-scale plants. The key to operation in constant flux mode is to operate below the critical flux condition when fouling is minimal and membrane permeability is not adversely affected. In the critical flux regime, the flux is almost directly proportional to feed pressure as discussed in Chapter 1 (see also Figure 2.27).

4.6.2 System equipment

The membrane filtration system shown in Figure 4.14 is a standard pressurised system (for a review of the various membrane filtration modules refer to Table 6.14). The PLC-controlled system is designed to treat 2700 m^3/h seawater or surface water and supply 2500 m^3/h filtered water to the RO desalination unit. The design recovery is greater than 90% based on a flux of 49 $l/m^2/h$ at 25°C. Major components of the skid-mounted system are detailed below:

1. Membrane unit: The hollow fiber membranes are PVDF with a pore size of 0.04 μm (nominal). Each unit can be isolated from the rest of the system using automatic bloc-and-bleed valves.
2. Feed system: VFD controlled centrifugal pumps rated for 1550 m^3/h at 5.5 bar g each. The feed system includes strainers rated for 250 μm.
3. Compressed air supply system: Rotary screw air compressors supply air at 9 bar g for air-assisted liquid backwash to remove particulates from the membrane surface. It also supplies air for the Membrane Integrity Test as well as various plant instruments and controls.

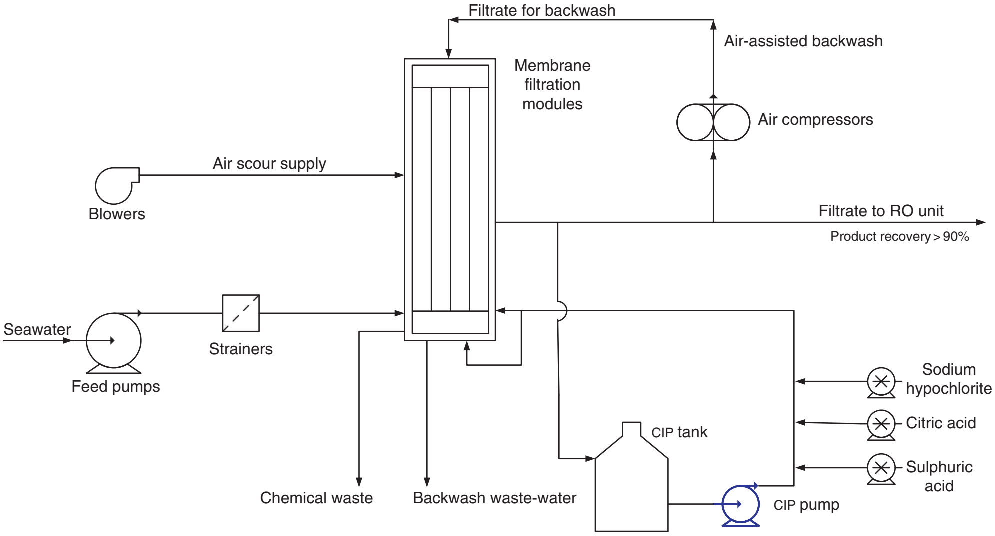


Figure 4.14 Process flow schematic of a semicontinuous dead-end UF/MF membrane system.

4. Air scour blowers: Positive displacement blowers supply low pressure air to the feed side to scour the membrane fibres during pre-backwash.
5. CIP system: The clean-in-place skid consists of a hot water tank, centrifugal transfer pump and an air-driven diaphragm pump. Diaphragm pumps for in-line addition of 12.5% sodium hypochlorite, 50% citric acid and 50% sulphuric acid.

4.6.3 Service and cleaning operations

Service cycle

Feed pumps transfer water through 250 μm strainers to the membrane units at 1550 m^3/h and 5.5 bar g, as shown in Figure 4.14. The pumps maintain a constant feed water flow rate. The operation is in constant flux mode. The feed water enters the shell side of the hollow fibre and flows through the membrane pores into the fibre bore or lumen as filtrate. The membranes reject particles and colloids larger than the nominal pore size. The filtrate flows to filtered water storage tank. Both feed water and filtered water are monitored for turbidity.

Backwash/cleaning cycle

The flow rate of the filtrate declines with time due to the build-up of particles on the membrane surface, and possibly due to some plugging inside the pores. This results in an increase in the TMP between the feed side and the filtrate side. To compensate for the reduced flux (constant flux mode), higher feed pressure is required by increasing the pump speed and/or opening the filtrate valve. Hence, a regime for restoring performance is required, consisting of the following typical steps:

1. Backwash – every 30–60 min for 4–5 min. First, the membrane surface is scoured with air to loosen up the debris formed on the membrane surface. Next, the flow direction is reversed with filtered water flowing backwards from the lumen side to the feed side with the aid of compressed air.
2. Maintenance wash – every 24 h with chlorine for ~30–40 min.
3. Pressure decay test (PDT) – every 24 h for ~4 min to test fibre integrity.
4. Sonic test – as required, typically when the PDT fails to determine which fibre has been damaged/broken and needs to be replaced.
5. Clean-in-place (CIP) – the membranes are cleaned with acid followed by sanitising with sodium hypochlorite solution when the TMP exceeds 1 bar, typically 4–6 weeks. Only one membrane unit is cleaned at a time. A combination of citric acid and sulphuric acid is injected by the dosing pump in the filtered water transferred from the CIP tank. The solution is circulated for 30 min followed by soak and aeration steps that last 90 min. Next, a dilute sodium hypochlorite solution is injected by the dosing pump in the filtered water transferred from the CIP tank. The solution is circulated for ~30 min followed by soak and recirculation steps that last 90 min.
6. Rinse the membranes to drain for 30 min and return the system to service.

The service, backwash and cleaning cycles described above are general in nature and depend on each membrane manufacturer's system design.

4.7 SUMMARY

The design and operation of two membrane plants are discussed in detail to familiarise the reader with the complexities of membrane-based water treatment plants. The design, equipment specification and operation of membrane plants depend on the quality and quantity of feed water and the product water. Often plants are modified or upgraded to meet newer demands. The initial or preliminary design is based on a simple line diagram incorporating mass balances followed by designing the plant based on feasibility and cost. Increasingly, RO membrane plants integrated with MF, UF, NF and in some cases, ED, are being built to supply potable water and treat wastewater [12,15,16]. Furthermore, integrated membrane systems are more competitive than conventional processes because of lower energy consumption, higher quality of final product and low environmental impact.

REFERENCES

[1] M. Cheryan, Ultrafiltration and Microfiltration Handbook, CRC Press, Boca Raton, FL, 1998.

[2] S.V. Cabibbo, D.B. Guy, A.C. Ammerlaan, A. Ko, R. Singh, Reverse Osmosis Technical Manual, NTIS Publication, Springfield, VA, USA, 1979.

[3] J.M. Douglas, Conceptual Design of Chemical Processes, McGraw-Hill, New York, NY, 1988.

[4] S.D. Strauss, Water treatment. Power, June (1993) 1–52.

[5] G.A. Pittner, High purity water production using reverse osmosis, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 334–363.

[6] W.V. Collentro, Pharmaceutical Water, CRC Press, Boca Raton, FL, USA, 1999.

[7] S.B. Applebaum, Demineralization by Ion Exchange, Academic Press, New York, NY, 1968.

[8] D.L. Owens, Practical Principles of Ion Exchange Water Treatment, Tall Oaks Pub, Littleton, CO, 1995.

[9] R. Bradley, Design considerations for reverse osmosis systems, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 104–137.

[10] D.R. Woods, Process Design and Engineering Practice, Prentice-Hall, Upper Saddle River, NJ, 1995.

[11] C. Branan, Rules of Thumb for Chemical Engineers, Gulf Publ. Co., Houston, TX, 1998.

[12] G. Pearce, Membrane filtration technology, Filtration + Separation 44 (8) (2007) 36–38.

[13] M.D. Kennedy, J. Kamanyi, S.G.S. Rodriguez, N.H. Lee, J.C. Schippers, G. Amy, Water treatment by microfiltration and ultrafiltration, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008.

[14] P. Cote, M. Liu, S. Siverns, Water reclamation and desalination, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 171–187.

[15] G. Pearce, Fouling behaviour for different module formats in membrane filtration applications for surface water treatment, Desal. Water Treat. 8 (1–3) (2009) 36–38.

[16] J.R. Pressdee, S. Veerapaneni, H.L. Shorney-Darby, J.A. Clement, J.P. Van der Hoek, Integration of Membrane Filtration into Water Treatment Systems, American Water Works Foundation, Denver, CO, USA, 2006.

[17] Wastewater treatment: reducing heavy metals in wastewater, Filtration + Separation 44 (8) (2007) 39–40.

CHAPTER 5

Design, Energy and Cost Analyses of Membrane Processes

> *"How did the biggest financial train wreck in human history come about? Arguably, one contributor was a mathematical equation."*
>
> **—Ian Stewart (In Pursuit of the Unknown, 2012)**

Since the 1990s, membrane-based separation processes integrated with traditional treatment systems have been successfully deployed in large desalination, wastewater and municipal water treatment plants [1–4]. More than a dozen large seawater RO (SWRO) plants with product water capacities greater than 200,000 m^3/day have been commissioned in the last decade.

Energy consumption, product water costs and technology reliability are key parameters that determine the viability of a process. Both cost and energy for desalination especially SWRO have fallen dramatically since the 1970s due to the development of higher permeability membranes, lower operating pressure, use of energy recovery devices and more efficient pumps as well as good RO feed water treatment practice. In addition, membrane plants have proven reliable in the field with longer life and lower plant maintenance costs.

Since 1980, the specific energy consumption (SEC) of SWRO has dropped from 10 kWh/m^3 to 3.0–5.0 kWh/m^3 and product water cost from \$2.00/m^3 to about \$0.75–1.25/m^3 [3]. The energy and cost figures for brackish water RO (BWRO) at 70–75% recovery today are 0.5–1.0 kWh/m^3 and \$0.15–0.75/m^3, respectively. The theoretical minimum energy of desalination for seawater at 35,000 mg/l (ppm) salt and at a typical recovery of 50% is 1.06 kWh/m^3 [5]. The actual energy consumption, however, is higher; for example, recovering 50% of a 35 g/l feed will have a practical minimum energy of 1.56 kWh/m^3. Further, more than 1 kWh/m^3 energy is required for pretreatment, post-treatment and pumping of feed water, product water and brine reject. Realistically, therefore, a minimum of 2.6 kWh/m^3 is consumed in a SWRO plant. Current state-of-the-art SWRO plants consume 3–5 kWh/m^3 of energy. The likelihood of reducing overall water cost and energy consumption of SWRO plants to $<$2.2 kWh/m^3 is unlikely due to several limiting factors such as membrane type and material, low product water recovery (PWR) (40–45%), concentration polarisation, fouling, membrane element hydrodynamics and RO system design [5,6].

Engineering analyses of typical commercialised and well-established membrane processes used for desalination and municipal and industrial water treatment are discussed and relevant data on energy consumption and water costs presented with special focus on seawater and brackish water desalination.

5.1 MEMBRANE SYSTEM PERFORMANCE CORRELATIONS

The transport properties of a semi-permeable membrane are determined by the permeability of the membrane and by a driving force both of which impact energy requirements. The flux of the solvent is directly proportional to the applied pressure and is given by the equation at constant temperature:

$$J_w = A(\Delta P - \Delta\pi) \tag{5.1}$$

where J_w is membrane water flux, A is membrane permeability coefficient, ΔP is hydraulic differential pressure across the membrane, and $\Delta\pi$ is osmotic pressure differential across the membrane. For liquids other than pure water the proportionality does not exist as shown in Figure 2.27 due to fouling and/or concentration polarisation.

The viability of a membrane process for potable water production depends on the energy consumption. The power input reflects the pressure energy required to pump water molecules through a size/charge selective membrane and is expressed as SEC in kWh/m^3 of product water. The following relationships are used to calculate energy consumption:

$$\text{Required pump power (kW)} = \frac{\text{feed water flow rate (m}^3\text{/h)} \times \text{feed pressure (bar g)}}{\text{pump efficiency} \times 36}$$

$$\text{Required motor power (kW)} = \frac{\text{pump power}}{\text{motor efficiency}}$$

$$\text{SEC} = \frac{\text{required motor power (kW)}}{\text{product water flow rate (m}^3\text{/h)}}$$

Membrane performance correlations are given below. For additional correlations refer to Section 2.4.7.

5.1.1 RO/NF systems

The performance of RO and NF membrane processes is typically determined by two key parameters, recovery and rejection, defined as follows:

$$\%\text{Recovery, Rec} = \left(\frac{F_p}{F_f}\right) \times 100 \tag{5.2}$$

$$\%\text{Rejection, } R = \frac{C_f - C_p}{C_f} \times 100 \tag{5.3}$$

where F_p and F_f are product and feed flow rates, respectively and C_f and C_p are feed and product water salt concentration, respectively. The product water (permeate) flow rate increases 3% per °C rise in water temperature because of lower viscosity (lower energy requirement) based on the general relationship between flux and temperature:

$$J_{\mathrm{m}} = J_{\mathrm{s}}\left[1.024^{(T_{\mathrm{m}}-T_{\mathrm{s}})}\right] \tag{5.4}$$

where J_s is the flux at standard temperature, T_s (e.g. 25°C) and J_m is the flux at process temperature, T_m.

The net driving pressure, NDP, across a RO/NF membrane is estimated from:

$$\mathrm{NDP} = (P_{\mathrm{feed}} + P_{\mathrm{brine}})/2 - P_{\mathrm{perm}} - \pi_{\mathrm{avg\ conc}} - \pi_{\mathrm{avg\ perm}} \tag{5.5}$$

where NDP is the net driving pressure, bar; P_{feed} is feed pressure; P_{brine} is reject pressure; P_{perm} is permeate pressure; $\pi_{\mathrm{avg\ conc.}}$ is average osmotic pressure on the feed side; $\pi_{\mathrm{avg\ perm}}$ is osmotic pressure of the permeate. $\pi_{\mathrm{avg\ conc.}}$ can be estimated from the log-mean average solids concentration, $C_{\mathrm{feed\ avg}}$:

$$C_{\mathrm{feed\ avg}} = C_{\mathrm{feed}} \times \ln\left[\frac{1}{1-\mathrm{Rec}}\right]\cdot\frac{1}{\mathrm{Rec}} \tag{5.6}$$

where C is the concentration, moles/l; and Rec is PWR, %. The expression $1/(1 - \mathrm{Rec})$ is the concentration factor, i.e. if the recovery is 75%, the solute concentration in the membrane feed channel is four times.

The osmotic pressure, π, of a saline solution is calculated from:

$$\pi = R(T + 273)\,\Sigma m_{\mathrm{i}} \tag{5.7}$$

where T is temperature, °K; Σm_i is summation of molarity of all ionic and non-ionic dissolved solids, and R is a constant = 0.0821 l bar/K mol. For solutions with total dissolved solids (TDS) less than 5000 mg/l, $\pi = (0.01) \times (\mathrm{TDS})$.

The amount of product water (permeate) is generally dependent on (i) total area of membrane within each pressure vessel, (ii) membrane pressure supplied by the high-pressure pump(s), (iii) reject flow rate, and (iv) feed water quality, as discussed in Chapter 2.

5.1.2 UF/MF systems

Flux across UF/MF membranes is defined based on Darcy's law as

$$J = \frac{Q_{\mathrm{p}}}{A_{\mathrm{m}}} = \frac{\mathrm{TMP}}{\mu R_{\mathrm{m}}} \tag{5.8}$$

where J is flux, lmh; Q_p is the flow rate of filtrate (permeate), l/day; A_m is membrane area, m^2; TMP is trans-membrane pressure, bar; μ is solution viscosity, cp; and R_m is hydraulic resistance of the membrane, bar/lmh. cp.

$$\mathrm{TMP} = \frac{1}{2}(P_\mathrm{f} + P_\mathrm{r}) - P_\mathrm{p} \tag{5.9}$$

where P_f is average feed pressure in the feed channel, bar; P_r is average pressure of the reject stream, bar; and P_p is average pressure in the permeate manifold, bar.

The expression for normalising flux for temperature is given in Equation (5.4).

PWR is the permeate (filtrate) flow as a percentage of feed flow defined in Equation (5.2). In the case of UF/MF, the relationship is modified to incorporate the filtrate used during backwashing:

$$\mathrm{PWR} = 100 - \left[100 \times \frac{Q_\mathrm{f} - Q_\mathrm{p}}{Q_\mathrm{f}}\right] \tag{5.10}$$

where Q_f is the feed flow rate over 24 h, $\mathrm{m^3/h}$ and Q_p is the net filtrate flow rate, $\mathrm{m^3/h}$ where Q_p is filtered water less filtrate used for backwash.

5.2 ENERGY AND COST SURVEY OF MEMBRANE PROCESSES

Membrane processes for this analysis include SWRO, BWRO, low-pressure RO (LPRO), brine recovery RO (BRO), pressurised MF/UF (pMF/UF), immersed membrane bioreactor (iMBR), cross-flow membrane filtration (XMF) and electrodeionisation (EDI). Membrane process characteristics for water treatment are detailed in Table 5.1. Typical process flow schematics of RO membrane plants are shown in Figures 5.1 and 5.2. RO/NF systems are typically multi-stage and single-pass or multi-stage and double-pass, as shown in Figures 2.21–2.23.

For our illustrative purposes we have assumed the plants are sized for feed water flow rates upto 1 million litres per day (MLD) at ambient temperature. Corresponding block flow diagrams with mass balances are shown in Figure 5.3. Pre-treatment and post-treatment technologies are discussed in detail in Chapters 2–4, but are also summarised in Table 5.1 and illustrated in Figures 5.1 and 5.2.

5.2.1 Energy consumption survey

SEC data for various membrane plants based on published data are given in Table 5.2 [3,5,7–16]. The effect of temperature on performance and SEC is discussed in Section 5.2.2. Estimates of total energy consumption and the power required for each plant are given in Table 5.3. Total energy consumption for the plant includes power consumed by the membrane unit, pre-treatment, post-treatment, and pumping of feed water, product water and brine reject. Energy consumption for a SWRO unit is typically 70–80% of the total plant energy and 40–50% of the total plant energy for a non-seawater RO unit [5,7,9,12–14].

Table 5.1 Membrane processes water treatment chart

Process/ technology	Application	Typical feed water type	Feed water TDS ppm	Max brine TDS ppm	Product water TDS ppm	Product water recovery (%)	Feed water constituents	Feed water pre-treatment	Notes
Seawater RO	Seawater desalination – single-pass; double-pass for boron removal	Seawater or similar brine water; medium TDS produced water	<50,000	80,000	<500	<50	Na, Cl, Ca, Mg, F, HCO_3, SO_4, boron, SS, organics	Clarifiers, media filtration, or MF; acid, anti-scalant, coagulant; dechlorination; organics removal	• Energy efficient vis-á-vis thermal desal • Limited by osmotic pressure • Pre-treatment important • Membrane life 3 years • Low recovery • Organic solvents not compatible
Brackish water RO	Brackish water desalination; industrial process water	Surface water, groundwater; low TDS produced water; industrial wastewater	<10,000	60,000	<100	70–75	Na, Cl, Ca, Mg, F, HCO_3, SO_4, Fe, Mn, silica, SS, organics	Clarifiers, media filtration, or MF; lime or IX softening, acid, anti-scalant, dechlorination, greensand filtration for Fe/Mn removal	• Energy consumption 1/3 of seawater RO • Pre-treatment critical • Membrane life 5 years • High recovery • Organic solvents not compatible
Low-pressure RO	City water purification; industrial process water; high-purity water	Low TDS surface water, groundwater; industrial wastewater	<1000	60,000	<20	75–85	Na, Cl, Ca, Mg, F, HCO_3, SO_4, Fe, Mn, silica, SS	Clarifiers, media filtration, or MF; lime or IX softening, acid, anti-scalant, dechlorination, greensand filtration for Fe/Mn removal	• Low energy consumption • Pre-treatment required • Membrane life 5–7 years • High recovery • Organic solvents not compatible

Continued

Table 5.1 Membrane processes water treatment chart—cont'd

Process/ technology	Application	Typical feed water type	Feed water TDS ppm	Max brine TDS ppm	Product water TDS ppm	Product water recovery (%)	Feed water constituents	Feed water pre-treatment	Notes
Nanofiltration	Water softening; RO pre-treatment; RO reject reclaim; partial desalination; textile wastewater	Seawater, brackish water, groundwater, RO reject; cooling tower blowdown; high TDS produced water	<60,000	80,000	<1000	75–85	Na, Cl, Ca, Mg, F, HCO_3, SO_4, SS, organics	Clarifiers, media filtration or MF, acid, anti-scalant, dechlorination	• Pre-treatment required, organic solvents not compatible • Membrane life 5–7 years • Energy consumption < RO; recovery same as RO • Effective for integration with RO • 70–98% rejection divalent ions; 20–75% monovalent ions
Membrane filtration – UF/MF	Turbidity reduction, particulate removal; RO pre-treatment	Seawater, surface and high turbidity water; secondary sewage	N/A	N/A	N/A	90–95	Suspended solids, colloids, particles, organics, bacteria, polymers	Coarse filtration; chlorination; in-line coagulation	• Highly efficient for clarification • Small footprint; modular • Superior product than clarifier • Higher Capex than clarifier • Best for RO/NF feed SS removal

Electrodialysis	Desalination; RO pre-treatment; RO reject treatment; sea salt recovery in Japan; metals recovery from wastewater; dairy industry; drinking water	Mostly brackish water; seawater; wastewater; dairy whey. Best for TDS <5000 ppm	500–80,000	200,000	<500	~95	Same as for SWRO and BWRO	Less than for RO; none required for silica and dechlorination	• Limited seawater application – energy consumption is 3–5 times SWRO • Requires less pre-treatment than RO • Not limited by osmotic pressure • Not affected by silica fouling • Organic fouling increases electrical resistance
Electro-deionisation	High-purity water; RO permeate polishing	RO permeate	<10	N/A	<0.5	88–95	See "notes"	Decarbonation of RO permeate if needed	• Feed water hardness <1 ppm; silica <1 ppm; heavy metals <10 ppb; chlorine <20 ppb; TOC <500 ppb as C

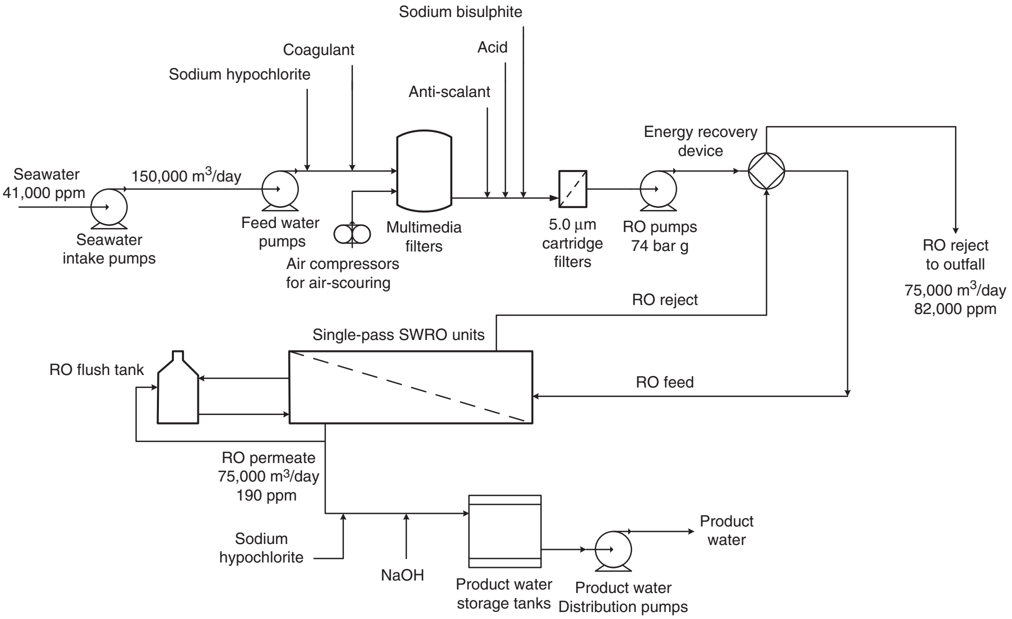


Figure 5.1 Process flow diagram of a typical single-pass seawater RO plant.

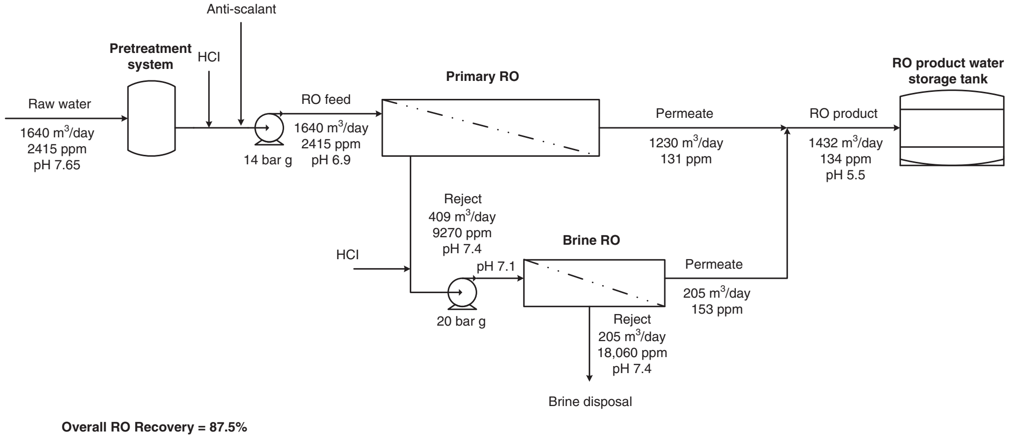


Figure 5.2 Process flow diagram and mass balance of a high-recovery brackish water RO plant. The brine RO increases the overall RO system water recovery from 75% to 88%.

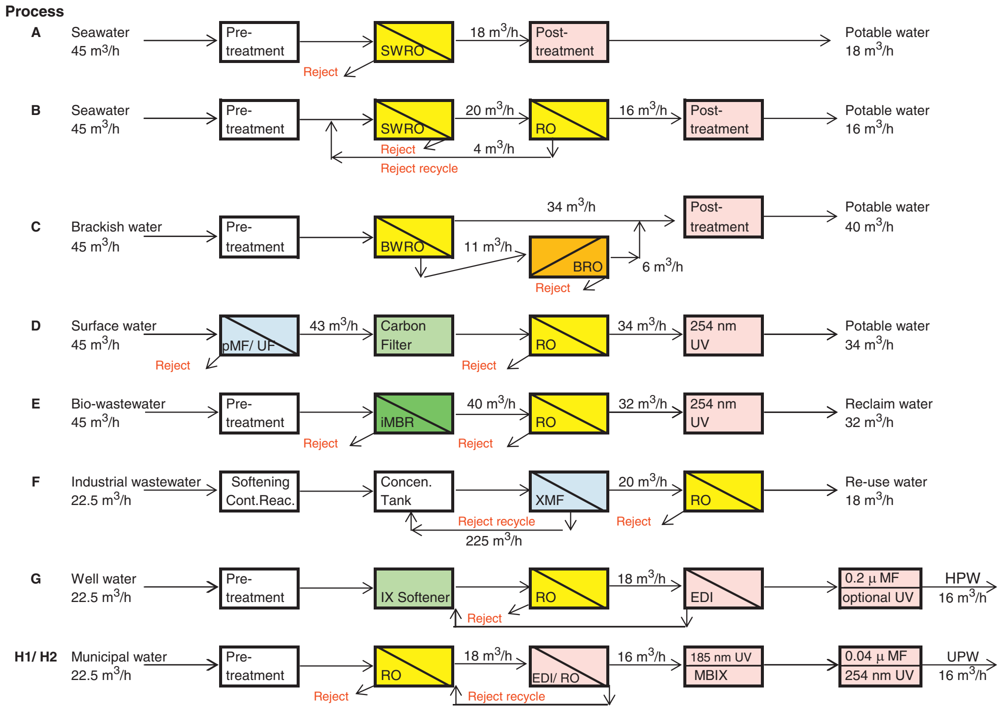


Figure 5.3 Process flow schematics of membrane plants. Process A is single-pass RO; process B is double-pass RO; process C is high-recovery RO; process D is pressurised MF/UF-RO integrated plant; process E is membrane bioreactor-RO integrated plant; process F is cross-flow MF-RO integrated plant; and processes G and H1 are RO-EDI integrated high-purity water plants. In process H2, second-pass RO replaces EDI, and no post-treatment after MBIX is required.

Process A – single-pass RO seawater desalination

The product water quality for a single-pass SWRO unit is typically 300–500 mg/l TDS, which is well below the World Health Organisation (WHO) drinking water limit of 1000 mg/l. The single-pass SWRO system is capable of producing 18 m^3/h potable water operating at 40% recovery based on a feed water flow rate of 45 m^3/h (see Figure 5.3). The total energy consumption is 59 kW given in Table 5.3 based on SEC of 3.3 kWh/m^3 with energy recovery.

The SEC of SWRO has dropped from 10 kWh/m^3 to typically <4.0 kWh/m^3 in the last 30 years [3,5,9,12–14] as a result of improvements in membranes, systems design and hardware. The process, however, is still energy intensive. Additional reductions of 10–20% may be achievable when operating with modified staged designs of membrane arrays [5,6,14] and/or operating in a combined heat and power mode [13].

The thermodynamic minimum energy independent of the desalination process is 1.06 kWh/m^3 [5,7,13,14]. The lowest energy consumption achieved in pilot studies

Table 5.2 Specific energy consumption of membrane plants[a]

Membrane process	Specific energy consumption (kWh/m^3)	Typical applications
SWRO	2.8–4.5	Seawater[b] desalination w/energy recovery
SWRO + RO	3.5–5.0	Two-pass seawater[b] desalination w/energy recovery
BWRO	0.5–1.0	Brackish water desalination; TDS > 1500 ppm
BWRO + BRO	0.9–1.4	High recovery, i.e. primary RO + brine RO
RO	0.3–0.7	Feed water TDS < 1000 ppm
NF	<0.5	Water softening, organics removal; RO pre-treatment
Pressurised MF/UF	0.1–0.2	Surface water, wastewater, RO pre-filtration
Submerged MF/UF	0.05–0.1	Surface water, wastewater, RO pre-filtration
External MBR	2.0–4.0	Landfill leachate, industrial wastewater, RO pre-filtration
Immersed MBR	0.3–0.9	Municipal/industrial wastewater, RO pre-filtration
Cross-flow MF	2.5–3.0	High hardness, high silica wastewater; metals wastewater
EDI	0.2–0.3	RO permeate polishing, high-purity water

[a] Includes energy consumption for the membrane unit, pre-treatment, post-treatment, and pumping of feed water, product water and brine disposal.
[b] Total dissolved solids ~34,000 ppm; Temperature = 25°C.

Table 5.3 Estimated energy consumption of integrated membrane plants in Figure 5.3.

Process no.	Integrated process	Total product recovery [b] %	SEC[a] (kWh/m^3)	Total energy consumption (kW)	Integrated SEC (kWh/m^3)
A	SWRO	40	3.3	59	3.3
B	SWRO + RO	36	3.7	72	4.53
C	BWRO + BRO	89	1.4	37	0.93
D	pMF/UF + RO	76	0.65	20	0.59
E	iMBR + RO	71	1.0	37	1.16
F	XMF + RO	80	3.3	65	3.61
G	RO + EDI	72	0.6	10	0.63
H1	RO + EDI + MBIX	72	0.7	12	0.75
H2	2-pass RO + MBIX	70	0.85	14	0.88

[a] Values based on data in Table 5.2.
[b] Product water recovery, %R: SWRO = 40%, BWRO = 75%, BRO = 55%, RO = 80%, pMF/UF = 95%, iMBR = 90%, XMF = 90%.

is 1.6 kWh/m^3 [5,17]. The likelihood of reducing the energy consumption of commercial SWRO plants to <2.0 kWh/m^3 is, however, unlikely [5,13,14] because of a number of reasons; system design, low PWR (<50%), high osmotic pressure and membrane concentration polarisation.

Process B – double-pass RO seawater desalination

A double-pass SWRO system is required to produce potable water with TDS less than 200 mg/l and to meet the WHO's drinking water standard for boron of 1.0 mg/l. Boron concentration in seawater is usually between 4.0 and 6.0 mg/l, depending on the location (in contrast, typical river water has a boron concentration of 0.05–0.2 mg/l). Since the boron concentration in the permeate from a single-pass SWRO is generally >0.8 mg/l, a second-pass RO is required with the feed water pH > 9.0. It is difficult to remove boron for the following reasons: boron exists as a weakly dissociated boric acid, H_3BO_3 at pH < 8.2, which is typically the pH of seawater, and the molecular size of boric acid is so small that it is difficult to remove by size exclusion. Boron rejection level is enhanced at the pH > 9.3 when the boron changes from boric acid to its salt resulting in high rejection by RO membranes that are generally negatively charged [18,19]. Rejection changes from approximately <30% to >90%:

$$H_3BO_3 + H_2O \Leftrightarrow H^+ + B(OH)_4^- \tag{5.11}$$

As shown in Figure 5.3, the first-pass SWRO unit permeate flows to the second-pass RO unit at 20 m^3/h operating at 45% recovery based on a feed water flow rate of 45 m^3/h. The pH of second-pass RO feed is raised to >9.0 with caustic soda. The second-pass RO unit produces 16 m^3/h operating at 80% recovery (recoveries >80% are typical for second-pass RO units). The second-pass RO reject flows to the SWRO inlet at 4 m^3/h (with TDS substantially lower than the first-pass RO seawater feed). The total energy consumption is 72 kW based on SEC of 3.3 kWh/m^3 for the SWRO unit with energy recovery and 0.4 kWh/m^3 for the second-pass RO unit (Table 5.3). The integrated system SEC is 4.53 kWh/m^3.

Process C – brackish water RO desalination

Typically, BWRO plants operate at 70–75% recovery so that 25–30% of feed water is wasted as concentrated brine. Product water recoveries greater than 80% are generally constrained by the solubility limits of sparingly soluble scale-forming compounds discussed earlier; as the feed/brine water gets concentrated in the channel above the membrane, e.g. by a factor of 4 at 75% recovery and 10 times at 90% recovery, the salt concentration also gets concentrated. The salt concentration is even higher at the membrane surface due to concentration polarisation, and must not be more than 20% higher than in the feed/brine channel. In the case of brackish waters, $CaCO_3$ and gypsum ($CaSO_4 \cdot 2H_2O$) are the most common scalants. Gypsum (solubility product,

$K_{sp} = 1.9 \times 10^{-4}$ at 25°C) is much more soluble than calcium carbonate ($K_{sp} = 8.7 \times 10^{-9}$ at 25°C). Limiting salts can be identified from their K_{sp} values. The deposition of the scale-forming compounds can be limited to an extent by reducing the pH with acid and/or by the use of anti-scaling chemicals, which interrupt crystal growth at the nucleation stage.

Because of high costs of disposing brine, and the need to reclaim and conserve water, primary RO (PRO) reject water can be purified using a brine RO (BRO) and/or NF system to recover additional potable water and reduce the volume of the brine stream, as shown in Figure 5.2. Such PRO + BRO systems can achieve overall product water recoveries of 87–96% for low to medium TDS (<4000 mg/l) brackish waters [20].

In the configuration shown in Figure 5.3, low salinity brackish water (TDS ~ 3000 mg/l) flows to the BWRO system, which produces 34 m^3/h potable water when operating at about 75% recovery based on a feed water flow rate of 45 m^3/h. In order to increase the yield, the reject (TDS ~ 12,000 mg/l) flows to the BRO unit at 11 m^3/h. The product water flow rate from the two RO units is 40 m^3/h, resulting in an overall recovery of 89%. The total energy consumption is 37 kW (Table 5.3). The integrated system SEC is 0.93 kWh/m^3.

Process D – surface water membrane filtration

Semi-dead end UF/MF membranes (effective pore size of the membrane is ≤ 0.1 μm) with intermittent backwash are being increasingly used for surface water and wastewater treatment for re-use, e.g. secondary or tertiary effluent is treated for industrial, non-potable and, in some cases, potable water reuse using UF/RO (or MF/RO) plus advanced oxidation techniques such as UV disinfection and hydrogen peroxide. The process is described in detail in Chapters 2 and 4 and several examples discussed in Chapter 3. Prominent examples of advanced reclamation plants include Water Factory 21 in California, NEWater Factory in Singapore and the Goreangab Reclamation plant in Namibia [2].

Wastewater reclamation for reuse by membrane filtration is more attractive than SWRO desalination due to much lower energy consumption and materials costs. For example the cost for producing RO product water from secondary effluent and seawater is estimated to be \$0.30/m^3 and \$0.70/m^3, respectively [9].

Depending on the quality of feed water, e.g. surface water or low TDS groundwater, MF or UF is sufficient for producing reuse quality water without RO or UV disinfection [15]. The pMF + RO system product water flow rate is 34 m^3/h at an overall recovery of 76% when the MF and RO recoveries are 95% and 80%, respectively (MF/UF system recoveries of up to 99% are achievable when the reject is also recycled to the feed water inlet [15]). The total energy consumption is 20 kW based on SEC of 0.15 kWh/m^3 for the pMF/UF unit and 0.4 kWh/m^3 for the RO unit (Table 5.3). The integrated system SEC is 0.59 kWh/m^3.

Process E – biological wastewater membrane bioreactor treatment

The integrated MBR + RO wastewater system produces 32 m^3/h reuse water with the MBR unit operating at 89% recovery and the RO unit operating at 80% recovery. The total energy consumption is 37 kW based on SEC of 0.5 kWh/m^3 for the iMBR unit and 0.4 kWh/m^3 for the RO unit (Table 5.3). The integrated system SEC is 1.16 kWh/m^3.

The configuration couples an MBR unit with an RO unit for wastewater treatment. Biological degradation of organic pollutants is carried out in the bioreactor by adapted microorganisms, and the microorganisms (biomass) are removed from the treated wastewater or mixed liquor (activated sludge) with MF/UF membranes. Since the effective pore size of the membrane is <0.1 μm, the MBR effluent is highly clarified and substantially disinfected [11]. For municipal wastewater treatment, MBRs are very attractive as compared to conventional treatment due to a small footprint and high effluent quality required for water reuse or as pre-treatment for RO or NF processes. Further, in recent pilot tests at NEWater Factory in Singapore, it has been shown that MBR + RO produces water with a slightly superior quality product water for industrial use and at lower cost than the existing MF + RO system for treatment of secondary sewage mainly because MBRs eliminate the need for secondary and/or tertiary filtration [2,11].

Process F – industrial wastewater cross-flow membrane treatment

For wastewater streams high in metals, hardness (>800 mg/l as $CaCO_3$) and/or silica (>60 mg/l), softening is required prior to recovering water by RO for reuse. For such streams, softening pre-treatment followed by clarification and filtration is used. The basis for softening is as follows: while temporary hardness (calcium and magnesium hardness due to carbonate) can be controlled by acidifying RO feed water, permanent hardness (due to sulphate) is relatively independent of the pH. When calcium sulphate and silica limit RO recovery, lime or caustic softening is necessary to achieve higher recovery. Softening ($pH = 10.5$–11 lowers hardness to 50 mg/l) and removes calcium as $CaCO_3$, whereas SiO_2 is partially sorbed by $Mg(OH)_2$ ($K_{sp} = 1.2 \times 10^{-11}$ at 25°C) floc and removed by co-precipitation with magnesium. Related applications are discussed in Chapter 3.

One process sometimes used for low flow rates (<50 m^3/h) is lime or caustic soda softening followed by cross-flow microfiltration (XMF) and RO polishing [21]. The MF membrane (pore size <0.2 μm) is tubular with a diameter of 1.27 or 2.54 cm. Due to the large diameter of the tubes, the membranes can handle feeds with solid levels of up to 5% at a very high membrane flux (375–500 lmh). The XMF filtrate is of high quality with turbidity <0.1 NTU and SDI < 3.0.

In the process configuration shown in Figure 5.3, wastewater flows to a contact reactor at 22.5 m^3/h. The supernatant from the concentration tank flows to the XMF membrane array and is recirculated at 225 m^3/h and 3–4 bar g with 10–15% recovery per recirculation/pass until 85–95% of the feed is recovered. In cross-flow MF/UF systems, operation at high velocity (shear rate) minimises solute cake build-up on the membrane surface and controls fouling. Ideally, the system should be operated at the critical flux region to reduce fouling as discussed in Chapters 1 and 2. The MF filtrate pH is lowered with acid to ~6.0 before it flows to the RO unit at 20 m^3/h. Because of the high quality of filtrate – turbidity < 0.1 NTU, SDI < 3.0, hardness < 50 ppm, silica < 20 ppm – the RO unit can operate at 85–90% recovery without fouling/scaling.

Thus, the XMF-RO integrated system recovers 75–85% of wastewater for reuse. The SEC of XMF is, however, much higher than semi dead-end membrane filtration processes (Table 5.2) because of very high cross-flow recirculation rates. The total energy consumption is 65 kW based on SEC of 3.0 kWh/m^3 for the XMF unit and 0.3 kWh/m^3 for the RO unit (Table 5.3). The integrated system SEC is 3.61 kWh/m^3.

Process G – high-purity water

The water treatment system is designed to supply 16 m^3/h high-purity water (HPW) to a pharmaceutical plant. Typical treatment steps follow the sequence given below, not all of which are shown in Figure 5.3:

$$\begin{aligned}&\textit{Well water} \Rightarrow \textit{Duplex MMF} \Rightarrow \textit{Duplex IX softeners} \Rightarrow \textit{Carbon filter} \Rightarrow \textit{Holding tank}\\&\Rightarrow \textit{254 nm UV} \Rightarrow \textit{Single-pass RO} \Rightarrow \textit{EDI} \Rightarrow \textit{0.2}\,\mu\textit{m final filter}\\&\Rightarrow \textit{HPW to point-of-use}\end{aligned}$$

Pre-treated RO feed water combines with RO reject recycled water and flows to the RO skid through a 5.0 μm pore size (nominal) cartridge filter. The single-pass RO unit is a three-stage (1:1:1) array designed to produce purified water at an overall recovery of ~80%. The TFC RO membrane average rejection is 98% and permeate conductivity is <10.0 μS/cm. The permeate is polished in an EDI unit. The product water conductivity is <1.0 μS/cm. EDI product water flows through a 0.2 μm (absolute) cartridge final filter to the point-of-use at 16 m^3/h, and the reject flows back to the holding tank. The total energy consumption is 10 kW based on an SEC value of 0.4 kWh/m^3 for the RO unit and 0.25 kWh/m^3 for the EDI unit [22]. The integrated system SEC is 0.63 kWh/m^3 (Table 5.3).

Process H1 – ultrapure water

The purified water system is designed to supply 16 m^3/h ultrapure water (UPW) to a semiconductor plant. Typical treatment steps follow the sequence given below, not all of which are shown in Figure 5.3:

$$\begin{aligned}&\textit{Filtered city water} \Rightarrow \textit{Carbon filter} \Rightarrow \textit{IX softener} \Rightarrow \textit{Single-pass RO}\\&\Rightarrow \textit{185 nm UV} \Rightarrow \textit{Membrane degasifier} \Rightarrow \textit{EDI}\\&\Rightarrow \textit{Polishing MBIX} \Rightarrow \textit{254 nm UV}\\&\Rightarrow \textit{0.04}\,\mu\textit{m MF} \Rightarrow \textit{UPW to point-of-use}\end{aligned}$$

Dechlorinated and softened water flows to the RO skid via a 5.0 μm (nominal pore size) cartridge filter. The RO unit is a three-stage (2:1:1) array designed for 80% recovery.

The permeate conductivity is <10 μS/cm. The TOC level in the RO permeate can vary between 50 and 500 ppb. Irradiation with 185 nm UV light is very effective in oxidising residual organic matter (TOC), thereby reducing the organic load on anion resins in the EDI unit. RO product water flows through a 185-nm rated ultraviolet (UV) unit and is degasified in a membrane contactor (MC). The MC removes any traces of dissolved gases from water with nitrogen flowing in the permeate side as sweep gas. Degassed water flows to an EDI unit. The EDI product water conductivity is <1.0 μS/cm. The EDI product water is polished in a mixed-bed ion exchanger (MBIX), producing UPW with resistivity = 18.2 MΩ-cm. The MBIX effluent flows through a bacteria-reducing 254 nm UV unit to deactivate bacteria and destroy any traces of organic matter. The irradiated water flows through MF cartridges rated for 0.04 μm (absolute) to the water distribution loop. The total energy consumption is 12 kW based on the SEC of 0.4 kWh/m^3 for RO and 0.25 kWh/m^3 for EDI (Table 5.3). The integrated system SEC is 0.75 kWh/m^3.

Process H2 – power plant water

Process H2 is an alternate to H1 for producing high-purity water for power plants with resistivity = 16.0 MΩ-cm. The energy consumption is slightly higher (Table 5.3), but the process is simpler as shown below. The RO system is two-pass; second-pass RO replaces EDI.

Filtered city water ⇒ Chemical in-line treatment ⇒ First-pass RO ⇒ NaOH dosage
⇒ Second-pass RO ⇒ Polishing MBIX ⇒ HPW to point-of-use

The illustrative examples summarise conceptual design and application of integrated membrane plants based on simple assumptions and typical performance data. The overall SEC of the two-pass SWRO system (Process B) was the highest while the SEC of the membrane filtration-RO integrated system (Process D) was the lowest with high-purity water systems (Process G and H) close behind. The cross-flow MF-RO system (Process F) was more energy intensive than single-pass SWRO, which is not unexpected because of the energy expended in recirculating the reject stream at very high flow rates, i.e. high shear rate to minimise cake build-up on the membrane surface. Because of high energy consumption, high Capex and a large footprint – low surface area tubular membranes – cross-flow MF systems are only used in limited wastewater treatment applications.

5.2.2 Temperature effect on energy consumption and membrane performance

Membrane productivity increases with feed water temperature albeit at a slight penalty in product water quality. A rule of thumb is that permeate flow rate increases 3% per °C rise in temperature as a result of reduced viscosity, e.g. the product water of a 100,000 m^3/day desalination plant is 39% at 20°C and 43% at 28°C. Higher productivity, in turn, means fewer membrane elements to achieve the same product water flow rate, resulting in reduced Capex and Opex. Design and performance of SWRO and BWRO systems operating at 20 and 30°C is detailed below. For general details of membrane systems design refer to Section 2.4.

SWRO design

The seawater RO unit design was based on the following assumptions [8]:

- Feed water flow rate = 45 m^3/h
- Feed water TDS = 34,262 mg/l
- Feed water temperature = 20 and 30°C
- Thin-film composite RO membrane; membrane life = 3 years
- PWR = 35%, 40%, 45% and 50%
- Product water flux constant for each temperature sub-set
- Pelton Wheel energy recovery turbine

The SWRO unit was modelled using Hydranautics Membrane Solutions Design software, version 8.8 (2004), based on a known seawater water analysis. The optimal spiral-wound membrane element was SWC5, which is one of the lowest energy consumption RO membrane elements for seawater. The design data are presented in Table 5.4. In all cases, the SWRO unit was a single-pass, single-stage membrane array (6:0; 7:0; 8:0), i.e. six, seven and eight parallel pressure vessels, similar to the one shown in Figure 3.33. Each pressure vessel contained six membrane elements. The RO pump, motor, and energy recovery turbine efficiency was assumed to be 80%, 90% and 88%, respectively.

The product water TDS increased with PWR due to higher concentration polarisation. There was a slight drop in TDS at 45% recovery possibly due to a slight increase in flux. The increase in product water TDS was nearly 38% when the feed water temperature increased from 20 to 30°C. The product water quality decreases slightly with rise in temperature due to higher osmotic pressure and because solute (ions) flow through the membrane has a higher activation energy than water flow (see Chapter 1).

The feed pressure and net energy required dropped by 6–7% while maintaining the same product water flux when the feed water temperature increased from 20 to 30°C. The feed pressure increased with recovery due to higher energy required to pump water through larger arrays, e.g. the number of pressure vessels increased from six at 35% recovery to eight at 50% recovery. The SEC for the RO unit varied between 2.63 and 2.96 kWh/m^3. For SWRO plants, energy is 70–80% of total plant energy consumed [3,4,9]. Assuming a value of 75%, the plant SEC was in the range of 3.51–3.95 kWh/m^3. The SEC was minimum for Case D when the recovery was 40% at 30°C. The optimum operating point most likely is between 40% and 45% recovery. Further, the efficiency of the Pelton Wheel energy recovery device used in the analysis is 88%. The SEC value would be slightly lower with more efficient isobaric ERD ($\eta = 95\%$) [4,23].

Table 5.4 Seawater RO unit design parameters

Case	Membrane type[a]/ membrane array[b]	Feed temp. (°C)	Feed pressure (bar g)	Reject/ brine pressure (bar g)	Product flow (m^3/h)	PWR[c] (%)	Avg. flux. (l/m^2/h)	Product TDS[d] (mg/l)	RO pump power (kW), (1)	Energy recov. (kW), (2)	Energy recov. (%)	RO motor energy (kW), (1) − (2)	Specific energy (kWh/ m^3)
A	SWC5 6:0	*20*	47.1	44.4	15.9	35	11.9	183	73.6	31.*6*	*42.9*	*42*	*2.94*
B	SWC5 6:0	30	44.3	43	15.9	35	11.9	250	69.2	30.2	43.6	39	2.73
C	SWC5 7:0	20	49.3	46.7	18.2	40	11.7	199	77	30.6	39.7	46.4	*2.83*
D	SWC5 7:0	30	46.8	45.*6*	18.3	40	11.7	274	73.1	30.1	41.1	43	*2.63*
E	SWC5 7:0	*20*	54	51.1	20.5	45	13.1	190	84.4	30.6	36.2	53.8	2.*92*
F	SWC5 7:0	*30*	50.9	*49.6*	20.5	45	13.1	262	79.5	30.1	37.9	49.4	2.68
G	SWC5 8:0	*20*	57.6	54.7	22.5	50	12.7	213	90	30.1	33.4	59.9	2.96
H	SWC5 8:0	*30*	54.7	53.5	22.5	50	12.7	295	85.5	29.8	34.9	55.7	2.75

Notes: Feed water flow rate = 45 m^3/h. Feed water TDS = 34,252 mg/l. Reject/brine osmotic pressure range = 38 (A) – 51 (H) bar. RO pump $\eta = 80\%$. RO pump motor $\eta = 90\%$. Energy recovery turbine $\eta = 88\%$. Calculated specific energy for the SWRO unit only. *Source:* Singh [8].

[a] Hydranautics TFC membrane rating: 30.3 m^3/day at 99.8% rejection. Membrane element surface area: 37.16 m^2.

[b] One-stage array. Six spiral-wound modules/vessel.

[c] Product water recovery.

[d] Total dissolved solids.

BWRO design

The brackish water RO unit was based on the following assumptions [8]:

- Feed water flow rate = 45 m^3/h
- Feed water TDS = 1656 and 3674 mg/l
- Feed water temperature = 20 and 30°C
- Thin-film composite RO membranes; membrane life = 3 years
- PWR = 70 and 75%
- Product water flux constant for each temperature sub-set
- No energy recovery device
- No brine recovery RO unit

As in the case of SWRO, the BWRO unit was modelled using Hydranautics Membrane Solutions Design Software, version 8.8 (2004), based on a known brackish water analysis. The optimal spiral-wound membrane elements were ESPA2 (energy-saving polyamide) and CPA2 (standard pressure polyamide). The design data are presented in Table 5.5. In all cases, the BWRO unit was a single-pass, two-stage membrane array (6:3 or 6:4). The RO pump and motor efficiencies were assumed to be 80% and 90%, respectively.

The product water TDS increased with PWR due to higher concentration polarisation. The increase in product water TDS was nearly 44% when the feed water temperature increased from 20 to 30°C. The feed pressure and net energy required dropped by 8–11% with an increase in feed water temperature while maintaining the same product water flux. The higher gain in pressure drop in the case of BWRO as compared to SWRO is a result of lower osmotic pressure in the brine reject stream. The SEC for the RO unit was lowest = 0.42 kWh/m^3 for lower TDS brackish water (Case III) and lowest = 0.56 kWh/m^3 for higher TDS brackish water (Case VI). For BWRO plants, energy is 40–50% of total plant energy consumed [3,4]. Assuming a figure of 45%, the plant SEC was 0.93 and 1.24 kWh/m^3 for Cases III and VI, respectively.

Post-analysis

The analyses showed that raising the RO feed water temperature from 20 to 30°C reduced the RO plant energy usage by 7–11%. Reduction in the cost of energy through such several incremental innovative design and operation techniques is possible [5]. However, for operation at higher temperature to be meaningful, a source of waste heat is required [8]. Co-location of SWRO plants with conventional power plants for utilising power plant waste heat is one option – the cooling water is used as the SWRO plant feed water [4]. Warmer temperature results in reduced RO feed pressure and concomitant power cost savings. Increase in permeate flux of up to 60% was reported when feed water temperature was increased from 20 to 40°C possibly due to changes in membrane morphology and higher solvent flow [24]. However, at greater than 30°C range, higher membrane permeability is adversely affected by increased osmotic pressure and higher salt passage [25].

The data show that the energy consumption of the SWRO units was about five times higher than the BWRO units, which is consistent with other reported data [3]. This is further evident from the data in Table 5.6.

Table 5.5 Brackish water RO unit design parameters

Case	Membrane type[a]/ membrane array[b]	Feed TDS[c] (mg/l)	Feed temp. (°C)	Feed pressure (bar g)	Reject/ brine pressure (bar g)	Product flow (m^3/h)	PWR[d] (%)	Avg. flux (l/m^2/h)	Product TDS (mg/l)	RO pump power (kW)	RO motor energy (kW)	Specific energy (kWh/m^3)
I	ESPA2$^{(1)}$ / 6:3	1656	20	9	4.9	31.8	70	15.9	28.5	14.1	15.7	0.49
II	ESPA2$^{(1)}$/ 6:3	1656	30	8	3.9	31.8	70	15.9	41.3	12.5	13.9	0.44
III	ESPA2$^{(1)}$/ 6:4	1656	30	8.1	4.5	34	75	15.3	51.2	12.7	14.1	0.42
IV	ESPA2$^{(1)}$/ 6:3	3674	20	11.6	7.7	31.8	70	15.9	90.4	18.1	20.1	0.63
V	CPA2$^{(2)}$/6:4	3674	20	11.6	8.9	31.8	70	15.6	82.9	18.1	20.1	0.63
VI	CPA2$^{(2)}$/6:4	3674	30	10.3	7.9	31.8	70	15.6	119	16.1	17.9	0.56

Notes: Feed water flow rate = 45 m^3/h. Reject/brine osmotic pressure range = 3.1 (I)–7 (VI) bar. RO pump $\eta = 80\%$. RO pump motor $\eta = 90\%$. Calculated specific energy for the BWRO unit only. *Source:* [8].

[a] Hydranautics TFC membrane rating: (1) 34.1 m^3/day at 99.6% rejection; (2) 37.9 m^3/day at 99.7% rejection.

[b] Two-stage array. Six spiral-wound modules/vessel.

[c] Total dissolved solids.

[d] Product water recovery.

Table 5.6 RO system specification and estimated cost data for typical select cases

Case	Feed water flow rate (m^3/day)	Feed water TDS (ppm)	RO system	Feed pressure (bar g)	Product water flow rate (m^3/day)	Product water recovery (%)
I	1637	2500	Primary RO: two-stage 7:4 array; 66 membrane elements Brine RO: single-stage 2:0 array; 12 membrane elements	Primary RO = 14 Brine RO = 19	Primary RO = 1310 Brine RO = 163 Total = 1473	Primary RO = 80 Brine RO = 50 Overall = 90%
II	1992	7200	Primary RO: two-stage 8:4 array; 72 membrane elements Brine RO: single-stage 4:0 array; 24 membrane elements	Primary RO = 24 Brine RO = 55 w/ reject recycle	Primary RO = 1495 Brine RO = 295 Total = 1790	Primary RO = 75 Brine RO = 60 Overall = 90%
III	2180	23,000	Two-stage SWRO 7:4 array; 66 membrane elements	72	1526	70
IV	10,360	40,200	Single-stage SWRO 58:0 array; 348 membrane elements	66	5180	50
V	10,360	40,200	Single-stage SWRO 63:0 array; 378 membrane elements	79	6216	60

Case	RO Product water TDS (ppm)	Brine concentrate TDS (ppm), flow rate (m^3/day)	RO unit energy consumption (kWh/m^3)[a]	Capex ($)	Opex ($/$m^3$)[a]	Comments
I	Primary RO = 133 Brine RO = 568 Combined = 181	TDS = 23,930, flow rate = 164	Primary RO = 0.61 Brine RO = 1.36	0.55 M	0.724	• Mid-level TDS brackish water • Brine RO for high recovery
II	Primary RO = 336 Brine RO = 522 Combined = 367	TDS = 68,821, flow rate = 202	Primary RO = 1.13 Brine RO = 4.13	0.75 M	1.147	• High TDS brackish water. Primary RO and brine RO. • Higher BRO pressure • Brine RO membrane: seawater
III	125	TDS = 76,511, flow rate = 654	3.76	0.88 M	1	• Brackish-seawater mix feed water
IV	465	TDS = 79,870, flow rate = 5180	4.79	4.0 M	1.124	• Seawater RO. Utilises energy recovery (ER) device. 50% product water recovery is higher than normal.
V	535	TDS = 99,720, flow rate = 4144	4.89	4.5 M	0.96	• Utilises energy recovery (ER) device. Higher recovery and feed pressure than Case IV. 60% product water recovery is extremely high, hence high energy consumption.

[a] Product basis.

5.2.3 Capital and operating costs assessment

Water desalination costs

There is a broad variation in the cost of water produced by membrane processes due to the type of feed water, plant size and energy source. For example, the cost of SWRO desalted water is reported to be in the range of \$0.53–\$1.53/m^3 [3], \$0.525–\$0.75/m^3 [4,9], and \$0.75–\$1.25/m^3 [26]. The cost of BWRO desalted water in the 1978 dollars was in the range of \$0.33–\$0.47/m^3 [27]. It was in the range of \$0.1–\$1.00/m^3 in 2007 dollars [3]. Both the source and salinity of brackish water are highly variable, unlike seawater. Also, the cost of brine concentrate disposal can be considerable for inland brackish water desalting plants today, which was not a serious issue in the 1970s. The O&M costs are also strongly affected by the price of electricity.

The capital cost of a seawater RO unit is between \$600 and \$800/m^3/day while for brackish water RO unit it is between \$250 and \$400/m^3/day [3]. The capital costs of entire seawater plants are five times higher than brackish water plants partly due to a more extensive pre-treatment system required as well as larger pumping and piping required to move larger volumes of feed water and RO concentrate (because of lower RO PWR). The capital cost of reclaim water membrane plants is typically one-half of seawater RO plants [9]. Typical breakdown of operating costs of SWRO plants by components is as follows [3,4]:

- Power, 46%
- Fixed costs, 36%
- Maintenance and spare parts, 6%
- Membrane replacement, 5%
- Labour, 4%
- Chemicals, 3%

Typical breakdown of operating costs of BWRO plants by components is as follows [3,27]:

- Power, 11%
- Fixed costs, 54%
- Maintenance and spare parts, 9%
- Membrane replacement, 7%
- Labour, 9%
- Chemicals, 10%

RO design for cost analyses

Capex and Opex of RO systems with feed water TDS from 2500 to 40,200 ppm and flow rates from 1640 to 10,360 m^3/day were analysed for performance, capital and operating costs. The data are summarised in Table 5.6. The RO unit designs were modelled using Hydranautics Membrane Solutions Design software, version v. 2010.

Pre-treatment included sodium hypochlorite dosing, multimedia filtration, carbon filtration and/or sodium bisulphate dosage, ion-exchange softening or anti-scalant dosing for scale control (see Table 5.1). RO feed water turbidity was <0.2 and Silt Density Index ≤ 4. Membrane life was assumed to be 3 years. The primary RO skid included a 5.0 μm cartridge filter. The high-pressure RO pumps were multi-staged. An energy recovery device was a part of SWRO. All high-pressure piping was 316 L SS except duplex steel was used in Cases IV and V.

Cases I and II are based on "high recovery" brackish water RO, i.e. primary RO + brine RO (PRO + BRO). Cases III covers intermediate TDS (23,000 ppm) water. Cases IV and V are based on SWRO.

Desalination – Capex and Opex calculation basis

Capex:
- \$250–400/m^3/day for brackish water RO
- \$600–1200/m^3/day for seawater water RO

Opex:
- BWRO energy consumption ~1.0 kWh/m^3 product
- SWRO energy consumption ~3.8 kWh/m^{3}product
- Energy cost ~ \$0.111/m^3 (based on a typical energy cost of \$0.12/kWh)
- Long-term spares/consumables/membrane replacement/maintenance/labour ~ \$0.137/m^3
- Installation: 15% of equipment cost ex-works

Primary RO (PRO) Opex basis (\$/m^3):
- Labor at \$280/day (8-h shift). Labour cost doubled for Cases IV and V
- Chemicals = \$0.033/m^3
- Membrane replacement = \$0.01/m^3
- Miscellaneous = \$0.077/m^3
- Energy = \$0.12/kWh

Brine RO (BRO) Opex basis (\$/m^3):
- Labour = N/A
- Chemicals = \$0.033/m^3
- Membrane replacement = \$0.01/m^3
- Miscellaneous = \$0.077/m^3
- Energy = \$0.12/kWh

RO cost calculation equation:

$$\text{Total opex}\left(\$/\text{m}^3\right) = [\text{PRO opex}\,(\$/\text{day}) + \text{BRO opex}\,(\$/\text{day})]/\left[\text{m}^3/\text{day feed}\right]$$

In summary, the data presented in Table 5.6 provide an overview of general cost estimates of RO modelled systems. In desalination, costs are sometimes difficult to compare across projects because they are rarely reported consistently and some cost parameters are often not reported. Further, project costs can vary significantly especially for water desalination, depending upon factors such as source water quality, plant size, cost and availability of power, project financing terms, permitting requirements, distribution lines, and brine concentrate or waste sludge disposal/transportation [3,26–28].

UF/MF water treatment cost figures

The design of a membrane filtration water treatment plant requires a clear selection of flux in order to achieve a stable cost-effective design to ensure that fouling can be controlled at an acceptable level [29]. Flux data and specifications for various MF/UF systems are provided in Table 3.13. The cost of reclaimed water from secondary and wastewater using integrated membrane systems (MF/UF + RO/NF) is in the range of \$0.25–\$0.40/m^3 [9,28]. According to another study, the Capex for full-scale MF systems as pre-treatment for RO units in wastewater reclamation was \$140–215/m^3/day for a 10,000 m^3/day plant with Opex approximately \$0.10/m^3 [30]. Process design of a cross-flow tubular UF plant for treating industrial wastewater was discussed in Chapter 2. Specifications for a tubular UF system are given in Table 2.12.

In one case study on seawater desalination in the Mediterranean Sea, the total cost of conventional pre-treatment SWRO system and membrane pre-treatment SWRO system was about the same, \$0.90/m^3 [3]. Even though membrane filtration pre-treatment is more expensive than conventional treatment, potential savings were a result of: (i) RO permeate flux increase of 25%, (ii) footprint and RO membrane replacement costs decrease of 33%, and (iii) chemical costs decrease of 45–65%.

5.2.4 Electrodialysis energy consumption and costs

Electrodialysis (ED) is mainly used for brackish water desalting and wastewater treatment with feed salinity less than 5000 mg/l. It is typically not used for desalting seawater because of high energy consumption. The theoretical energy consumption for normal seawater desalination is 1.05 kWh/m^3, but the actual energy consumption range is 10–25 kWh/m^3. For brackish water desalination (2000–10,000 mg/l) the theoretical energy consumption range is 0.05–0.33 kWh/m^3, but the actual energy consumption is 0.4–4 kWh/m^3 [31]. Based on the relative specific cost vs. salt concentration the economic cut-off point for ED vis-à-vis RO lies between 3500 and 7000 mg/l [32,33].

Energy consumption is strongly affected by salt concentration and cell voltage, V_{cell}. For example, the SEC at $V_{\text{cell}} = 0.4$ V and 1000 mg/l salt concentration is 0.18 kWh/m^3 and 0.8 kWh/m^3 at 4000 mg/l salt concentration. The relationship is linear. At $V_{\text{cell}} = 0.2$ V and 1000 mg/l salt concentration, SEC is 0.15 kWh/m^3 and increases linearly to 0.45 kWh/m^3 at 4000 mg/l salt concentration. However, operation at low cell voltages results in increase in capital investment [34]. A large fraction of total power is consumed by the pumps required to circulate feed and concentrate solutions through the stacks (see Figure 2.35). The pumping energy is estimated to be 0.5 kWh/m^3 [35]. Nearly complete de-gassing of water substantially increases its electrical conductivity. This suggests that the use of de-gassed salt solution could increase the overall efficiency of the ED process by increasing the electrical conductivity of the ion depletion layers within the ED stack [7], especially in the case of dilute electrolyte solutions.

Even though RO is the dominant process for brackish water desalination as compared to ED, EDR is preferred to RO in certain applications [33]. Several examples where EDR was the preferred process are discussed below (see also Chapter 3):

1. The city of Suffolk in Virginia, USA deployed EDR instead of RO for treating well water with TDS ~ 700 mg/l. Both RO and ED are suitable for reducing high level of fluoride, 4.6 mg/l (4.0 mg/l max.) and reducing sodium to 50 mg/l for potable water. However, EDR was selected because the volume of brine concentrate discharge was an important consideration [36]. ED had a higher PWR, 94% vs. 85% for RO. For a plant size of 14,240 m^3/day, the brine concentrate from the RO plant would have been 2136 m^3/day vs. 855 m^3/day for ED, i.e. 2.5 times more volume in the case of RO plant.

   The ED plant consists of three units (GE/Ionics Aquamite 120) each rated for 4747 m^3/day product water. Each unit contains eight parallel lines of membrane stacks with each line consisting of stacks in series. Three stages are required to reduce the fluoride level to 1.4 mg/l. The product water cost is \$0.25/m^3 based on the following costs: fixed = \$0.132/m^3, chemicals = \$0.02/m^3, EDR stack replacement = \$0.23/m^3, utilities = \$0.21/m^3 (at \$0.05/kWh), maintenance = \$0.17/m^3, and professional services = \$0.06/m^3 [34].
2. EDR was selected over RO to treat river water in Barcelona, Spain (TDS = 2000 mg/l) containing high levels of bromide, which along with the dissolved organic matter, creates a precursor for chlorination disinfection byproducts called trihalomethanes (THMs). The Capex of the 200,000 m^3/day EDR system and including a pre-treatment system was \$79 M. The SEC was 0.8 kWh/m^3 and the Opex was ~ \$0.26/m^3. The EDR system consists of nine modules of 32 lines and two stages. Six hundred cell pairs are assembled horizontally and in parallel between two electrodes. The PWR is 90% with salt reduction 60–80%. The system reduces bromides by 80% and achieves a THM formation potential of <100 μg/l [34,36].
3. An EDR plant was installed for the treatment and reuse of tertiary water (TDS = 1250 mg/l) in San Diego, CA. The reclaimed water was needed for irrigation purposes. EDR was selected since its cost was 25% lower than MF-RO and it consumed less energy [37]. The pumping power consumption was ~0.264 kWh/m^3 and the DC power requirement was 0.362 kWh/m^3 at 55% salt rejection. The EDR plant consistently produced 347 m^3/h at the product water TDS between 355 and

664 mg/l. The EDR system was designed for 85% water recovery without chemical treatment, whereas the RO system required acid dosing and a scale inhibitor to achieve the same recovery. In addition, the EDR stack tolerated continuous exposure to 0.5 ppm residual chlorine.

These examples show that for certain applications and feed waters (TDS = 700–2000 mg/l), EDR is superior to RO.

High salinity feed waters

An ED-RO integrated system for treating high salinity waters is shown in Figure 5.4. Scaling by sparingly soluble salts is controlled by pre-treatment and the ED reversal system (EDR) [33]. EDR uses a polarity reversal feature to prevent the accumulation of organic and inorganic foulants and prevent scaling, as discussed in Chapters 1 and 3. The SEC for concentrating RO reject (TDS ~ 70,000 mg/l) with ED to 200,000 mg/l is estimated to be 18.8 kWh/m^3 (30% for pumping) with $V_{\text{cell}} > 0.22$ and current efficiency = 90%.

5.2.5 Energy-saving options

The efficiency of seawater desalination plants is low, 10–25% as compared with the efficiency of other major industrial plants [7]. For example, the efficiency of cogeneration power generating plants is 50%. The efficiency of small desalination plants such as used on ships is in the low range. The energy consumption of the wind-powered 140,000 m^3/day SWRO plant in Perth is 3.56 kWh/m^3 [38]. Using the same feed and outlet conditions, the minimum work consumed is 0.951 kWh/m^3. Hence, the second law efficiency of the plant is about 26.7% [7]. The SWRO plant efficiency would increase if the plant energy consumption of 2.2 kWh/m^3 is achieved [5]. Alternate SWRO plant and system designs

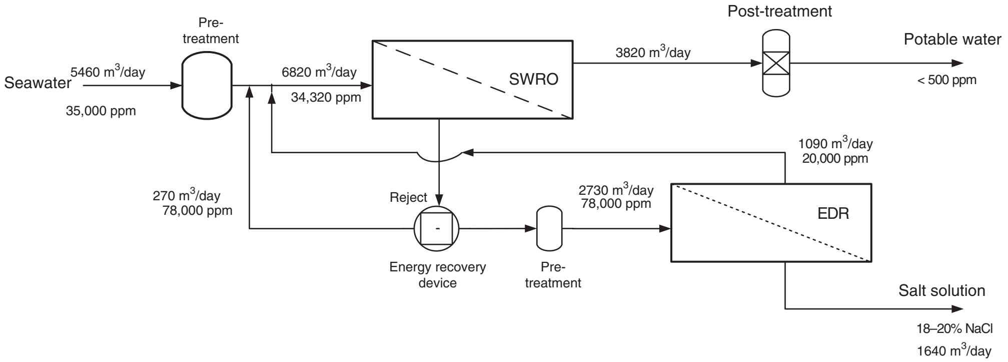


Figure 5.4 Process flow diagram and mass balance of a RO-EDR integrated desalination plant. Seawater desalination by ED is rare – used in Japan to recover sea salt.

and membrane array configurations that enhance performance and reduce product water costs are discussed in Chapter 3.

Membrane fouling problems in RO were addressed early in the 1970s and largely solved by site-specific feed water treatment systems [39,40]. Modifications to pre-treatment and post-treatment designs are, however, deemed necessary for reducing both energy consumption and total costs especially for seawater RO desalination [5]. A novel solution suggested for decreasing the energy consumption of and cost of seawater desalination involves forward osmosis (FO) integrated with RO. In this process, investigated in the laboratory, both pre-treatment and post-treatment operations would be minimised [41]. However, for the process to be viable, development of fouling-resistant FO membranes and improved module designs are required.

Seawater pre-treatment costs may be reduced by 15–25% with new kinds of filtration intakes [4,42]. One such design is a seabed filter intake that uses screened laterals (a non-metallic header-lateral arrangement with 0.6 m diameter laterals attached to two 1.8 m diameter headers) [43]. The intake pipes are installed about 3.9 m below the seabed, under 1.5 m of graded sand, 0.3 m of graded gravel and 2.1 m of coarse gravel.

Raising the RO feed water temperature from 20 to 30°C reduces the plant energy usage by ~10%. Overall costs could also be decreased if the brine concentrates are processed to recover valuable products. A few such cases are discussed in Chapter 3. Deployment of high recovery brackish water RO systems, i.e. a primary RO (PRO) plus a brine recovery RO (BRO) increases the overall PWR from 70–75% to 85–90%. A 10% reduction in energy consumption is achievable when the BRO unit is replaced by a NF unit [44]. The NF feed pressure is about 30% lower than the BRO feed pressure.

Besides energy consumption, the resulting greenhouse gas emissions are significant factors in the operation of membrane desalination plants [5,7]. Renewable energy sources such as wind power and solar energy have been successfully integrated with RO desalination plants of small to large capacity in the last decade to lower energy costs, e.g. the wind-powered 140,000 m^3/day SWRO plant in Perth mentioned earlier [38].

Another option to reduce SWRO energy consumption is to use diluted seawater. For example, the London desalination plant shown in Figure 5.5 draws water from the Thames River estuary during the last 3 h of the ebb tide. The feed water TDS is less than half of normal seawater. The $400 M plant commissioned in 2010 has a capacity of 150,000 m^3/day, enough to supply 400,000 households, and operates on 100% renewable energy with a water recovery >75% [45].

The seawater could also be diluted with sewage reclaimed water. In this scheme, RO reject from an integrated MBR-RO system is used to dilute SWRO feed [46]. At a demonstration plant in Kitakyushu, Japan, the RO feed pressure was reduced by more than 30% from 55 to 35 bar g. Based on the actual data, energy-saving efficiency for the total system was estimated to be 32%; the proposed system reduces energy consumption from 4.3 to 2.9 kWh/m^3.

Figure 5.5 Photograph of the 150,000 m^3/day Thames River seawater-brackish water RO desalination plant. *Source: [45].*

Membrane cleaning is a regular feature of membrane plants operation and maintenance. Frequent cleaning cycles with chemicals, however, have an adverse impact on membrane life and operating costs. Osmotic backwash based on FO for cleaning RO/NF membranes has been investigated to increase plant efficiency [14]. FO is a promising seawater desalination process described in Chapter 1 [5]. The basis of FO is osmosis, a natural and spontaneously occurring process. Thin-film composite membranes cannot be backwashed because the top thin layer can get detached. However, since FO transfers pure or fresh water through an RO/NF membrane under osmotic pressure, it can be used to backwash and clean the membrane with the permeate without the risk of damaging the membrane. Thus, operating costs of RO/NF plants can be reduced. The osmotic backwash process is described in Chapter 1.

ED for treating low TDS brackish waters and industrial waters is a proven and cost-effective technology, and in some applications superior to RO and NF [33,34,37]. Integrated RO/EDR, NF/EDR [47] and RO-ZDD [48] systems can reduce the cost of treated water by achieving higher recovery, e.g. in the case of inland brackish water desalination, higher total recovery results in minimising brine concentrate volume for disposal (see Chapter 3).

REFERENCES

[1] N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura, (Eds.) Advanced Membrane Technology and Applications, John Wiley & Sons, Hoboken, NJ, USA, 2008.

[2] A.L. Schafer, A.G. Fane, T.D. Waite, (Eds.) Nanofiltration: Principles and Applications, Elsevier, Oxford, UK, 2004.

[3] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[4] N. Voutchkov, R. Semiat, Seawater desalination, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 47–86.
[5] M. Elimelech, W.A. Phillip, The future of seawater desalination, Science 333 (2011) 712–717.
[6] B. Penate, L. Garcia-Rodriguez, Current trends and future prospects in the design of seawater reverse osmosis desalination technology, Desalination 284 (2012) 1–8.
[7] National Centre of Excellence in Desalination. National Desalination Research Roadmapping Workshop, October 2009, Freemantle, Western Australia. Australian Government National Water Commission, Emerging Trends in Desalination: A Review, Waterlines Report Series No. 9, University of New South Wales, 2008.
[8] R. Singh, Sustainable fuel cell integrated membrane desalination systems, Desalination 227 (2008) 14–33.
[9] P. Cote, M. Liy, S. Siverns, Water reclamation and desalination by membranes, in: N.N. Li, A.G. Fane, W.S.W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 171–187.
[10] G. Pearce, Water and wastewater – RO pre-treatment, Filt, + Sep 44 (7) (2007) 28–31.
[11] S. Judd, The MBR Book, Elsevier, Oxford, UK, 2006.
[12] S. Veerapaneni, B. Long, S. Freeman, R. Bond, Reducing energy consumption for seawater desalination, J. AWWA 99 (2007) 95–102.
[13] R. Semiat, Energy issues in desalination processes, Environ. Sci. Technol. 42 (22) (2008) 8193–8201.
[14] R. Semiat, J. Sapoznik, D. Hasson, Energy aspects in osmotic processes, Desal. Water Treat. 15 (2010) 228–235.
[15] J. Furlong, Siemens WT/Memcor, Personal communication, January, 2009.
[16] M. Wilf, Future of the osmotic processes, Desal. Water Treat. 15 (2010) 292–298.
[17] J. MacHarg, ADC spreads the facts, Filt. + Sep. (Desal. supplement) 1 (1) (2006) 12–14.
[18] The HERO Process, Desal. Water Reuse 18 (1) (2008) 43–44.
[19] H. Koseoglua, N. Kabayb, M. Yükselb, S. Sarpb, Ö. Ararc, M. Kitisa, Boron removal from seawater using high rejection SWRO membranes – impact of pH, feed concentration, pressure, and cross-flow velocity, Desalination 227 (2008) 253–263.
[20] R. Singh, Brine recovery at industrial RO plants – conceptual process design studies. Paper presented at the 2nd Oxford Water and Membranes Research Event, June 2008, Oxford, UK.
[21] M. Mierzejewski, D. Guendert, Industrial applications using microfiltration as RO pretreatment, Ultrapure Water 21 (7) (2004) 29–35.
[22] J. Wood, J. Gifford, J. Arba, M. Shaw, Production of ultrapure water by continuous deionization, Desalination 250 (3) (2010) 973–976.
[23] R.L. Truby, Seawater desalination by ultralow-energy reverse osmosis, in: N.N. Li, A.G. Fane, W.S. W. Ho, T. Matsuura (Eds.), Advanced Membrane Technology and Applications, Wiley, Hoboken, NJ, 2008, pp. 87–100.
[24] M.F.A. Goosen, S.S. Sablani, S.S. Al-Maskari, R.H. Al-Belushi, M. Wilf, Effect of feed temperature on permeate flux and mass transfer coefficient in spiral-wound reverse osmosis systems, Desalination 144 (2002) 367–372.
[25] M. Wilf, C. Bartels, Optimization of seawater RO systems design, Desalination 173 (2005) 1–12.
[26] R. Raucher, J. Clements, True costs of desalination projects, World Water: Water Reuse Desal, Spring (2011) 26–28.
[27] S.V. Cabibbo, D.B. Guy, A.C. Ammeralaan, A. Ko, R. Singh, Parametric study on brackish water membrane desalting plants, NWSIA J, July (1979) 17–36.
[28] J.R. Pressdee, S. Veerapaneni, H.L. Shorney-Darby, J.A. Clement, J.P. Van der Hoek, Integration of Membrane Filtration into Water Treatment Systems, American Water Works Foundation, Denver, USA, 2006.
[29] G. Pearce, Fouling behaviour for different module formats in membrane filtration applications for surface water treatment, Desal. Water Treat. 8 (1–3) (2009) 36–38.
[30] S. Khan, T. Wintgens, P. Sherman, J. Zaricky, A. Schafer, A performance comparison of individual and combined treatment modules for water recycling, Environ. Prog. 24 (4) (2005) 383–391.
[31] L.H. Shaffer, M.S. Mintz, Electrodialysis, in: K.S. Speigler, A.D.K. Laird (Eds.), Principles of Desalination, Part A, second ed., Academic Press, New York, NY, 1980, pp. 257–357.

[32] US Bureau of Reclamation, 2003. Desalination and Water Purification Technology Roadmap, Washington, DC, March 2003.

[33] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination 264 (3) (2010) 268–288.

[34] Y. Tanaka, Ion Exchange Membrane Electrodialysis: Fundamentals, Desalination, Separation, Nova, New York, NY, 2010.

[35] W. Eykamp, Section 22, Alternative separation processes, in: D.H. Perry, D. Green (Eds.), Perry's Chemical Engineers' Handbook, seventh ed., McGraw-Hill, New York, NY, 1999.

[36] Water Desalination Report, 45, 16 February 2009.

[37] J. Kiernan, A.J.M. von Gottberg, Selection of EDR desalting technology rather than MF/RO for the City of San Diego Water Reclamation Project, Paper presented at the 1998 American Desalting Association, North American Biennial Conference & Exposition, August, 1998.

[38] G. Crisp, Australia's first big plant thinks "green", Desal. Water Reuse 16 (3) (2006) 19–26.

[39] S.V. Cabibbo, D.B. Guy, A.C. Ammerlaan, A. Ko, R. Singh, RO Technical Manual, NTIS Publications, Springfield, Virginia, USA, 1979.

[40] R. Singh, Surface properties in membrane filtration, Chem. Eng. Prog. 85 (6) (1989) 59–64.

[41] D.L. Shaffer, N.Y. Yip, J. Gilron, M. Elimelech, Seawater desalination for agriculture by integrated forward and reverse osmosis: improved product water quality for potentially less energy, J. Memb. Sci. 415–416 (2012) 1–8.

[42] T.M. Missimer, R.G. Maliva, M. Thompson, W.S. Manahan, K.P. Goodboy, Reduction of seawater reverse osmosis treatment costs by improvement of raw water quality: innovative intake designs, Desal. Water Reuse 20 (3) (2010) 12–22.

[43] Water Desalination Report, 50 (2) 13 January, 2014.

[44] R. Singh, Analysis of high recovery brackish water desalination processes using fuel cells, Sep. Sci. Technol. 44 (2009) 585–598.

[45] http://www.theguardian.com/environment/2011/jun/28/water-desalination-plant-beckton-london (accessed 13.02.14).

[46] M. Kurihara, M. Hanakawa, Mega-ton water system: Japanese national research and development project on seawater desalination and wastewater reclamation, Desalination 308 (2013) 131–137.

[47] A. Sharbat, N.E. Moe, J. Loya, J. Barber, A. Ghassemi, Reducing the cost of inland desalination: pushing the conventional design limits in EDR and EDR/RO/NF hybridization efforts, Paper presented at the 2012 AIChE Annual Meeting, Pittsburgh, USA, November 2012.

[48] T. Davis, B. Biagini, M.A. Capelle, B. Mack, H. Johnson, E. Gilbert, et al., Collaborative development of zero discharge desalination technology, Paper presented at the 2012 AIChE Annual Meeting, Pittsburgh, USA, November 2012.

CHAPTER 6

Appendix: Engineering Data and Notes

> *"Anyone who believes that exponential growth in a finite world can go on forever is either a madman or an economist."*
>
> ***— (Economist) Kenneth Boulding***

6.1 GLOSSARY/TERMINOLOGY

Activation energy Energy barrier that the reactants must overcome in order react. It is the energy difference between the reactants and the activated complex.

Absorption It involves the dissolution (partitioning) of a contaminant from one phase into another without chemical reaction, e.g. absorption of oxygen gas in water or the absorption of DDT in hexane, an organic solvent.

Acidity, water All waters – natural, domestic wastewater and also frequently industrial wastewater – with pH less than 8.5 contain acidity. Acidity in natural waters is caused mainly by dissolved carbon dioxide that produces a weak acid, carbonic acid. Natural waters are buffered by a CO_2–bicarbonate system. See carbon dioxide.

Activated diffusion The process by which a penetrant molecule moves through a membrane from one transient vacancy to another with an energy interaction between the penetrant and the membrane.

Adsorption The process by which ions or molecules present in one phase condense and concentrate on the surface of another phase (surface phenomena), e.g. adhesion of the molecules of gases, dissolved substances, or liquids to the surfaces of solids or liquids with which they are in contact. There are three general types of adsorption: physical (activated carbon), chemical and exchange (ion exchange).

Aeration Air introduced into water and/or to release dissolved gases from water.

Aerobic Conditions where oxygen acts as electron donor for biochemical reactions.

Agglomerate To gather fine particulate matter together into a larger mass.

Algae Primitive autotrophic plant-like single-cell organisms. Use sunlight and photosynthesis to grow.

Alkalinity A measure of the buffer capacity to resist drop in pH when acid is added, i.e. it is the measure of the chemical constituents of water that react with hydrogen ions, and thus resist a decrease in pH. The major portion of alkalinity is due to hydroxide, carbonate and bicarbonate. Other contributors include salts of weak acids such as borates, silicates, phosphates, and organic acids such as humic acid. Alkanitiy can be expressed as "M" alk. to a methyl orange titration end point (pH 4.2) or "P" alk. to a phenolphthalein end point ($pH \geq 8.2$).

Amphoteric Compounds such as amino acids that form salts with acids or bases. The hydroxides of aluminium, zinc, chromium and a few other elements are soluble in both acid and bases. Hence used to accomplish separations in water treatment.

Anaerobic Conditions where biochemical reactions take place in the absence of oxygen.

Anion A negatively charged ion resulting from the dissociation of a salt, acid, or an alkali in an aqueous solution.

Anion-exchange membrane Membrane containing a fixed positive polar group that will permit passage of anions and reject cations.

Anisotropic (asymmetric) Defines a particular type of ultrastructure of microporous membranes. The surface of the membrane where separation occurs is more dense than the rest of the membrane body. The pore diameter increases in a direction perpendicular to the membrane surface, with the pore opening near the separation surface being smaller than the pore opening on the bottom of the membrane. This "skin" layer is typically present in polymeric membranes made by the phase-inversion process. Some asymmetry is also present in many inorganic membranes.

Anoxic Conditions where some species other than oxygen act as the electron donor for biochemical reactions.

Aqueous chemistry Also called solution chemistry, aquatic chemistry, water chemistry, electrolyte chemistry – any chemical system that involves water and dissolved salts.

ATD (anti-telescoping device) A circular ring with spokes fitted to the ends of a spiral module to prevent the membrane from pushing itself outward under a high-pressure drop.

Autofiltration The formation of a secondary or a dynamic membrane by retention of solutes or particles on the membrane surface affects separation or fractionation in UF. The higher the pressure, the more severe the polarisation.

Autotrophic Microorganisms that do not need to use organic matter as a source of energy.

Attrition Breakage or wear of ion-exchange resins.

Back-pressure Pressure exerted against flow.

Backwash Reverse (upward) flow of water through a packed bed to remove foreign material from the bed and clean and expand the bed.

Backpulse Brief reversal of flow from permeate to feed side of the membrane.

Base The hydroxyl form of a cation or a compound that can neutralise an acid.

Bicarbonate alkalinity The bicarbonate ion concentration expressed in "ppm" as $CaCO_3$ equivalents. To convert ppm of bicarbonate to ppm of $CaCO_3$ equivalents multiply by 0.82.

Biological treatment (biotreatment) Process whereby dissolved organic chemical constituents are removed through biodegradation.

Biomass Viable (living) microorganisms used to achieve removal of organics through biotreatment.

Biomimetic membrane A potential synthetic membrane under development incorporating *aquaporins* (proteins functioning as water-selective channels in biological cell membranes) that results in superior water transport efficiency than conventional RO membranes.

Bioreactor A vessel for conducting biological reactions.

Bipolar membrane The membrane consists of an anionic membrane and a cationic membrane laminated together. The membrane is used for generation of hydroxyl and hydrogen ions by water splitting. Used to split sodium chloride into sodium hydroxide and hydrochloric acid.

BOD (biochemical oxygen demand) A measure of the amount of oxygen required to support growth of bacteria during the breakdown of organic compounds in a sample. Usually expressed in parts per million (ppm). It is a bioassay procedure that involves the measurement of oxygen consumed by living organisms (mainly bacteria) while utilising the organic matter present in waste under conditions that simulate natural conditions.

Boundary layer The region near a sold surface where fluid motion is affected by the surface. The boundary layer is a major resistance to transport (e.g. by heat, mass, or momentum). In order to improve transport, the thickness of this boundary layer must be reduced.

Brackish water Generally, water having a dissolved solids content of 1000–10,000 mg/l.

Buffers Substances in solution that resist change in pH as acids or bases are added to or formed in the solution. Buffer solutions usually contain mixtures of weak acids and their salts (conjugate bases) or weak bases and their salts (conjugate acids).

Calcium carbonate equivalents The impurities of naturally occurring waters are frequently expressed as $CaCO_3$ equivalents (Table 6.9). To convert the ppm (mg/l) of a given constituent to ppm expressed as $CaCO_3$, multiply "ppm" by the ratio of the molecular weight (MW) of $CaCO_3$ to that of the constituent. For example, to convert ppm of carbonate to ppm of $CaCO_3$ equivalents multiply by 1.67. The MW of $CaCO_3$ is 100.

Capacity Operating – the fraction of total capacity used in an ion-exchange operation. Total – the ultimate or maximum ion-exchange capacity of a resin.

Carbonate alkalinity The carbonate ion concentration expressed in "ppm" as $CaCO_3$ equivalents.

Carbon dioxide CO_2 gas is a natural component of natural waters. It is also generated by biological oxidation of organic matter, especially in polluted water. Carbon dioxide is very soluble in water above pH 5 and forms bicarbonate and carbonate buffers by exposure to atmosphere. In the case of surface waters it can enter water from the atmosphere when its concentration in water is less than that in equilibrium with CO_2 in the atmosphere in accordance with Henry's law. Free CO_2 is dissolved carbon dioxide gas in water.

Carbonate hardness Carbonate hardness is chemically equivalent to the bicarbonate plus carbonate hardness (formerly called "temporary hardness"). It is expressed as ppm $CaCO_3$.

Carbon nano-tube membrane CNT membrane made by catalytic vapour deposition on the surface of quartz substrates. Observed flow velocities are four to five orders of magnitude higher than predicted by the Hagen–Poiseuille equation.

Catalyst A substance that lowers activation energy of a reaction but is not consumed. It reduces the time needed for a reaction to reach equilibrium but does not affect the composition of the equilibrium reaction.

Cation A positively charged ion resulting from the dissociation of molecules in solution.

Cation-exchange membrane Membrane containing a fixed negative polar group that will permit passage of cations and reject anions.

Cell potential Voltage produced by an electrochemical cell.

cfu Colony forming units, a measure of the number of microorganisms in a sample that are capable of forming colonies on a plate.

Channelling Liquid flow through a path of least resistance in a packed bed.

Chelating agent Organic compounds having the ability to form soluble complexes with ions in an aqueous solution. The solubility of metal ions is increased by chelating agents. See EDTA. Natural chelates include haemoglobin (contains iron), vitamin B-12 (containing cobalt), and chlorophyll (containing iron). Natural organic substances, e.g. humic are capable of chelating.

Chemical potential Defined in terms of Gibbs free energy, it is a measure of how the Gibbs function for a system changes when a specified amount of component is added to the system.

Chlorination Addition of chlorine in the form of free chlorine or sodium hypochlorite. Chlorine, hypochlorous acid and hypochlorite ions are called "free chlorine residuals," whereas the chloramines are referred to as "combined chlorine residuals."

Cryptosporidium A microbial pathogen found in surface water. Ingestion can cause cryptosporidiosis, an abdominal infection.

Coagulant A chemical (e.g. alum of iron salts) used to form a floc; used in the clarification of turbid or coloured water, and as an aid in removing colloids. See also Zeta potential.

COD (chemical oxygen demand) A chemical measure of the amount of oxygen required to break down organic matter in a sample expressed in parts per million (ppm). It does not differentiate stable from unstable organic matter. COD values are greater than BOD values.

Colligative properties Properties of a solution that depend only on the number of solute molecules and not the identity of the solute. They include osmotic pressure, freezing point depression, boiling point elevation and Raoult's law.

Colloids Particles (0.001–1.0 μm) that form a suspension or emulsion and cause turbidity in water. All colloidal particles are electrically charged (+ve or −ve), have very large surface areas, and are too stable to be removed by gravitational settling (can be removed by UF in their original state). However, if they are destabilised by charge neutralisation or allowed to form aggregates with coagulating agents, they can be removed by filtration. Hydrophilic colloids such as protein compounds have minimum solubility at their iso-electric point (pH = 4.0–6.5).

Colloidal solutions Stable two-phase systems with fine particles of one phase dispersed in a second phase. Solid particles suspended in a liquid – *sols*; liquid/liquid systems – *emulsions*; gas/liquid systems – *aerosol*.

Concentrate That portion of the feed solution that is retained (on the high-pressure side) of the membrane. As a result, the retained components are usually more concentrated than they were in the original feed solution. The terms concentrate, reject and retentate are used interchangeably.

Concentration polarisation Accumulation of solutes within the boundary layer above the membrane surface. Solutes that do not pass through the membrane accumulate on the membrane surface causing either an increased resistance to solvent transport or an increase in local osmotic pressure (either of which may decrease flux), and possibly a change in the separation characteristics of the membrane. See also Gel Layer and Polarisation Modulus.

Concentration ratio or concentration factor The ratio of the initial feed volume (or weight or flow rate) to the concentrate volume (or weight or flow rate).

Contact angle Acute for hydrophilic and obtuse for hydrophobic at solvent–solid interface.

Continuous diafiltration A mode of processing where water is added continuously to the feed tank or the retentate loop at the same rate as permeate flux. The total volume of the system and the concentration of the retained solute remain constant during CD. The concentration of the permeable solutes decreases in proportion to the volumes diluted and their individual rejections.

Critical flux Membrane flux below which flux decline is minimal. Operation at below critical flux condition results in minimal fouling. See also Flux-step.

Cross-contamination Inter-mixing of one resin with another of opposite charge.

Cross-linking The "setting up" of chemical links between two or more polymer chains.

Cross-flow The flow of fluid across a membrane surface, parallel to its surface or tangential flow. These modules have one inlet (feed) and two outlets (concentrate and permeate). This is in contrast to dead-end modules.

Cryoto – Cryptosporidium A protozoan parasite found in cattle and sheep. Causes severe diarrhoea in humans.

DE Diatomaceous earth, which is the fossilised skeletal remains of microscopic prehistoric plants; used as a filter aid in conventional filtration.

Dead-end Mode of operation where there is only one feedstream and one outlet stream (the filtrate of permeate). Refers to modules that do not have a means for cross-flow, e.g. stirred cells. Cross-flow modules could be operated in the dead-end mode by shutting off the reject outlet of the module.

Deionisation See Demineralisation.

Demineralisation Any process used to remove mineral salts from water, commonly restricted to an ion-exchange process.

Denitrification Biochemical reduction of nitrate to nitrogen gas.

Desalination The process of removing salts from water by reverse osmosis or distillation.

Detergents Organic materials that have the property of being "surface active" in aqueous solution. See Surfactants.

Diafiltration The convective elimination of permeable solutes by the addition of fresh solvent (water) to the retentate. Two modes of operation may be used in diafiltration: continuous or discontinuous.

Diffusivity/diffusion coefficient A measure of a solute's diffusive mobility in a solvent, cm^2/s.

Discontinuous diafiltration Permeable solutes are first eliminated by conventional UF or MF. Water is then added to the concentrated retentate to dilute it back to a certain volume and reprocessed by MF or

UF. This process of repetitive MF/UF and dilution to eliminate permeable solutes is called discontinuous diafiltration.

Dissolved air flotation (DAF) The process that introduces fine bubbles of air into water. The bubbles tend to form using solid particles as nuclei, which then float to the surface where they are removed as a foam.

Dissolved oxygen All atmospheric gases are soluble in water to some degree. Oxygen and nitrogen are poorly soluble, and since they do not react with water chemically, their solubility is directly proportional to their partial pressures. The solubility of atmospheric oxygen in fresh water ranges from 14.6 mg/l at 0°C to 7 mg/l at 35°C at 1 bar atmosphere pressure. The equilibrium concentration of oxygen in water at 20°C at 1 bar air is 9.2 mg/l. The low solubility of oxygen restricts the purification capacity of natural waters, necessitating treatment of wastes to remove pollutants prior to discharge. The solubility of oxygen is also less in saline water than in clean water.

Divinylbenzene A di-functional monomer used to cross-link polymers.

Donnan phenomena Fixed charged groups on the membrane polymer backbone tend to exclude ions of the same charge, especially multivalent ions, while permeable to ions of opposite charge particularly multivalent ions.

Drawback The process of natural osmosis that occurs when an RO system is shut down.

EDTA Ethylene-diamine-tetra-acetic acid; the Na^+ salt is the usual form of this chelating agent.

Eductor An in-line static mixing device that, by flow of water through it creates a vacuum, thereby drawing a solution into the water stream.

Electric double layer Most substances acquire a surface electric charge when brought into contact with a polar (e.g. aqueous) medium possibly due to ionisation, ion adsorption and ion dissolution. Ions of opposite charge (counter-ions) are attracted toward the surface, and ions of like charge (co-ions) are repelled away from the surface. This together with the mixing tendency of thermal motion leads to the formation of an electric double layer made of the charged surface and a neutralising excess of counter-ions over co-ions distributed in a diffuse manner in the polar medium. The theory of the electric "double layer" deals with this distribution of ions and the magnitude of the electric potentials, which occur in area of the charged surface. See also Zeta potential.

Electrochemical cell Device that uses an electrochemical reaction to generate an electric current at a constant voltage.

Electrochemistry The study of chemical reactions that produce electricity, and the use of electricity to facilitate non-spontaneous chemical reactions.

Electron donor Species capable of donating an electron to a suitable acceptor, which is oxidised as a result.

Electroneutrality When the positive charges equal the negative charges.

End point (breakthrough) A pre-selected value or measurement used to determine when the service cycle is completed or that a break-through has occurred.

Enzymes, catalysts Temperature sensitive, organic catalysts produced by living cells. Enzymes are proteinaceous catalysts that permit biochemical reactions at room temperature. Catalysts increase the rate of a chemical reaction by lowering the activation energy of the reactions.

Equivalent Equal valence is the weight in grams of a substance that combines with or displaces one gram of hydrogen, usually obtained by dividing the molecular weight by the valence.

Eutrophication The process whereby nutrients and biological growth increase with time in a body of water.

Exchange sites Reactive groups on an ion-exchange resin.

Exothermic Giving off heat in a chemical reaction. Reverse of endothermic.

Feed-and-bleed A continuous cross-flow mode of UF or MF operation where the feed is pumped into the recirculation loop of the membrane system at the same rate as the sum of the concentrate flow and permeate flux out of that loop. The feed concentration within the recirculation loop is determined by the concentration factor.

Filter aid A material added to a liquid to be filtered or on to the filter medium to improve the separation of solids from the liquid.

Fines Particles smaller than 50 mesh in size.

Floc A gelatinous precipitate formed by a coagulant.

Flocculants Materials that can form gelatinous clouds of precipitate to enclose fine particles of suspended dirt.

Fluoropolymers See Thermoplastics.

Flow rate The volumetric rate of flow of fluid parallel to the membrane surface. This is expressed in terms of volume/time (e.g. l/min or gal/min). Flow rate is velocity (v) × cross-sectional area of the feed channel. Also sometimes termed recycling rate or recirculation rate. This is the major determinant of the state of turbulence in a membrane module.

Flux Membrane permeate throughput (flow rate per unit area) usually expressed as volume per unit membrane area per unit time, e.g. $l/m^2/h$, $m^3/m^2/h$, or $gal/ft^2/day$.

Flux-step Critical flux identification method whereby flux is increased incrementally and the TMP or permeability response recorded.

FMA Free mineral acidity; the sum of the mineral acids.

Fouling Phenomenon in which the membrane adsorbs or interacts in some manner with solutes in feed resulting in a decrease in membrane performance (lowering of the flux and/or increase in rejection of solutes). This is usually irreversible and time-dependent, which distinguishes it from concentration polarisation.

Freeboard The space above a packed bed in a vessel that allows for bed expansion during backwashing.

Functional groups See Exchange Sites.

Gel layer Precipitation of sparingly soluble macromolecules, colloids and particles on the membrane surface.

Gellular A jelly-like appearance with no apparent physical pores, e.g. gellular resins.

Giardia *Giardia lamblia* is a protozoan organism that causes severe diarrhoea, carried by animals.

Glass transition temperature (T_g) The temperature where the polymer transits from a rubbery state to a glassy state. The thermal expansion coefficient in the rubbery state is two to three times greater than in the glassy state because of greater molecular (chain) mobility. T_g varies between −120 and +130°C, depending on the type of polymer. Rubbery polymers such as elastomers have −ve T_g, i.e. T_g is well below their use temperature, whereas common plastics such as polyvinyl chloride (PVC) polymers have +ve T_g, i.e. T_g is well above their use temperature. However, if used above its T_g, PVC would display the usual rubber-like behaviour.

Hardness It is caused by multivalent metallic cations. The main cations promoting hardness in water, Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}, Mn^{2+}, and the major anions associated with them are HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, and SiO_3. Can include iron and other multivalent cations. A rough classification of water in terms of hardness (mg/l as $CaCO_3$) is soft = 0–100; medium hard = 100–300; hard = 300–500; and very hard > 500.

Henry's law The law states that the amount of a gas that dissolves in a given volume of a liquid at constant temperature is directly proportional to the pressure the gas exerts above the liquid. The Henry's law constant, H, reflects the relationship between gas phase over a solution and dissolved species. Hence, Henry's law can be used to calculate the amount of gas present at saturation at any temperature.

Heterotrophic Requiring an organic substrate to obtain carbon for growth and development.

Housing A pressure vessel in which a membrane element is placed with ports and fittings to direct the feed, concentrate and permeate streams through the membrane element.

Humic substances High molecular weight polymeric substances, phenolic in character, that are formed by the decomposition of plant materials that release coloured substances of a highly refractive nature. The macromolecular structure is composed largely of aromatic building blocks that have been heavily substituted with carboxylic acid (–COOH) and alcoholic (–OH) functional groups, as shown in Figure 6.1. It has an amphiphilic character due to the hydrophilicity of the –COOH and –OH functional groups, and the hydrophobicity of the aromatic and aliphatic groups in the core of the molecule.

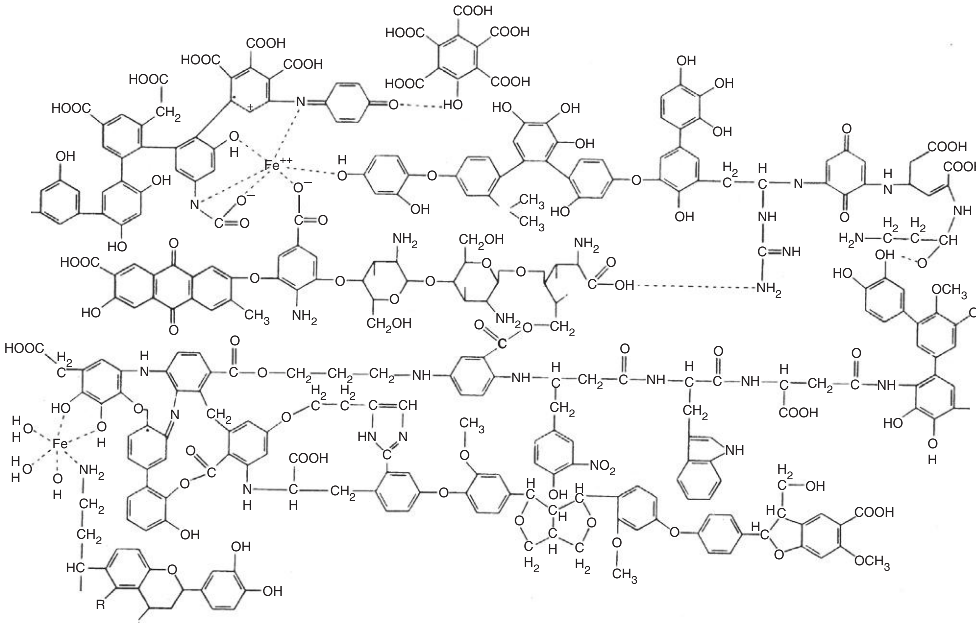


Figure 6.1 A suggested structure of humic acid. Humic materials are highly surface active, which is the basis for much of their fouling characteristics in membrane systems. *Source: C.E. Harland, Ion Exchange, Royal Society of Chemistry, Herts, UK, 1994.*

Hydrolysis The addition of water to split a chemical bond, e.g. the splitting of a salt and water into its ions and formation of a weak acid or base, or both.

Hydrophilic A material that is compatible with or preferentially interacts with water ("water loving"). See Contact Angle.

Hydrophobic A material that is incompatible with and cannot interact with water ("water hating"). These materials preferentially interact with oils and other hydrophobic components. See Contact Angle.

Hydroxide alkalinity The carbonate ion concentration expressed in "ppm" as $CaCO_3$ equivalents.

Hyperfiltration Same as reverse osmosis.

Inert media A resin with no reactive groups.

Ion exchange The inter-change of one ion in solution with another ion on an insoluble material.

Iso-electric point Substances such as proteins acquire their charge mainly through the ionisation of carboxyl and amino groups to give COO^- and $NH_3{}^+$ ions. The ionisation of these groups and the net molecular charge depend strongly on the pH of the solution. At low pH a protein molecule is positively charged, and at high pH, it is negatively charge. The pH at which the net charge is zero is called the "iso-electric" point.

Isotropic Refers to the ultra-structure of a membrane, where the pores are essentially uniform in size from the top to the bottom of the membrane body, and the body is more or less of a uniform density.

Jackson turbidity units (JTU) A measure of turbidity or suspended particles by optical obstruction of light rays passed through a water sample. See NTU.

Langelier Saturation Index (LSI) It is a means of expressing the degree of saturation of water as related to calcium carbonate solubility. The difference between the actual pH and the pH at which the water would be saturated with calcium carbonate, pH_s. It quantifies $CaCO_3$ scaling potential. If LSI is positive,

$pH > pH_s$, $CaCO_3$ will precipitate from water. If LSI is negative, $pH < pH_s$, water will dissolve $CaCO_3$ and will be corrosive. The LSI value must be negative to ensure the scaling potential is nil. Common practice is to feed sufficient acid or an anti-scalant to reduce the LSI in the concentrate stream to <1. See Section 6.14.

Leakage Leakage or slippage is the amount of an ion or ions in the effluent from an ion-exchange bed during the service cycle.

"Like dissolves like" (i) A solute dissolves when the attraction of solvent molecules to solute molecules (or ions) overcomes the intermolecular forces (or ionic bonds) holding solute molecules (or ions) together. (ii) For a solute to dissolve in a solvent, the cohesive forces that hold the solute molecules together (e.g. London forces, dipole–dipole interactions) should be the same as those that hold the solvent molecules together. (iii) Non-polar solvents dissolve non-polar solutes, while polar solvents dissolve polar solutes.

Macroporous A material with large pores, e.g. macroporous resins for removing organics.

Mass transfer coefficient (*k*) A measure of the solute's mobility due to forced or natural convection in the system. Analogous to a heat transfer coefficient, it is measured as the ratio of the mass flux to the driving force. In membrane processes the driving force is the difference in solute concentration at the membrane surface and at some arbitrarily defined point in the bulk fluid. When using the "film theory" to model mass transfer, k is also defined as D/δ, where D is solute diffusivity and δ is the thickness of the concentration boundary layer.

Membrane element Refers to a membrane module without the pressure vessel housing.

meq/L Milli-equivalents per litre.

Membrane bio-reactor (MBR) A system for simultaneous reaction and separation with a membrane. Could be conducted in the same physical enclosure or in separate enclosures if the reaction vessel and membrane unit are coupled in a semi-closed-loop configuration.

Mesh The number of strands in a linear inch of filter material. Higher numbers mean finer particles are retained.

Micrometre (μm) Indication of size of microscopic particles; $1.0\ \mu m = 0.0001$ cm.

Microfiltration (MF) Membrane separation process using microporous membranes with a pore size range of 0.1–10 μm.

Mil One-thousandth of an inch. $1\ \text{mil} = 0.0254$ mm. A common way of expressing the thickness of spacers in flat-sheet membrane elements.

Molality One mole of solute per kilogram of solvent.

Molarity One mole of solute per litre of solvent.

MWCO Molecular weight cut-off, a term used to describe the potential separating capabilities of a UF membrane; molecular weight of a theoretical solute with 90% rejection by the membrane.

Mixed-matrix membranes A combination of organic and inorganic materials. The objective is to combine the high packing density, good permselectivity and long operational experience of polymeric membranes with superior chemical, biological and thermal stability of inorganic membranes, e.g. nanocomposite membranes made by adding zeolite nanoparticles to polyamide films that boost permeability without sacrificing rejection.

Nanofiltration (NF) Originally called "loose RO." NF operates at lower pressure than RO but at a higher flux. A process that rejects multivalent ions and organic compounds >200 molecular weight but rejection of monovalent ions is <70%.

Neutral Neither acidic nor basic, i.e. pH 7.0.

Nitrification An aerobic respiration process in which ammonia is converted into nitrate in the presence of oxygen. Biochemical oxidation of ammonia to nitrate.

Non-carbonate hardness The amount of hardness that is in excess of carbonate hardness, i.e. hardness in water caused by chlorides, sulphates and nitrates of calcium and magnesium (formerly called "permanent hardness"). See Hardness.

Non-reactive silica Polymerised colloidal silica.

NTU Nephelometric turbidity units. A measure of turbidity in water by scattering of light from particles. Replaces JTU.

Oleophilic Same as hydrophobic.

Osmosis It is the movement of a solvent through a membrane that is impermeable to a solute, from the more dilute to the more concentrated solution. Water passes through the membrane in both directions, but it flows more rapidly in the direction of the salt solution resulting in a difference in hydrostatic pressure. The tendency of the solvent to flow can be stopped by applying pressure to the salt solution. The excess pressure that must be applied to the solution to produce equilibrium is known as "osmotic pressure." The pressure exerted in excess of the osmotic pressure "reverses" the flow of the solvent and is called "reverse osmosis."

Oxidation A chemical reaction in which an element or ion is increased in positive valence, losing electrons to an oxidising agent. Oxidants such as chlorine and ozone are added to water and wastewater to bring about the desired inorganic and organic transformations as well as to disinfect.

Oxidation–reduction reactions Many reactions in wastewater treatment including organic oxidation, methane fermentation, nitrification, and denitrification are mediated by bacteria. They are important in the solubilisation of iron and manganese.

Permeate That portion of the feed solution that passes through the membrane.

pH A measure of the hydrogen ion concentration in solution. pH of water determines the percentage of inorganic carbon that is in the form of carbon dioxide, bicarbonate, or carbonate. It also determines the extent to which carbon dioxide is in the permeate water, or whether calcium carbonate is likely to precipitate.

Poiseuille's law Describes the behaviour of liquids flowing through capillary tubes in relation to their viscosity $[V = (\pi P r^4)/(8\,\mu\,L)]$.

Polarisation modulus Ratio of solute concentration in the boundary layer above the membrane surface and the bulk feed once the steady state is reached. In the case of UF and MF membranes solute concentration at the membrane surface is very high for macromolecular and colloidal solutes. The modulus is >50 for proteins and colloidal as compared to <1.5 for desalination.

PPM An acronym for "parts per million" (mg/l). Similarly, PPB = μg/l.

Protonation It is the addition of a proton (H^+) to an atom, molecule, or ion, forming the conjugate acid.

PWR Product water recovery defined as: permeate flow rate/feed water flow rate, %.

Pyrogen Any substance capable of producing a fever when injected into mammals. Produced by bacteria and not necessarily inactivated by conventional heat treatment methods.

Reaction rate The rate of change in concentration in a reactant or product over time.

Redox conditions Conditions defined by the presence of either dissolved oxygen or some other species capable of providing oxygen bioactivity (reduction–oxidation).

Reduction A chemical reaction in which an element or compound gains electrons, being reduced in positive valence.

Regenerant solution A chemical used to restore the ion-exchange resin back to its desired or original form.

Rejection A measure of how well a membrane retains or allows passage of a solute. When based on concentrations in the bulk of the permeate and retentate streams, it is the "apparent" rejection. The "intrinsic" rejection is based on concentrations at the membrane surface. Sometimes used interchangeably with retention factor.

Reject stream Also called "retentate," it is the concentrated feed stream that does not flow through the membrane.

Retention factor Defined in the same manner as rejection, except retention refers to the feed, permeate, and retentate streams entering and leaving a module, while rejection should ideally refer to local concentrations close to the membrane surface.

Reynolds number (Re) A measure of the state of turbulence in a fluid system. It is calculated as the ratio of inertia effects to viscous effects. Reynolds number is dimensionless. Flow systems with Re values <2200

Table 6.1 Reynolds numbers for various flow systems

Flow system	Re[a]
Flow past wing of a jumbo jet	5×10^7
Spin-down of a stirred cup of tea	5×10^3
Finger moved through water	3×10^2
Golden syrup draining from a spoon	2×10^{-3}
Swimming spermatozoan	1×10^{-3}
Spiral-wound membrane elements[b]	$<1 \times 10^3$

[a] $Re < 2.1 \times 10^3$ is laminar; $Re > 4 \times 10^3$ is turbulent. The transition from laminar to turbulent flow in porous channels and tubes, e.g. tubular membranes, $Re < 2 \times 10^3$.
[b] Flow is considered turbulent because of mesh spacers.
Source: Adapted from Acheson, From Calculus to Chaos, Oxford, 1997.

are considered to be laminar flow, while $Re > 4000$ are considered to be fully turbulent. See Table 6.1 and Section 6.5.

Salt-splitting To replace the cation (or anion) of a neutral salt such as sodium chloride (NaCl) with hydrogen (or hydroxyl) ion.

Schmidt number (Sc) A measure of the ratio of momentum transfer to mass transfer. See Section 6.5.

Silt Density Index (SDI) It is an empirical measurement (*ASTM Standard D-4189-82, 1987*) used for measuring the colloidal fouling potential of RO/NF feed water. It is not a direct measure of the particle concentration, which is more properly measured by turbidity. The SDI value is based on the time required to filter a volume of feed water through a 0.45 μm filter pad at a feed pressure of 2.1 bar g. The SDI value is calculated from the formula:

$$SDI = \frac{P_{30}}{T_t} = 100\left(\frac{1 - T_i/T_f}{T_t}\right)$$

where P_{30} is % plugging, which should not exceed 75%; T_t the total test time, usually 15 min; T_i the initial time in seconds required to obtain a sample; and T_f is the time required to obtain a sample after 15 min.

A value <1 is indicative of a system that will run for several years without problems; a system with a value in the range of 3–5 is considered a "problem" and requires regular cleaning, and a value >5 indicates a system with severe fouling potential. Most spiral-wound RO/NF membrane systems require a $SDI < 3$.

Sherwood number (Sh) A dimensionless measure of the ratio of convective mass transfer to molecular mass transfer. If the mass transfer coefficient k is defined in terms of the "film theory," then Sh is a measure of the ratio of hydraulic diameter to the thickness of the boundary layer. See Section 6.5.

SHMP Sodium hexametaphosphate, a sequestering agent used for complexing calcium sulphate, thereby preventing $CaSO_4$ from precipitating on the membrane surface.

SI Units International System of Units was established in 1973–74 to develop a uniform method of reporting results worldwide. The basic units are metre (m), kilogram (kg), second (s), ampere (A), Kelvin (K), mole (mol) and candela (cd). Acceptable units outside the SI system are litre (l), grams per litre (g/l), moles per litre (M), day (d), hour (h) and minute (min).

Solubility product Solubility product constant, K_{sp}, reflects the relationship between dissolved species and precipitated species. Each ionic compound has its own solubility limit, which is the maximum amount of the compound that can remain in solution. K_{sp} is commonly used in solubility calculations to determine the precipitation potential of mineral salts. Certain combinations of cations and anions form sparingly soluble salts in water, and scaling in RO/NF may occur when the salts are concentrated beyond their solubility limits. See Table 6.10.

Solute The solid (e.g. salt) that is dissolved in water (solvent) to form a solution.

Solution A homogenous mixture of more than one substance in one phase (solute – minor component of a solution; solvent – major component of a solution).

Spacers A mesh-like material used in flat-sheet modules (e.g. plate, spirals, pleated sheet) to separate successive layers of membranes. Spacers control the feed channel dimensions in these modules. Serve as turbulence promoters in spiral-wound membrane elements.

Space velocity Flow per unit volume of media, $m^3/h/m^3$ or gpm/ft^3.

Superficial linear velocity Flow per unit area, $m^3/h/m^2$ or gpm/ft^2.

Surfactant "Surface active agent" is a compound that alters the surface tension of a liquid in which it is dissolved. All surfactants have large polar molecules. One end of the molecule is soluble in water (due to carboxyl, sulphate, hydroxyl, or sulphonate groups) and the other end is readily soluble in oils (organic groups). Synthetic surfactants are of three types: anionic, cationic and nonionic.

Sustainable flux The flux at which TMP increases gradually at an acceptable rate and chemical cleaning required is minimal.

Total dissolved solids (TDS) in mg/l or ppm is a measure of the total weight of impurities found in a water supply. The measure permits a quick, rough estimate of RO/NF permeate quality and feed pressure requirements.

Thermoplastic Polymers such as polyethylene (PE) and polypropylene (PP) can be processed and fabricated in the molten state. When actually used they are in the crystalline state so that the desired physical properties can be exploited. The replacement of all the hydrogen atoms from the linear PE with fluorine atoms results in a *fluoropolymer* such as polytetrafluoroethylene (PTFE) with a much higher melting temperature.

TFC Thin-film composite RO and NF membranes. A typical TFC membrane consists of three layers: a polyester web structural support (120–150 μm thick), a micro-porous inter layer (~40 μm thick), and an ultra-thin polyamide (or other polymer) top layer (0.2 μm thick). See Figure 6.15.

TOC Total organic carbon is a measure of the organic, carbonaceous material in water. Under normal circumstances, TOC concentrations are less than 15 ppm, ranging in most water supplies from 2 to 6 ppm. Under unusual circumstances or in wastewater streams, the TOC level can be 50 ppm or higher. Organic compounds with a molecular weight greater than 200 are easily rejected by RO and NF membranes. Compounds of lower molecular weight such as trihalomethanes are removed only 40%. TOC is not a key parameter in the design of RO systems. It can, however, be a source organic or bacterial fouling of the membrane.

Trace contaminants Contaminants in ground water or drinking water that are carcinogenic when present in excess of minute concentrations as set by the US government maximum contaminant levels. Mostly halogenated hydrocarbons (typically 1–100 μg/l or ppb) and heavy metals (typically 0.1–1.0 mg/l or ppm).

Transmembrane pressure (TMP) The driving force for flux. In cross-flow systems, it is measured as the average of the feed inlet and concentrate outlet pressures minus the permeate back-pressure.

Trihalomethanes (THM) Compounds formed by the reaction between the halogen elements of chlorine and bromine and methane forming chloroform, bromoform, dibromochloromethane and bromodichloromethane. The methane (CH_4) molecule has three of its hydrogen atoms replaced by either bromine or chlorine.

Turbidity A measure of the extent to which light is scattered by particulate matter in the water. It is caused by a wide variety of suspended materials ranging in size from colloidal to coarse dispersions. Municipal water supplies normally have a turbidity level of less than 1 NTU indicating a content of less than 0.5 ppm of suspended solids. The turbidity should be less than 1 NTU to avoid particulate fouling of RO/NF membrane elements.

Turbulence promoter Devices that are inserted into the feed/retentate channel of a module to improve mixing characteristics, increase turbulence, and thus improve flux. Typical turbulence promoters are spacers, spiral wires, static Kenics®-type mixers, spheres, or balls.

Ultrafiltration (UF) Membrane separation process using membranes with a pore size range of about 0.005–0.1 μm, corresponding to MWCO of 1000–500,000. See Section 6.12.

Valence The number of positive or negative charges of an ion. It is measured by the number of atoms or ions of hydrogen it takes to combine with or be replaced by an element or radical.

Vapour pressure The pressure exerted by a vapour in equilibrium with a liquid or solid.

Velocity The linear rate of flow of fluid parallel to the membrane, expressed in units of length/time (e.g. m/s). This is calculated as flow rate/cross-sectional area of feed channel.

Void The openings or spaces, e.g., in the body of a membrane, underneath its surface.

Void volume The space between particles of a settled packed bed, or “interstitial volume.”

Water hammer Instantaneous surges of water pressure caused by sudden interruptions in water flow in pipe or tank systems.

WHO Water Guidelines Drinking water: TDS < 1000 mg/l; chloride concentration <250 mg/l; boron concentration <2.4 mg/l. Irrigation water: TDS < 450 mg/l; chloride concentration <105 mg/l; boron concentration <0.5 mg/l.

Zeolite A mineral composed of hydrated silicates of aluminium and sodium or calcium. The term has been used, sometimes improperly, to describe softening by synthetic IX resins.

Zeolite membrane Ceramic membranes made up of a micro-porous support layer and a meso- or micro-porous active layer. Made from alumina, silica, titania, zirconia, or any other mixtures of these materials.

Zero discharge desalination (ZDD) ZDD is based on electrodialysis metathesis (EDM). EDM stacks utilise the same types of anion and cation-exchange membranes as conventional ED stacks, but there are four membranes and solution compartments in the repeating unit of an EDM stack.

Zeta potential (ζ) It is the magnitude of the charge at the surface of shear – the boundary surface between the fixed ion layer and the solution serves as a shear plane when the particle undergoes movement relative to the solution. $\zeta = 4\pi\delta q/D$ where q is the charge at the shear surface, δ is the thickness of the diffuse layer, and D is the dielectric constant of the liquid. Zeta potential gives an indication of the effectiveness of added electrolytes in lowering the energy barrier between colloids (i.e. reducing surface potential and electrical double-layer thickness), and thus can be used to select the optimum conditions for coagulation. Most colloids in natural water sources have a negative charge that helps to repel each other and to keep them suspended in solution. Overall, the colloidal water has a negative ζ value. The negative charge can be neutralised by the addition of cationic coagulants such as aluminium sulphate (alum) and ferric chloride. The coagulants are added until ζ reading is zero (neutral). The colloids without charges do not repel each other and coagulate into larger particulate groups, which can be easily filtered out by filtration. See also Electric Double Layer.

6.2 MEMBRANE POLYMER PERFORMANCE

Membrane morphology and performance are altered by changing the chemical structure of the membrane polymer. The permeability of synthetic membranes is dependent on both the chemical and physical structure of the membrane. High permeability may be realised by (a) increase in porosity, (b) decrease in thickness, (c) increase in operating pressure, and (d) increase of hydrophilicity. Water flux of polyamide (PA) membranes can be enhanced by the introduction of highly hydrophilic pendant carboxylic (–COOH) or sulphonic acid (–SO_3 H) groups. Nitration of polymers also imparts hydrophilicity to the polymer. However, it was found that the nitrated PA membranes had the opposite effect; the membrane shrank slightly and there was a reduction in flux [1] when thin-film composite (TFC) PA membranes were nitrated to produce a chlorine-resistant membrane (Section 6.3).

The drop in flux can be shown quantitatively by the drop in the value of the membrane constant, A. For a perfectly semi-permeable membrane with feed-side mixing or flow conditions such that the boundary layer is insignificant,

$$A = \frac{J}{\Delta P - \pi} \tag{6.1}$$

where A is the membrane constant, g/cm^2 s atm; J the permeate flux, g/cm^2 s; ΔP the pressure drop across the membrane; and π the osmotic pressure of the salt solution, atm. The membrane constant is based on the membrane properties alone [2]. The value of A decreased for the TFC membrane from 1.92×10^{-5} to 0.47×10^{-5} g/cm^2 s atm or four-folds after nitration, most likely due to morphological changes in the membrane (discussed next) qualitatively. Any shrinkage in membrane would lead to a decrease in porosity (ε) and an increase in skin-layer thickness (λ). These in turn would lead to higher tortuosity (τ). In other words, the term ($\lambda\tau/\varepsilon$) defined here as a "morphology constant" would increase. This is further evident (J decreases as $\lambda\tau/\varepsilon$ increases) if we consider the equation for the special case of Poiseuille flow through membrane pores, which have the ideal critical diameter (2 t) for desalination given by

$$J = \frac{\varepsilon \pi P \gamma^4}{8 \eta \lambda \tau} \tag{6.2}$$

where t is the thickness of a monomolecular layer of pure water on the membrane surface based on the preferential-sorption capillary flow model of Sourirajan, J the permeability of water, P the effective pressure, γ the effective pore radius, and η the average viscosity [3]. Typical values for homogenous PA membranes are reported in the literature to be $\lambda = 0.1$–0.3 μm, $\tau = 2.5$ and $\varepsilon = 0.005$–0.052 [4].

It was also reported that membrane permeability decreased while membrane selectivity increased in the case of nitrated polysulphone (PS) membranes [5] due to increasing packing density. Since the packing density is a common measure of polymer "free volume," an increase in packing density was believed to be due to an increase in polymeric inter-chain attraction caused by the polar nature of the nitro (–NO_2) group, and/or an increase in chain packing efficiency. Further, the addition of nitro groups to the backbone of the PS polymer most likely decreases polymer permeability by stiffening the polymer matrix, thereby restricting chain torsional mobility. The stiffening of the PS polymer by nitration was due to an increase in the glass transition temperature (T_g) of the highly nitrated PS polymer. Hence, a lower flux after nitration of the PA membrane was most likely due to morphological changes playing a far more dominant role than hydrophilic factors. Similar behaviour was also noted when a polysulphone UF membrane was nitrated by a gas phase technique [6]. The UF membrane shrank, transforming into a NF membrane.

6.3 CHLORINATION OF PA MEMBRANES

In order to form suitable membranes, the membrane polymer must possess glass transition temperatures (T_g), and melting temperatures (T_m) that are well above the used temperature. TFC PA membranes in spiral-wound elements are the workhorse of RO and NF systems, as discussed in Chapter 1. These membranes have remarkable properties for separations in aqueous streams; high flux, high rejection (RO membranes), low fouling, satisfactory thermal properties and tolerance to operating conditions over a wide pH range. In the last few years, TFC PA membranes have been developed that are sanitisable with hot water at 80°C, an essential requirement for applications in the pharmaceutical and beverage industries.

As remarkable as the performances of these membranes are, all aromatic PA membranes have one severe drawback: their susceptibility to degradation by chlorine. The removal of chlorine prior to membrane separation by activated carbon, sodium sulphite (Na_2SO_3), or sodium bisulphite ($NaHSO_3$) addition is, therefore, mandatory. Dechlorination by $NaHSO_3$ in stoichiometric excess can, however, be ineffective in seawater feed because dissolved oxygen in seawater reacts with the chemical. Further, the absence of chlorine can lead to biofouling that is often irreversible.

Aromatic PA polymers used for RO membranes are essentially random copolymers consisting of repeat units as shown in Figure 6.2. The amide ring is sensitive to attack by chlorine because it is an electron-rich region [1,7]. Hence, deleterious ring chlorination occurs only on the electron-rich phenylenediamine rings and not on the electron deficient phthalate rings, as shown in Figure 6.3. The bulkiness of the halogen substituents on the amide ring results in changes in hydrogen-bonding modes from inter-molecular to intra-molecular. This results in chain deformation and alteration of the average inter-chain displacement within the membrane skin structure. The damage to the skin layer of TFC composite membranes is severe, rendering the membrane useless with rejections dropping to as low as 20% [8–10]. A reaction scheme for chain cleavage is shown in Figure 6.4.

The effect of oxidative chain cleavage on PA polymer can be investigated by exposing the polymer to a sodium hypochlorite solution over a period of time and measuring the viscosity of the dissolved polymer after chlorination. The severe drop in viscosity after several exposure times confirmed the breakdown of the polymer [7]. Why viscosity? Solution viscosity is a well-recognised measure of the molecular weight of a polymer. According to the Mark–Houwink equation, for example, the relationship between the intrinsic viscosity $[\eta]$ and the average molecular weight, M, is expressed as:

$$[\eta] = K \cdot M^x \tag{6.3}$$

where K is a proportionality constant [3]. Hence the breakdown of the PA polymer due to chlorination, i.e. lower molecular weight is reflected in lower viscosity measurements.

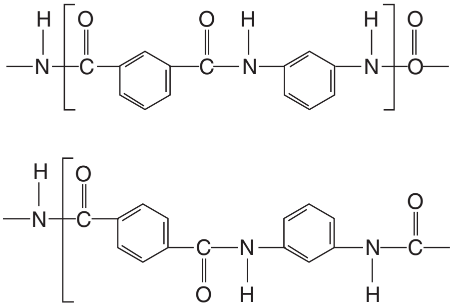


Figure 6.2 Aromatic polyamide polymer structure. *Source:* [1].

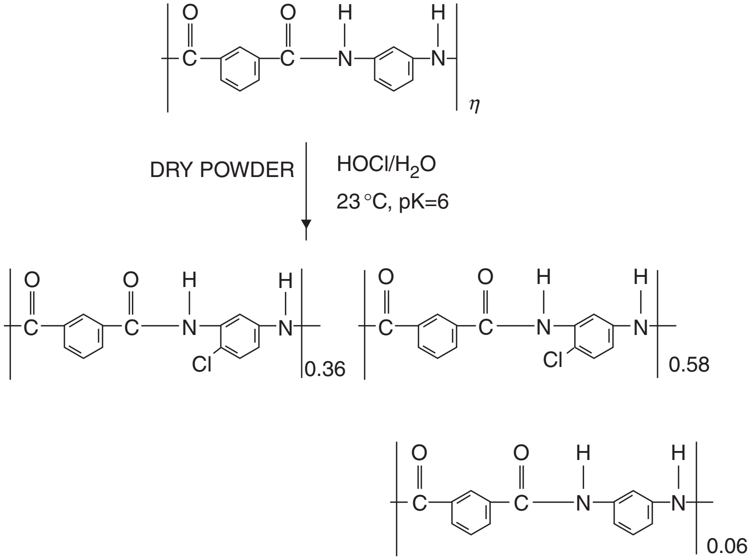


Figure 6.3 Polyamide ring chlorination based upon chlorine analysis and NMR evidence. *Source:* [1].

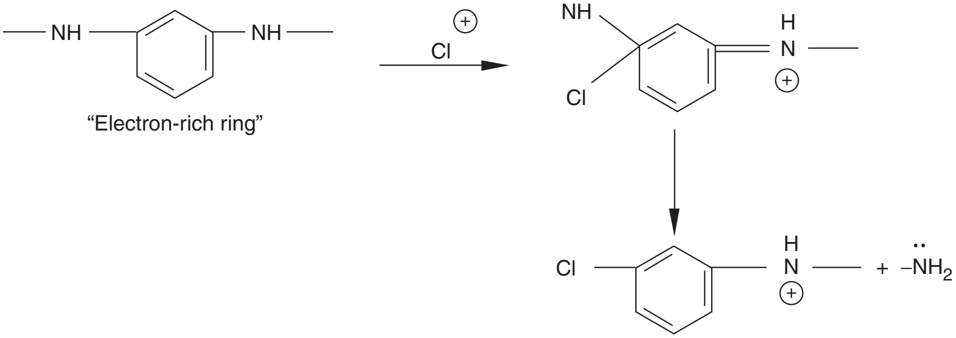


Figure 6.4 PA polymer chain cleavage reaction. *Source:* [8].

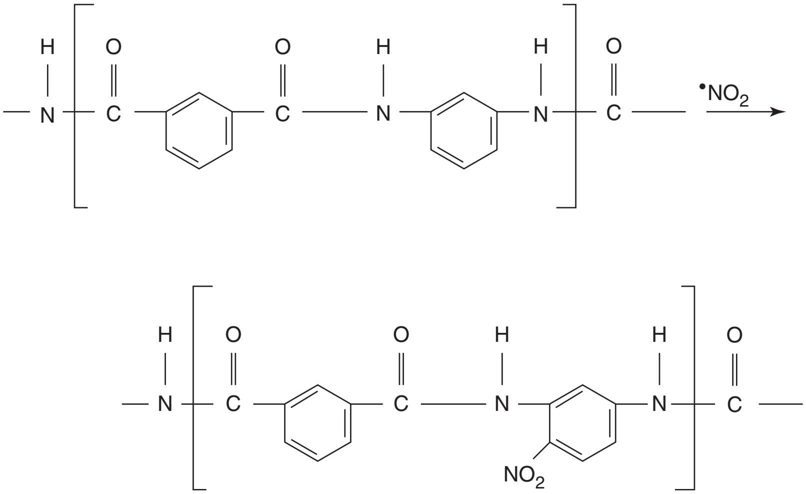


Figure 6.5 PA polymer nitration reaction. *Source:* [1].

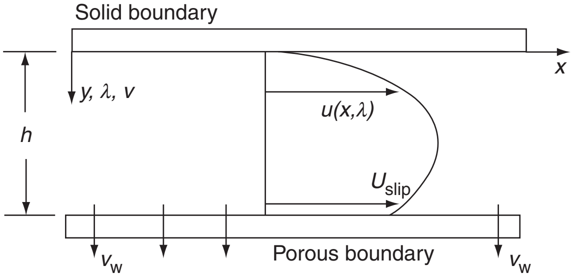
One way to suppress the ring chlorination reaction is to make the diamine rings less electron rich. Nitro (–NO_3) groups are powerful electron acceptors and are known to drastically deactivate aromatic rings toward electrophilic substituents. Nitration of an aromatic ring is known to reduce its reactivity by 10 for further ring addition reactions such as chlorination. A reaction scheme where an NO_2 molecule attaches itself to an aromatic ring containing the amide groups is shown in Figure 6.5.

6.4 FLUID FLOW IN MICROPOROUS MEMBRANES

In the analysis of fluid flow in microporous membrane tubes and channels, it is tacitly assumed that the no-slip boundary condition that characterises flows with solid bounding walls is applicable. This postulate is incorrect because the surface velocity at a porous wall is in fact not zero but proportional to the shear rate at the permeable boundary, i.e.

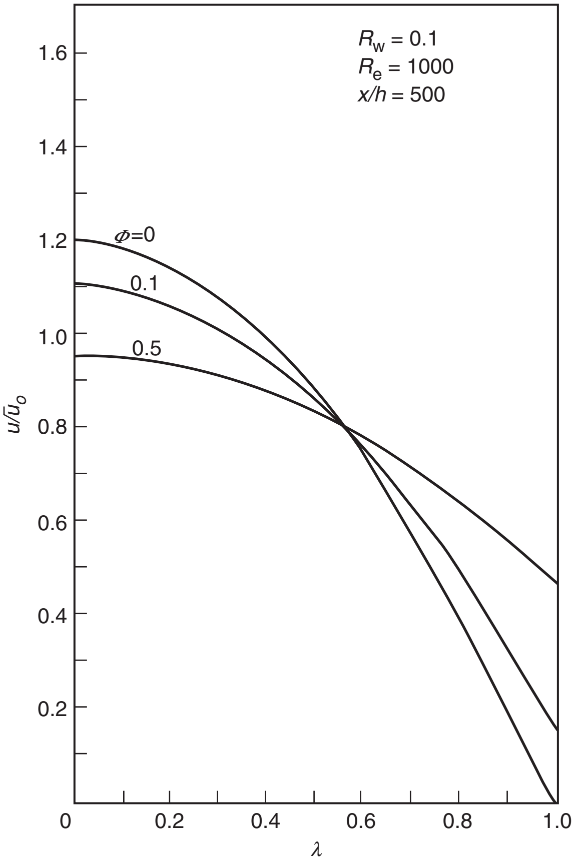
$$U_s = \phi \cdot \left.\frac{du}{dy}\right|_{y=0} \tag{6.4}$$

where U_s is slip velocity, ϕ is slip-flow coefficient, and du/dy is shear rate at wall boundary. Slip velocity and slip coefficient for a UF membrane were measured with a dye-tracing photographic technique by Kohler [11]. Laminar flow velocity profiles in tubes and channels using slip coefficients measured by Kohler were subsequently investigated [12,13]. Profiles for channel flow (Figure 6.6) are shown in Figure 6.7, which is a plot of normalised velocity as a function of channel height [U ($=u/u_{avg}$) vs. λ ($=y/h$)] for an entrance Reynolds number of 1000 ($Re = 4\, u_{avg} h/\nu$) and a longitudinal position, x/h, equal to 500. The curves are plotted for a slip coefficient equal to 0, 0.1, and 0.5, and



Coordinate system for the laminar flow in a channel bounded by one porous surface operating under a uniform suction velocity V_w.

Figure 6.6 Schematic of a channel with a porous wall.



Velocity profiles for $Re_w = 0.1$ based on entrance Reynolds number for channel flow.

Figure 6.7 Slip-flow velocity profiles. *Source:* [12].

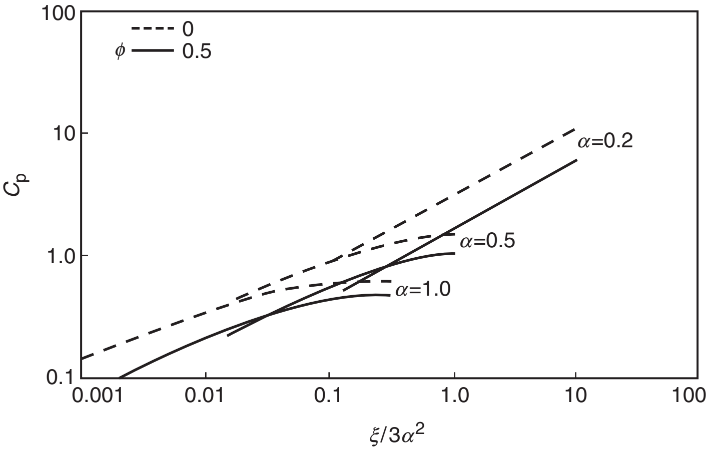
a wall Reynolds number, Re_w of 0.1 (($\mathrm{Re}_w = v_w h/\nu$), where v_w is the fluid velocity through the membrane).

The curves show that the velocity at the membrane surface ($\lambda = 1$) is 0 when ϕ is 0 as expected. As the slip velocity increases with increasing ϕ, the wall shear decreases, and the velocity profiles become flatter, approaching those for plug flow [12–14]. The effect of slip coefficient on axial pressure gradient (P) is as follows: an increase in ϕ results in a decrease in wall shear stress so that P also decreases. In addition, the transition from laminar to turbulent flow at a porous surface occurs at a Re of less than 2000, which is also the case with membrane systems.

The effect of slip coefficient on concentration polarisation (CP) was mathematically modeled for flat membrane and tubular membrane systems [12,13,15,16]. Lowering of CP due to slip coefficient ϕ as a function of product water recovery (ξ) for different normalised diffusion coefficients (α) is shown in Figure 6.8. The data show that CP decreases both with ϕ and α. Since α is a measure of particle diffusion from the membrane surface to the bulk solution, slip-flow possibly augments diffusive back-transport of particles from the membrane surface to the bulk solution. Thus, the slip-flow velocity model possibly accounts for higher or actual UF/MF flux, which is under-predicted by the gel polarisation model discussed in Chapter 1.

6.5 CP AND MASS TRANSFER COEFFICIENT

CP is the accumulation of rejected solutes on the membrane surface. It reduces membrane permeability of the solvent and can lead to a limiting flux. Hence, controlling



Concentration polarisation, C_p, as a function of slip coefficient, ϕ. ξ is fraction of water removed (1 - R_w/R_e *(x/h) or channel length.* α *is normalised diffusion coefficient, (D/*v_w*h).*

Figure 6.8 Concentration polarisation profiles in a membrane channel. *Source: [12].*

or reducing CP is necessary to maintain design flux or throughput. It can be controlled by raising cross-flow velocity and/or by increasing turbulence at the membrane surface resulting in increasing the diffusive back-transport of the solutes from the membrane surface, i.e. increases the mass transfer coefficient. According to Equation (1.3) in Chapter 1, for 100% rejection (solute concentration in permeate is zero), the equation for CP reduces to:

$$J = k\ \ln\left(\frac{C_\mathrm{w}}{C_\mathrm{b}}\right)$$

where J is the solvent flux, k is the mass transfer coefficient, C_w (or C_g) and C_b is the concentration of the solute at the membrane surface and in the bulk solution, respectively. $k = D/\delta$, where D is the solute diffusivity and δ is the boundary layer thickness. Mass transfer correlations can be used to estimate the k for various membrane configurations [17]. It can also be estimated empirically (see Chapter 1).

For *turbulent flow* in a circular tube, the correlation is (Chilton–Colburn),

$$\mathrm{Sh} = 0.023\ \mathrm{Re}^{0.8}\mathrm{Sc}^{0.33}$$

For *laminar flow* in a circular tube, the correlation is (Leveque),

$$\mathrm{Sh} = 1.62\ (\mathrm{Re}\,\mathrm{Sc}\,d_\mathrm{h}/L)^{0.33}$$

where Sherwood number, $\mathrm{Sh} = \frac{k\,d_\mathrm{h}}{D} = \frac{\text{convective mass transfer coefficient}}{\text{diffusive mass transfer coefficient}}$

$$\text{Schmidt number, Sc} = \frac{\nu}{D} = \frac{\text{momentum diffusivity}}{\text{mass diffusivity}}$$

$$\text{Reynolds, Re} = \frac{V d_\mathrm{h}}{\nu} = \frac{\text{inertial forces}}{\text{viscous forces}}$$

where V is the fluid velocity; d_h the hydraulic diameter $= d$ for tubes $= 4$ (cross-sectional area/wetted diameter); L the axial length of tube; and ν is the kinematic viscosity (μ/ρ).

An alternate correlation for k uses the shear rate (γ):

$$k = 0.816\gamma^{0.33}D^{0.67}L^{-0.33}$$

where $\gamma = 8\ V/d$ for tube (d is tube diameter) and for channel, $\gamma = 6\ V/b$ (b is channel height).

6.6 SURFACTANT MICELLES SIZE CORRELATION

Surfactant-based ultrafiltration (SBUF) has been investigated since the 1980s for removing dissolved organic compounds, especially hazardous wastewater, as discussed in Chapter 1. The basis of SBUF is that at concentrations above the critical micelle concentration (CMC), surfactant micelles attach to each other to form organised aggregates called micelles. These aggregates average 30–200 monomers and are easily rejected by UF membranes. Thus sodium dodecyl sulphate, an anionic surfactant with a molecular weight of 288, is too small to be rejected by a UF membrane [18]. However, the anionic surfactant micelles were easily rejected by a 10,000 MWCO membrane. The micelles form in such a way that the hydrophobic portions of the molecules align toward the centre, away from the surrounding hydrophilic aqueous solution.

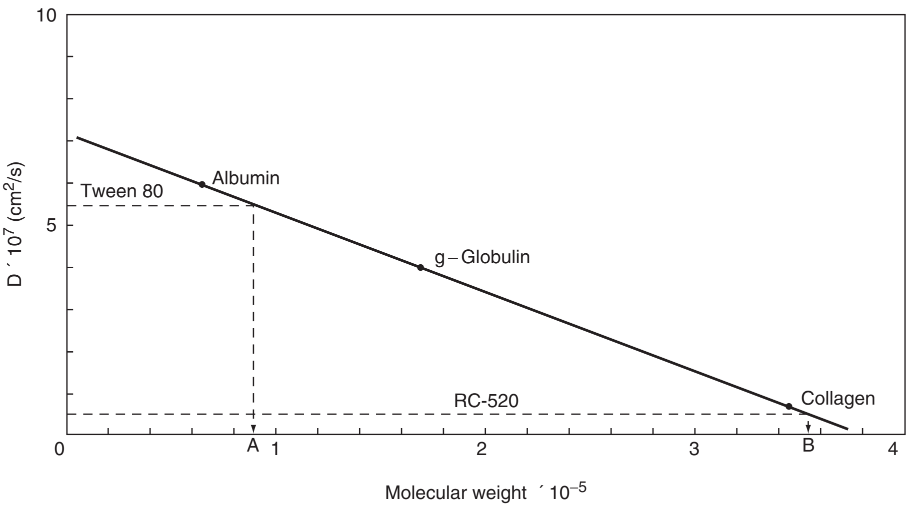
Surfactants, both ionic and non-ionic, are commonly available. Non-ionic surfactants form larger micelles with aggregation numbers an order of magnitude higher than ionic surfactants but at a much lower CMC, e.g. the CMC value for sodium dodecyl sulphate is 2360 mg/l (MW = 288) as compared to 16 mg/l in the case of Igepal RC-520 (MW = 526), a non-ionic surfactant. Since only micelles are rejected by UF membranes, a high CMC value results in a substantial leakage of surfactant monomers through the membrane. Hence the size of micelles is an important parameter for selecting a UF membrane with the largest MWCO in order to achieve both high flux and high rejection.

The micelle diameter can be calculated by measuring the micelle diffusion coefficient using the technique of dynamic light scattering (DLS). If one assumes that all micelles are spherical in shape, the radius of a micelle in solution may be calculated by using the Stokes–Einstein relation:

$$D = \frac{kT}{6\eta R} \tag{6.5}$$

where D is the diffusion coefficient, k is Boltzmann's constant, T the absolute temperature, η the solvent viscosity, and R the hydrodynamic radius of the micelle. Using the DLS technique, the hydrodynamic radius of micelles of ionic surfactants, Tween 80 and Igepal RC-520 was found to be 37–39 and 400–600 Å, respectively [19]. The diffusion coefficient of the two non-ionic surfactants calculated using Equation (6.5) was 5.5×10^{-7} and 4.5×10^{-8} cm^2/s, respectively. The diameter of the anionic surfactant was considerably smaller, 24 Å, which was in good agreement with the value in the literature.

The surfactant diffusion data were compared with the molecular weight (MW) and diffusion data of selective proteins from the literature to estimate pseudo-molecular weights (PMW) of the surfactant micelle in Figure 6.9 [19]. The correlation indicates that the PMW of Tween 80 and RC-520 micelles was 92,000 and 346,000, respectively. A rule of thumb is that the MWCO of a UF membrane should be at least one-half of the solute to be separated. Thus, a new tool was developed where the relationship between the micelle diameter, diffusion coefficient and a PMW could be used to screen high MWCO membranes for SBUF applications.



Diffusion coefficient vs. molecular weight plot for macromolecules. Diffusion coefficients for Tween 80 and RC-520 Points A and B refer to pseudomolecular weights of Tween 80 and RC-520, respectively.

Figure 6.9 A correlation between the size of surfactant micelles and molecular weight of macromolecules. *Source: [18], Copyright® 1996 from Separation Science and Technology by R. Singh. Reproduced by permission of Taylor & Francis Group, LLC, http://www.taylorandfrancis.com.*

6.7 DEIONISER DESIGN

Deionisation (DI) requires replacement of all cations and anions in the aqueous, as discussed in Chapter 2. The simplest DI system is a dual-bed system consisting of a strong acid cation exchanger followed by a strong base anion exchanger operating in series. For higher purity water production, a mixed-bed deioniser is required downstream of the two-bed cation–anion exchanger system or an RO system. A general rule of thumb is that when the TDS exceeds 300 mg/l, RO becomes more economical than dual-bed IX systems. IX system capabilities are listed below [20]:

- Sodium cycle softeners with co-flow regeneration: softened water hardness = 1–3 mg/l.
- Sodium cycle softeners with counter-flow regeneration: softened water hardness = 0.5 mg/l.
- Dual-bed IX systems with co-flow regeneration: DI water conductivity = 5–10 µS/cm and silica = 50 µg/l.
- Dual-bed IX system with counter-flow regeneration: DI water conductivity = 1–3 µS/cm and silica = 10–20 µg/l.
- A dual-bed IX system with co-flow regeneration followed by mixed-bed IX: DI water conductivity = 0.06–0.1 µS/cm and silica 5–10 µg/l.

6.7.1 DI system design basis

Design a dual-bed IX system for producing DI water with 1.0 μS/cm conductivity for a medium pressure (25–60 bar g) boiler [21,22]. The feed water has the following components: $Ca^{2+} = 75$ mg/l; $Na = 50$ mg/l; $Mg^{2+} = 25$ mg/l; $Cl^{-} = 30$ mg/l; $SO_4{}^{2-} = 80$ mg/l; $HCO_3 = 40$ mg/l; and $SiO_2 = 10$ mg/l where concentrations are in ppm as $CaCO_3$ equivalent. The feed water flow rate is 57 m^3/h at 20°C. The design procedure is given in Sections 6.7.2 and 6.7.3 using the resin manufacturer's data given below:

Strong acid cation resin bed:

- Regeneration level of 6 lb H_2SO_4 per ft^3 (96 kg H_2SO_4 per m^3) for maximum sodium leakage of 2.0 ppm, and an operating capacity of 15.6 kgr/ft^3 (35 kg/m^3);
- Pressure drop per foot (per 0.305 m) of bed depth at a linear velocity of 8.6 gpm/ft^2 (21 m^3/h/m^2) is 0.75 psi (5.2 kPa);
- Backwash flow rate of 6.4 gpm/ft^2 (15.6 m^3/h/m^2) for a bed expansion of 60%; and
- Rinse water flow is 25–50 gal/ft^3 (3.34–6.68 m^3/m^3) using DI water or RO permeate. The rinse water flow rates should be 1 gpm/ft^3 (8 m^3/h/m^3) to 1.5 gpm/ft^3 (12 m^3/h/m^3).

Strong base anion resin bed:

- Regeneration level of 4 lb NaOH per ft^3 (64 kg NaOH per m^3) for maximum silica leakage of 0.05 ppm and an operating capacity of 15.3 kgr/ft^3 (35 kg/m^3);
- Pressure drop per foot (per 0.305 m) of bed depth at a linear velocity of 8.5 gpm/ft^2 (20.8 m^3/h/m^2) is 0.85 psi (5.9 kPa);
- Backwash flow rate of 2.6 gpm/ft^2 (6.34 m^3/h/m^2) for a bed expansion of 60%; and
- Rinse water flow is 40–90 gal/ft^3 (5.34–12.0 m^3/m^3) using DI water or RO permeate. The rinse water flow rates should be 1 gpm/ft^3 (8 m^3/h/m^3) to 1.5 gpm/ft^3 (12 m^3/h/m^3).

6.7.2 Cation ion-exchanger design

Quantity of water to be treated per service cycle. The amount of process water deionised per service run cycle is (250 gpm)(60 min/h)(12 h/cycle) = 180,000 gal (681 m^3).

Cation load. Since the influent cation load is expressed as ppm equivalents as $CaCO_3$, it is necessary to convert to units consistent with resin manufacturer's capacity data expressed as kilograins (as $CaCO_3$) per ft^3 of resin. Total cation load in this case is 75 + 50 + 25 = 150 ppm. Convert to kgr: (150 ppm)(180,000 gal/cycle)/(1000 gr/kgr) (17.1 ppm/g/gal) = 1580 kgr as $CaCO_3$ per cycle.

Quantity of cation-exchange resin. The cation load per cycle is 1580 kg from above, and the resin capacity is given as 15.6 kgr/ft^3 in Section 6.7.1. Therefore, the amount of resin needed is 1580 kgr/(15.6 kg/ft^3) = 101 ft^3 (2.86 m^3).

Bed velocities. For water treatment the space velocity (SV) is usually between 1 and 5 gpm/ft^3 resin (8 and 40 m^3/h/m^3). Therefore, the SV is 250 gpm/101 ft^3 = 2.5 gpm/ft^3. The normal linear velocity range is 4–10 gpm/ft^2 (9.75–24.4 m^3/h/m^2). Assuming a bed depth of 3.5 ft (1.07 m), the cross-sectional area is 101 ft^3/3.5 ft = 28.9 ft^2. The linear velocity therefore is 250 gpm/28.9 ft^2 = 8.6 gpm/ft^2, which is within range. If either SV or linear velocity is considerably greater than the normal range, more resin would be required.

Vessel dimensions. The vessel diameter is $(\text{X-n area} \times 4/\pi)^{1/2} = (28.9 \times 4/\pi)^{1/2} =$ 6.1 ft (1.86 m). In order to determine the vessel side-shell height (SSH), assume 100% bed expansion; hence, the vessel SSH is 7 ft (2.13 m) or twice the bed height.

Resin bed pressure drop and backwash flow rate. A minimum head-space (freeboard) is required for bed expansion at the design backwash flow rate. Typically, the bed expansion is 50–60%. The flow rate required for this expansion is specified as 6.4 gpm/ft^2. Thus the backwash flow rate is 6.4 gpm/ft^2 × 28.9 ft^2 = 185 gpm (42 m^3/h). The pressure drop (ΔP) per foot of bed depth is specified as 0.75 psi. Thus ΔP for the cation-resin bed is (0.75 psi/ft) × (3.5 ft) = 2.6 psi (17.9 kPa). This excludes the pressure drop due to valves, fittings, or liquid distributors or collectors. Overall, the ΔP should be <10 psi (68.9 kPa).

Regeneration calculations. The H_2SO_4 regeneration level to hold Na^+ leakage to 2 ppm is 6 lb/ft^3 (96 kg H_2SO_4 per m^3), as specified in Section 6.7.1. The total acid required per cycle, therefore, is (6 lb/ft^3)(101 ft^3) = 606 lb (275 kg) per cycle. To avoid precipitation of $CaSO_4$, regenerate in two steps. First, use 50% of the regenerant as a 2% solution, and then the rest as a 4% solution. For the 2% step process: (1/2 × 606 lb H_2SO_4)/(8.43 lb solution per gallon)(0.02 lb H_2SO_4 per lb solution) or about 1800 gal (6.8 m^3) of 2% acid solution. The 4% step requires (1/2 × 606)/(8.54 × 0.04), or about 890 gal (3.37 m^3) of 4% acid solution. Note 8.43 and 8.54 lb/gal are densities of the 2% and 4% acid solution, respectively.

Rinse water flow rates. The column must be rinsed with DI/RO water after regeneration to remove traces of acid. Bed rinse is done at two flow rates to remove all traces of acid. The rinse water requirements are specified as 25–50 gal/ft^3 resin. For the resin volume of 101 ft^3, the rinse water requirement is about 2500–5000 gal (9.5–19 m^3). For the slow rinse step, the flow rate is (one bed volume – 101 ft^3 × 7.48 gal/ft^3, or ~750 gal) at 50 gpm (11.4 m^3/h) for 15 min. For the fast rinse step, the flow rate is based on the remainder volume, i.e. at 150 gpm (34.1 m^3/h) for ~50 min.

6.7.3 Anion ion-exchanger design

Quantity of water to be treated per service cycle. The amount of process water deionised per service run cycle is (250 gpm)(60 min/h)(12 h/cycle) = 180,000 gal (681 m^3).

Anion load. Total anion load is 30 + 80 + 40 = 150 ppm. Convert to kgr as follows: (150 ppm)(180,000 gal/cycle)/(1000 gr/kgr)(17.1 ppm/g/gal) = 1580 kgr as $CaCO_3$ per cycle.

Quantity of anion-exchange resin. The anion load per cycle from above is 1580 kgr, and the resin capacity is 15.3 kgr/ft^3 from Section 6.6.1. So the amount of resin needed is 1580/15.3 = 103 ft^3 (2.91 m^3).

Bed velocities. The space velocity is 250 gpm/103 $\text{ft}^3 = 2.4$ gpm/ft^3 resin (19.2 m^3/h/m^3). The normal linear velocity range is 4–10 gpm/ft^2 (9.75–24.4 m^3/h/m^2). Assume a bed depth of 3.5 ft (1.07 m). Then the bed cross-sectional area is 103 ft^3/3.5 ft = 29.4 ft^2, and the linear velocity is 250 gpm/29.4 ft^2 = 8.5 gpm/ft^2, which is within range. If either SV or linear velocity is considerably greater than the normal range, more resin would be required.

Vessel dimensions. The vessel diameter is $(\text{area} \times 4/\pi)^{1/2} = (29.4 \times 4/\pi)^{1/2} =$ 6.12 ft (1.86 m). In order to determine the vessel side-shell height (SSH), assume 100% bed expansion; hence, the vessel SSH is 7 ft (2.13 m) or twice the bed height.

Resin bed pressure drop and backwash flow rate. A minimum head-space (free-board) is required for bed expansion to permit the requisite backwash flow rate. Typically, the design bed expansion is 50–60%. The flow rate required for this expansion is specified as 2.6 gpm/ft^2 (lower linear velocity because the anion resin is lighter than the cation resin). Hence, the backwash flow rate is (2.6 gpm/ft^2) × (29.4 ft^2) = 76 gpm (17.3 m^3/h).

The pressure drop (ΔP) per foot of bed depth is specified as 0.85 psi. Thus, ΔP for the anion-exchange bed is (0.85 psi/ft) × (3.5 ft) = 3 psi (2.07 kPa). This excludes the pressure drop due to valves, fittings, or liquid distributors or collectors. Overall, the ΔP should be <10 psi (68.9 kPa).

Regeneration calculations. The caustic soda regeneration level is 4 lb NaOH per ft^3 as specified. Total caustic soda requirement, therefore, is (4 lb/ft^3)(103 ft^3) = 412 lb (187 kg) NaOH per cycle. Regenerant concentration is typically 4% NaOH solution having a density of 8.68 lb/gal. Total regenerant solution requirement per cycle is (412 lb NaOH)/0.04 lb NaOH per lb of solution)(8.68 lb solution per gallon) or 1190 gal per cycle (4.5 m^3 per cycle). This should be applied at 0.5 gpm/ft^3 (4 m^3/h/m^3).

Rinse water flow rates. The column is rinsed with DI/RO water after regeneration to remove caustic remaining in the bed. Bed rinse is done at two flow rates to remove all traces of caustic. The rinse water requirements are specified as 40–90 gal/ft^3 resin, i.e. for a resin volume of 103 ft^3, the requirement is 4000–9000 gal (15.1–34.1 m^3). For the slow rinse step, the flow rate is (one bed volume – 103 $\text{ft}^3 \times 7.48$ gal/ft^3, or 750 gal) at 50 gpm (11.4 m^3/h) for 15 min. For the fast rinse step, the flow rate is based on the remainder volume, i.e. at 150 gpm (34.1 m^3/h) for ~50 min.

6.8 PROCESS CONTROLS

Microprocessor-based control systems generally consist of a programmable logic controller (PLC) along with sensors and alarms. The PLC controls the parameters and devices that are automated. The PLC is programmed in ladder logic and provides logic control in a step-wise fashion. PLCs are rugged and inexpensive and offer many options for interfacing with process equipment. This flexibility allows the PLC to control all the processes within the plant as well as provide data to external systems via analogue signals or serial data. The PLC itself, however, is not suited for memory-intensive requirements such as data logging or sophisticated operator interface functions.

An operator interface system (OIS) is used to indicate and record data as gathered by the PLC. The OIS may be a specialised machine with a built-in display or a personal computer (PC) with OIS application software and a PLC interface card. A PC-based system offers greater flexibility and storage capacity but is generally more expensive. The PLC system can provide PID functionality but without an interface system that allows the operator to directly adjust parameters. The PLC, however, can be connected via a digital communication link to an OIS computer. The computer can be programmed with graphical-equipment/process screens to enable the operator to view the system from a primary location and adjust the set point values of the control valves. This arrangement is capable of encompassing a whole plant. The operator and the plant, though, are completely dependent upon a functioning PLC and OIS computer. The operator must start and stop each equipment from the control panel. Once the system is running, it functions automatically. Systems are switched "on" and "off" by the PLC automatically based upon process feedback signals – unless there is a fault in the system, which then requires manual intervention to clear the fault and restart the equipment.

Most industrial sensors, including temperature, pressure, and flow transmitters, provide an analogue output in the form of a voltage or current signal. For example, a temperature sensor might generate 1 V at 10°C and 5 V at 50°C. Analogue signals in a current form (4–20 mA) are especially popular because they are more impervious to noise and can conveniently provide a power source for low demand instruments. Another advantage is that using 4 mA to represent zero for whatever is being measured allows the system to differentiate a faulty instrument from one that is simply reading zero.

An analogue signal cannot be used directly by the PLC, so it is transformed into a digital signal with the aid of an analogue-to-digital (A/D) converter. The accuracy of an A/D converter depends on the number of bits (the unit for binary information) it sends to the computer. A 10-bit converter will work in the range of 0–1024 and is, therefore, able to divide an analogue signal voltage into 1024 steps. This represents an accuracy of 1/1024, which is approximately 0.1%. Many A/D converters are capable of 12-bit resolution that represents an accuracy of 0.02%. The PLC generates analogue output signals for controlling the process such as valve position or motor speed in a similar manner using digital-to-analogue conversion. Most PLC systems also resolve the output signal into 12 bits.

More sophisticated instruments of many different types provide data in the form of a serial string. In such cases, A/D conversion is not necessary, but the PLC must be programmed to accept the format of the serial data. This method can provide much more data than just a single process value and eliminates the inherent inaccuracy of D/A and A/D converters. Addressable instruments utilise widely accepted protocols.

These devices have the advantages of multi-parameter data transfer of serial instruments but afford the ease of wiring and use of analogue instruments. In many situations a device that switches between only two states may be adequate to control a process. In such cases it is more cost-effective to use a digital sensor that changes from one state to another based on a change in the process; for instance, when the pump discharge pressure exceeds a preset value, a pressure switch may change its state to close a circuit and notify the PLC. A two-state sensor may also provide backup for an analog instrument in a critical process.

All instruments and control systems must provide a way to implement process control interlocks, alarms and algorithms to prevent a dangerous upset from occurring and to safely shut down the process equipment if one does occur. Alarms let an operator know when a process deviates far enough from normal conditions and immediate action is warranted to prevent safety or quality incidents. The tendency to over-alarm the system should be avoided. Individual warning lights or annunciator panels are commonly used to indicate specific system faults, which also may be indicated in the OIS system. The latter gives the operator the ability to see the time of occurrence and associate each alarm with other conditions in the system for troubleshooting purposes. System-wide alarm conditions are indicated with a visual beacon and an audible alarm. Alarms and graphical indicators are usually driven by the PLC.

6.9 CENTRIFUGAL PUMPS

Centrifugal pumps are the prime fluid movers in membrane plants for liquid separations. In general, centrifugal pumps are used in moderate-to-high flow under low head conditions and operate within the rated ranges of head and velocity. Pump specifications depend on process requirements; for example, fluid flow rate determines the capacity of the pump, whereas pump head depends on fluid density and viscosity. Pump head is commonly used as a measure of energy. The total dynamic head (TDH) is a reflection of the energy a pump imparts to a fluid, and takes into account differences in pressure, fluid elevation and velocity between source and destination. In addition, TDH accounts for pipe friction losses and the pressure drop through in-line items such as instruments, valves, strainers and static mixers.

6.9.1 Pump selection criteria

Material and energy balances are used to calculate the required flow rate while the maximum pump pressure or "shut-off" pressure is the maximum pressure a pump will develop under no-flow conditions, e.g. when the pump outlet line is fully blocked. The amount of work needed to drive the pump increases with increase in fluid density and viscosity. The maximum values of these properties usually occur during start-up, shutdown and process upsets. Similarly, fluid temperature and the presence of suspended solids are taken into consideration during pump specification.

Pump brake horsepower (BHP) is related to the flow rate (Q, gpm), TDH (or H, ft), specific gravity (S.G.) and efficiency (η) by the relationship,

$$\mathrm{BHP} = \frac{H \times Q \times \mathrm{S.G.}}{3960 \times \eta}$$

The efficiency is set by the pump manufacturer when the final pump selection is made. It is usually based on their shop tests for the same model and size pumps. The pump efficiency can vary between 10% and 80%. Pump electric motor specifications require mechanical and electrical requirements. Motors can vary in size depending upon power, speed (RPM), frame size, area classification, orientation, service factor and type of enclosure (e.g. totally enclosed fan closure).

Pumps are specified to avoid cavitation. When the suction pressure of the pump fluid drops below its vapour pressure, vapour bubbles form resulting in cavitation. When the fluid gets re-pressurised, these bubbles implode, which results in pitting of the impeller and other pump components. Further, since vapour has a lower density than liquid, cavitation results in lowering pump capacity and efficiency.

Pump manufacturers have established guidelines to ensure each pump they supply is not exposed to conditions that result in cavitation. The design standard is called NPSHR or net positive suction head required. The NPSHR takes into account any potential head losses that might occur between the pump's suction nozzle and impeller thereby ensuring the liquid does not drop below its vapour pressure (bubble point). The NPSH is a measure of the proximity of a liquid to its vapour pressure, and must exceed the pump manufacturer's pump NPSHR. There are two process variables that can be adjusted, in case the available NPSH is less than the NPSHR: raise the static head and lower friction losses. Conversely, the NPSHR can be reduced by using a larger, slower speed pump, a double suction impeller, a larger impeller inlet area, an oversized pump and a secondary impeller placed ahead of the primary impeller.

Every pump manufacturer provides a specific curve for a pump, as shown in Figure 6.10. The curve relates head, flow rate, power, NPSHR, and efficiency for specific impeller diameters for the particular pump. The pump should not be operated below the manufacturer's minimum continuous flow rate rating. The pump impeller size is indicated in horizontal lines. The pump curve shows the pump has a specific NPSHR that varies depending on the head and flow. The goal is to select a pump with a rated (or design) point as close as possible to the best efficiency point as determined by the manufacturer. Since pumps are rarely operated at their exact design point, flow rate and head need to be changed to increase pump efficiency or to accommodate changes in process requirements. Hence, the impeller selected should be one size smaller than the maximum size for the given pump casing so that it can be replaced with a larger one without replacing the casing.

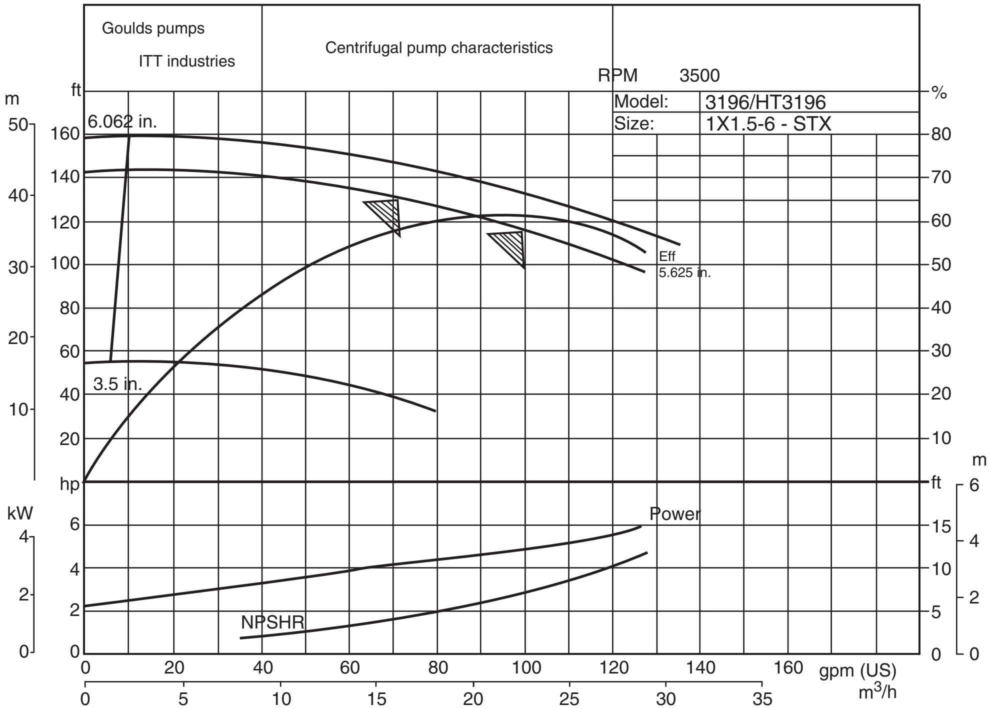


Figure 6.10 Typical centrifugal pump curves.

The construction materials of a pump depend on fluid properties such as corrosiveness, presence of dissolved gases and product application. Pump seals around the pump shaft are very important for preventing process fluid leaks. The seals are of two types: packing and mechanical. Mechanical seals are the most widely sealing method. Another class of pumps, the magnetically coupled pumps, are seal-less with no rotating shaft seals. These pumps, however, may not be suitable for high purity water (HPW) systems because of the potential for bacteria growth in the gap between the inner magnet and the containment can [23].

6.9.2 Pump controls

The purpose of pump control is to maintain a set of process conditions and operate it safely. These include adjusting (a) flow rate by throttling pump discharge, (b) controlling pump speed and (c) switching the pump on and off. Throttling is achieved with a flow controller and a control valve in the discharge line. Controlled flows are most often accomplished with a self-regulating (modulating) pressure-control valve on the pump discharge (as in a RO high-pressure pump discharge line), or a flow-control valve and controller with a flow configured at the set point (as in RO reject flow control), as discussed in Chapter 2.

The pump speed can be controlled by using a variable-speed driver (VFD) especially, when the capacity of the pump varies greatly. VFDs include electric, electromechanical, mechanical and hydraulic power recovery turbines.

Pump on–off control is achieved with level switches or level transmitters that have built-in dead bands on the suction vessel (storage tank) to start and stop the pump. Frequent starts and stops can damage the pump and the motor; hence, the storage tank is sized to accommodate changes in level by providing sufficient storage (residence time). Low suction pressure switches are used as safety interlocks for shutting off the pump when the suction pressure is below the set point. Conversely, high-pressure switches are installed on the pump discharge so as not to exceed the maximum allowable output pressure resulting in dead-heading the pump.

6.10 CONTROL VALVES

A control valve is a variable orifice used to regulate the flow of a process fluid. Control valves are a key component in any process plant. Proper selection of these valves can have a significant impact on how well the process is controlled and the overall cost of the plant. Characteristics of commonly used control valves in membrane plants are given in Table 6.2. In order to select a control valve, the following system operating conditions and fluid properties must be known: fluid state (vapour, liquid, or two-phase), vapour pressure, flow rate, inlet and outlet pressure, inlet temperature, fluid density, molecular weight and viscosity, specific heat ratio, critical temperature and critical pressure. In about 80% of applications, the valves are selected to be fail-safe closed under spring actuator action when there is a loss of power or signal. Hence, information about the valve's fail-safe position and maximum shut-off pressure is also required.

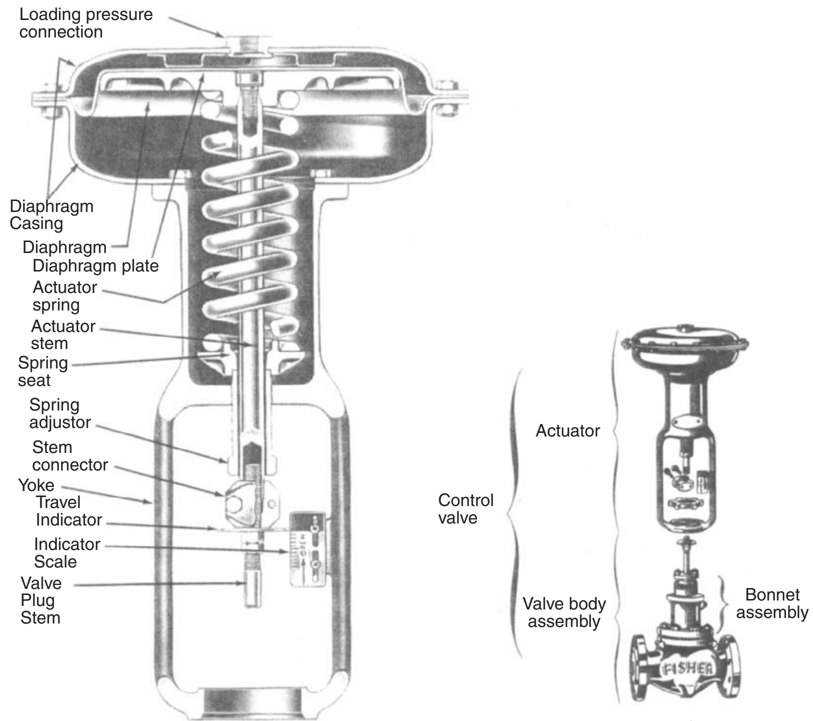
A valve should satisfy the following conditions to be effective: operate over a wide range of flows (wide range-ability), accurately respond to any signal across its operating range, exhibit little dead time (hysteresis), react to incremental adjustments from the controller (resolution), and respond with the required speed (stroking speed) [24]. The quality of a control valve is quantified in terms of its (a) gain, (b) time constant, and (c) dead-time lag. Gain is the ratio of the percentage change in a process variable to the percentage change of valve travel and depends on the valve characteristics and process conditions. The gain should never be less than 0.5.

The ability of a valve to control flow depends upon the quality of its actuator. A positioner is added when tighter control is required for the modulating valve, as shown in Figure 6.11. Positioners improve performance by amplifying the controller's signal, thereby achieving a more precise response. Control valves are either motorised (electrically operated) or pneumatic (air operated). A control valve should react instantaneously to any change in the signal. A fast response, however, may not be suitable for all applications. The signal is generated by a control loop, which consists of a sensing element,

Table 6.2 Characteristics of process valves

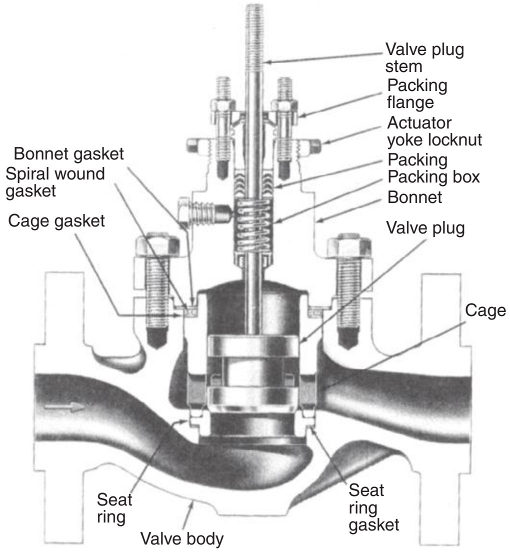
Ball	Globe	Butterfly	Diaphragm
• On/off (Rotary)	• Throttling	• Throttling	• Throttling
• Virtually no pressure loss across the valve face	• Good sealing characteristics	• Lightweight, compact design	• Almost no leakage; process fluid is isolated from valve stem
• Lightweight, compact design	• Can be used in frequent open/close service	• Minimal pressure loss across valve face	• Self-cleaning
• High capacity	• Quick change of trim without removing valve from line	• Low cost	
• Good rangeability	• High capacity	• High throughput capacity	
• Tight shut-off	• Good rangeability	• Smaller shaft and actuator	
	• Low-noise trim available		
	• Smooth control		
• Sealability poor with metal seats used at high temperatures	• High-pressure losses due to contorted path through the valve	• Poor sealing characteristics	• Limited operating pressure
• Limited temperature range with resilient seats	• Low-noise trim reduces capacity	• Good control limited to 60° opening	• Limited temperature
• Choke flow problems			
• Cavitation problems	• For flow regulation		
	• When tight shut-off is required.	• Tight shut-off requires special lining, plus over-sized shaft and actuators	• High wear and tear
			• Poor control over 50% opening
• Requires removal for maintenance		• Lining imposes temperature limitations	
		• Low-pressure applications	• Water treatment service
			• Chemical one abrasive service
• Not for service with highly corrosive fluids			
• Most suitable for slurries			

Source: Bishop et al., Reproduced with permission from Chemical Engineering Progress, Nov. 2002. Copyright® 2002 AIChE.



Direct-acting actuator

Relationship of major components



Push-down-to-close valve body assembly

Figure 6.11 A typical control valve assembly with actuator.

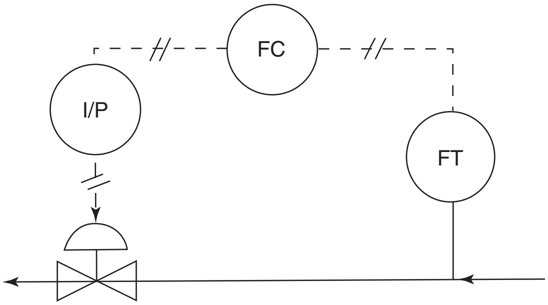


Figure 6.12 Control valve controller action.

a controller and the final control element, as shown in Figure 6.12. The sensing element transmits a signal to a local controller or a remote controller such as a PLC. The controller compares the signal with the set point and makes the required corrections by sending a signal to the control valve. The correction is measured and verified by the sensing element. Also shown in the figure is the I/P transducer converting the electronic signal to a pneumatic signal.

There are two main features of control valves: valve capacity and valve characteristics. The most important valve parameter for calculating the size of a control valve is the flow coefficient, C_v, which gives the flow rate of water through a valve for a unit pressure drop at standard conditions. It varies with size and style of valve. For liquids, the C_v value is calculated empirically using the equation:

$$C_v = \frac{Q}{(\text{S.G.}/\Delta P)^{1/2}} \tag{6.6}$$

where Q is flow rate, ΔP is pressure drop across the valve, and S.G. is fluid-specific gravity. The calculation of C_v depends on whether the fluid is incompressible, compressible, or mixed-phase. Valve manufacturers provide actual valve flow capacities in terms of C_v for various valve sizes and types. The valve should operate in the 10–80% range of its stroke range; otherwise, it is difficult to control the valve. System geometry, pipe size and schedule number, and materials of construction must be specified. The maximum flow rate should include a minimum design margin of 10%. The pressure drop through a valve should be greater than 1 bar at the rated flow rate in a pumped system. The size of the control valve should be one size smaller than the line size since the pressure drop due to reduced size helps it attain the correct C_v.

The fluid flowing through a valve or a flow restriction gets accelerated to some maximum velocity with corresponding minimum pressure downstream of the restriction where the cross-section area is minimum (vena contracta). This increase in velocity or kinetic energy occurs at the expense of the pressure or potential energy. If the pressure is lower than the liquid vapour pressure, flashing occurs, producing bubbles or cavities of vapour. The pressure rises or recovers downstream of the vena contracta. If the pressure exceeds the vapour pressure, the bubbles or cavities collapse, causing noise similar to gravel flowing through a line, vibration, loss of efficiency and physical damage. These gas pockets collapse violently; the resulting shock waves can generate impact pressure greater than 10,000 bar. The key to preventing damage due to cavitation is to avoid a sudden pressure recovery when the fluid emerges from the throat of the valve. Accelerating the fluid gradually maintains sufficient pressure to avoid cavitation. The initiation of cavitation can also be delayed by installing an orifice plate downstream of the valve. This builds up a back-pressure on the valve resulting in ΔP that is below the cavitation threshold. Orifice plates are useful in processes with fairly constant flow.

6.11 MATERIALS PROPERTIES

The key issue in selecting materials of construction for high purity plants such as pharmaceutical and semiconductor plants is contamination. Selecting the most suitable materials – stable and cost-effective – for equipment and piping is a complex and critical issue, e.g. in the case of seawater desalination plants.

6.11.1 Stainless steel

Stainless steel refers to steel alloys with a minimum chromium content of 10.5% that forms a thin chromium oxide film on the steel's surface to improve corrosion resistance, which makes the steel "stainless." Other alloying elements typically include nickel and molybdenum to improve materials properties, e.g. fabrication.

Type 304 and 316 stainless steel are used in the high-pressure pipes and pipe fittings in RO plants. The 300 series SS are also sensitive to chlorides at a pH of 6.5–8 and at temperatures below 60°C. Type 316 SS tolerates chlorides up to 1000 ppm, but concentrations can reach 26,000 ppm in dry zones (for $MgCl_2$), resulting in failure. In seawater RO desalination plants, duplex (2205) or super-duplex (2507) steels are used instead of 316 SS. The compositions of these steels are detailed below [25]:

- 304 SS: Contains 18% chromium and 8% nickel. It has good general corrosion resistance in moderately oxidising environments.
- 316 SS: Contains 16% chromium, 10% nickel and 2% molybdenum. Molybdenum increases corrosion resistance and improves chloride pitting resistance.
- 2205 SS: Duplex 2205 is an austentic–ferritic (duplex) stainless with 22% chromium, 4.5% nickel and 3% molybdenum with superior corrosion resistance lessthan 316. Its design strength is much higher than 316 L, often permitting lighter wall construction.
- 2507 SS: Contains 25% chromium, 7% nickel and 4% molybdenum. It is ideal for applications requiring exceptional strength and corrosion resistance. It has excellent resistance to chloride stress corrosion cracking and pitting and crevice corrosion.

Type 316 L is the preferred material of construction in pharmaceutical and other HPW plants. It contains about 70% iron and has less than 0.03% carbon (L is for low carbon). The rust deposits formed on SS surfaces are thin, called "rouge" due to their reddish-brown hue. Rouging is the result of dissolved ferrous ion (Fe^{2+}) oxidising to the insoluble ferric iron (Fe^{3+}) in the presence of oxygen and precipitating as either Fe_2O_3 or $Fe(OH)_3$. One gram of iron will cover an area of 390 m^2, three atoms deep [26]. Oxygen can enter a system through pump seals or by diffusion-sorption through plastics, as discussed in Chapter 1.

There are three types of rouge: (a) Type I is due to the dissolution of steel such as in the case of pump impellers; (b) Type II results from active corrosion, e.g. on non-stainless steel components; and (c) Type III is due to high temperature. Passivation is used to remove rogue, but it does not prevent Type I and III rogue from reoccurring if oxygen permeates the system. Type II rogue is usually the result of improper welding that leaves a heat-affected zone near the weld. Type II attacks the heat-affected zone only. Rogue can be avoided by using the thermoplastics discussed in Section 6.11.2. However, plastics are permeable to gases such as O_2, N_2, He, H_2, and CO_2 as well as many solvents. This permeability results in "blistering" behind plastic-lined vessels and pipes over time.

6.11.2 Plastics

Unlike stainless steel, the properties of plastics vary depending on the type of polymer. Polymers are substances formed by linking one or more species of atoms or groupings of atoms by covalent bonds. The method and type of linking converts simple molecules into macromolecular structures that determine the chemical and physical properties of the synthesised polymer. Polymer properties depend on many factors such as polymer chain length and conformation, cross-linking of chains, intense polar interactions and the type and size of attached side groups, to name a few controlling factors. For example, branched polyethylene (PE) has a lower melting point than linear PE even though they are chemically identical. For additional information refer to "Glass transition temperature" and "Thermoplastics" in the Glossary section.

Commonly used thermoplastics such as PE, polyvinyl chloride (PVC) and polypropylene (PP) are less costly than fluoropolymers, e.g. polyvinylidene fluoride (PVDF), but do not perform as well in high temperature conditions. They also include plasticisers, heat stabilisers and fire retardants that can leach out. PVDF in its virgin form is highly pure and does not contain additives.

Fluropolymers such as PVDF and perfluoroalkoxy (PFA) have excellent chemical resistance to deionised water, high thermal stability and are resistant to degradation by sunlight. They have a low coefficient of friction unlike metal surfaces, thereby preventing microorganisms (fungi and bacteria) from growing. This is critical since unlike chemical plants, biocides cannot be added to HPW to prevent microbial growth. PFA polymer can be used at temperatures up to 260°C. However, it is highly expensive, and PVDF is the preferred material. PVDF is the main competitor of 316 L SS in HPW systems and is widely used in high purity fluid loops in semiconductor plants. PVDF is among the hardest fluoropolymers and has the highest tensile strength of all plastics. It also has better abrasion strength than SS.

Since PVC and PP have low melting temperatures (<90°C), components using these materials can only be sterilised by chemicals such as hydrogen peroxide and chlorine, both of which require rinsing after sterilisation. The melt temperature of PVDF, on the other hand, is 178°C, which makes it amenable to steam sterilisation. PVDF can also be sterilised by ozone. Since ozone has a short half-life (minutes), PVDF systems do not need rinsing after sterilisation.

6.11.3 SS vs. plastics

Stainless steel is impermeable to oxygen unlike plastics; it has 10 times the thermal conductivity of plastics and does not creep at temperatures below 425°C (at room temperature for plastics). SS pipes can withstand high pressures (up to 110 bar for a 25 mm O.D. 300-series SS pipe vs. 5 bar for plastic pipe). Its yield and tensile stresses are an order of magnitude greater than those of thermoplastics.

6.12 PROCESS VALIDATION

Membrane plants used for producing HPW in pharmaceuticals manufacture require validation like other equipment and processes. The FDA has defined process validation as "establishing documented evidence which provides a high degree of assurance that a specific process will consistently produce a product meeting its predetermined specification and quality attributes." In other words, validation involves detailed testing and documentation of system equipment and components and system functional operation to ensure that design and regulatory specifications are met and that system performance will be consistently acceptable during service.

Process validation is part of current good manufacturing practices (cGMPs) and is required in the US and EU for a manufacturing license. It involves the identification, monitoring, and control of sources of variation that can contribute to changes in the product. Process development normally involves identifying critical variables, defining set points for each unit operation, and establishing operating ranges. Cleaning validation shows the ability of cleaning procedures to allow reuse of processing components and equipment without deterioration of product quality.

In the case of pharmaceutical plants, a HPW system must comply with the rules of the US Food and Drug Administration (FDA) as stated in the 21 CFR (Code of Federal Regulations), Parts 210, 211 and 820. According to the FDA regulatory code, validation implies "the conformation by documented examination and provision of objective evidence that the particular requirements for a specific intended use can be consistently fulfilled." These regulations specify minimum cGMP. Compliance, which must be validated, ensures that drugs meet the requirements of safety, identity, strength, quality and purity.

The system validation documentation includes but is not limited to Quality Assurance Plan (QAP), Operation and Maintenance Manual (O&M), and Factory Acceptance Test (FAT) reports. A properly developed QAP and its supporting documentation help to reduce cost, boost product quality, ensure regulatory compliance and increase profitability. The FAT validation is the first verification step of the customer's validation process, which may include design qualification (DQ), installation qualification (IQ), operational qualification (OQ), and performance qualification (PQ).

6.13 RO/NF FEED WATER ANALYSIS

Feed water constituents must be analysed prior to designing a membrane system. The ASTM Designation D4195-88 "Standard Guide for Water Analysis for Reverse-Osmosis Applications" for components and properties that require analysis is given below. Water treatment processes are discussed in Chapter 2.

Carbon dioxide (CO_2) is not rejected by RO/NF membranes. If it is the major dissolved constituent in the permeate, it will increase the ionic load on downstream ion-exchange polisher anion resins.

Free chlorine (Cl_2) is an oxidant. Polyamide RO and NF membranes are sensitive to chlorine. Hence, water must be dechlorinated by passing it through an activated carbon filter or by the addition of a reducing chemical such as sodium sulphite, sodium bisulphite, or sodium metabisulphite to feed water. However, it is necessary for CA membranes to protect them from bacterial attack.

Hydrogen sulphide (H_2S) is not present in chlorinated water supplies because it is quickly converted to sulphite. It is, however, associated with some sub-surface water supplies that have been depleted of oxygen. H_2S forms sulphur particles in the water and contribute to membrane fouling. Sulphide ion may form insoluble metal sulphides.

Langelier Saturation Index. See Section 6.14.

Oxygen (O_2) is indicative of the character and source of the water supply. Water depleted in oxygen/air is likely to contain soluble iron, manganese and hydrogen sulphide, often in appreciable quantities. When oxygen is added to such a water supply, precipitates (e.g. ferric compounds) are formed.

Silt Density Index. See Glossary.

Silica. The solubility of silica (SiO_2) is a function of pH and temperature. Exceeding the saturation level in cold water (<10°C) is not a serious problem because the precipitation is very slow. However, exceeding 120 ppm in any temperature presents a potential problem. Since water supplies often contain >20 ppm silica, silica very often limits recovery. Precipitated silica is virtually impossible to remove from the elements and must be avoided. Metal hydroxides (e.g. iron, aluminium, magnesium) absorb or complex silica and catalyse the precipitation.

Turbidity. See Glossary.

Bicarbonate (HCO_3^-) results from the chemical decomposition of dissolved CO_2 with the hydroxide ion in water. A portion of the bicarbonate present in the feed water can be converted to carbonate as a result of pH changes owing to concentration of salts on the concentrate side of the membrane. Such cases require the addition of acid or a crystal growth inhibitor to avoid calcium carbonate scaling.

Carbonate (CO_3^{2-}) forms a sparingly soluble salt with calcium, which readily fouls RO membranes. Calcium carbonate can easily be removed by lowering the pH below 5.0 or raising the pH above 8.0.

Chloride (Cl^-) does not generate insoluble salts. Because it passes through RO membranes more easily than most anions, it is one of the predominant ions in the permeate.

Fluoride (F^-) forms insoluble salts with divalent metal ions such as calcium, magnesium, barium and strontium.

Nitrate (NO_3^-) is similar to chloride in that it is not aggressive to the membrane nor does it tend to form insoluble salts.

Phosphate (PO_4^{3-}) forms a low solubility salt with calcium. Water containing phosphate generally requires the addition of an antiscalant.

Sulphate (SO_4^{2-}) forms a sparingly soluble salt with calcium, strontium, or barium. Sulphate does not usually limit the cycles of concentration, unless one or more of these three cations are present in high concentrations.

Aluminium (Al^{3+}) is generally found as the hydroxide, which causes particulate fouling of the RO membrane. Aluminium-based compounds such as sodium aluminate and aluminium sulphate are common coagulants used in potable water treatment. Under proper circumstances, the aluminium precipitate formed in the water treatment plant is completely filtered. Occasional fluctuations in pH can cause excessive amounts of dissolved Al^{3+} to pass into the distribution system.

Barium (Ba^{2+}) forms a low solubility compound with sulphate ion. Strontium and barium tend to occur together (see Strontium).

Calcium (Ca^{2+}) forms insoluble or slightly soluble salts with common ions such as carbonate and sulphate. Both can be adequately controlled through crystal growth inhibitors or, if the precipitate is allowed to form, can readily be removed by cleaning the RO membrane. Calcium concentration, in conjunction with alkalinity and sulphate concentration, often establishes the upper limit to the water recovery of the RO system.

Iron is generally present in the dissolved ferrous (Fe^{2+}) form, but can oxidise to the ferric (Fe^{3+}) state and precipitate as the hydroxide. Municipal potable water supplies contain <0.3 ppm of iron, but sub-surface supplies may contain levels of iron in excess of 10–20 ppm. Prior to use in an RO system, a water supply containing iron should be treated to remove the iron, or steps should be taken to avoid contact of the water with air or oxidising substances such as chlorine.

Magnesium (Mg^{2+}) forms sparingly soluble salts such as magnesium silicate and, under high pH conditions, magnesium hydroxide. Both are uncommon in RO systems.

Manganese (Mn^{2+}) like iron is usually at levels of less than 0.3 ppm in public water supplies. Private well water supplies often contain higher manganese levels, often in a dissolved form, which precipitates on exposure to air. A well water supply containing manganese should be pre-treated, or steps should be taken to eliminate contact with air or oxidants to assure the manganese remains soluble.

Potassium (K^{+}) is present in small quantities. It is soluble like sodium, and no operating or fouling problems are caused by potassium.

Sodium (Na^{+}) forms relatively soluble salts with most anions, including bicarbonate, sulphate and chloride, and thus seldom presents a fouling issue. However, since the cation passes most readily through the RO membrane, it is present at the highest concentrations in the permeate. It generally controls overall salt rejection.

Strontium (Sr^{2+}) is found in less than 20% of water supplies. It forms a salt with sulphate ion that is soluble up to 1 ppm in concentration. It is kept in suspension with a crystal growth inhibitor.

When the feed water is secondary effluent from a municipal plant, analyses of total oil, grease and surfactants are also required.

6.14 CHEMISTRY OF FEED WATER TREATMENT IN MEMBRANE PLANTS

6.14.1 Mineral precipitation

Conditions within an RO unit are typically not at equilibrium with respect to supersaturated ion precipitation. Hence, it may be feasible, depending on the feed water chemistry, to operate RO units under supersaturated conditions when precipitation kinetics are substantially lower than the residence time in the RO system. Ideally, this requires the use of short flow-path membrane elements, as shown in Figure 1.24.

As amply discussed in previous chapters, product water recovery (<75%) in brackish water RO systems is constrained by the solubility of sparingly soluble salts. Precipitation of $BaSO_4$ (barite), $CaSO_4$ (gypsum), $SrSO_4$ (celestite), $CaCO_3$ (calcite), $CaMg(CO_3)_2$ (dolomite) and silica are generally the most critical. Additionally, $MgCO_3$ may precipitate instead of $CaMg(CO_3)_2$. High RO recoveries (80–90%) are achievable, depending on feed water chemistry, by using a brine RO/NF system with or without intermediate chemical treatment such as lime softening or caustic soda [27]. Addition of $Ca(OH)_2$ (hydrated lime) generates twice the amount of $CaCO_3$ solids as NaOH (caustic soda), although it is half as expensive.

Raising the pH to 10.3 by adding Na_2CO_3 (soda ash) promotes the precipitation of non-carbonate hardness resulting in the highest removal of Ca^{2+} and Sr^{2+}, whereas adding $Ca(OH)_2$ and Na_2CO_3 aids in the removal of Ba^{2+}, Mg^{2+} and silica. When the pH is

10.3, barium, magnesium and strontium can co-precipitate with $CaCO_3$. The principal sink for Ca^{2+} can also be $CaSO_4$ and $CaMg(CO_3)_2$, and the principal sink for Mg^{2+} can also be $MgSO_4$.

6.14.2 Calcium carbonate chemistry

Calcium carbonate ($CaCO_3$) is a common scale component in desalination plants because of its very low solubility; 18 mg/l in pure water at 15°C. The solubility product of $CaCO_3$ is 8.7×10^{-9} at 15°C, which is one of the lowest among sparingly soluble salts. See Table 6.9.

Relatively high concentrations of calcium and carbonate in natural waters result from the composition of geological formations in aquifers. Calcium carbonate exists in three different crystalline forms in the order of increasing solubility: calcite, aragonite and vaterite. Calcite is thermodynamically the most stable polymorph of $CaCO_3$ and forms tenaciously adhering hard mineral deposits. Vaterite is the least stable and tends to transform to aragonite or calcite. The presence of foreign ions or impurities has a destabilising influence; for example, Mg^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, and Cu^{2+} encourage aragonite formation over calcite. Magnesium has the strongest influence on $CaCO_3$ precipitation, favouring the formation of aragonite or vaterite over calcite [28]. In the absence of additives and over a range of temperatures up to 80°C, a mixture of all three polymorphs exists. The presence of Mg^{2+} favours the stabilisation of aragonite, while organic compounds tend to stabilise the formation of vaterite.

Total hardness comprises all divalent salt ions in solution (mainly calcium and magnesium), while carbonate hardness is the fraction of total hardness that relates to dissolved CO_2. The actual concentration of dissolved Ca^{2+} (or Mg^{2+}) in water depends on the availability of CO_2, which solubilises $CaCO_3$ ($MgCO_3$) according to the equation:

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3) \tag{6.7}$$

A concentration of CO_2 corresponding to its partial pressure yields a carbonate hardness of about 100 mg/l (2 meq/l). Scale inhibitors such as polymeric phosphates can sustain a concentration of 250 mg/l. WHO hardness recommendation for drinking water is 2 meq/l (max.) and a permissible total hardness of 10 meq/l (max.). Carbonate hardness is reduced by the addition of lime, $Ca(OH_2)$, which precipitates $CaCO_3$, as discussed under lime softening in Chapter 2.

The ratios of carbonate containing species in aqueous solution are a function of pH value as depicted by the well-known carbonate speciation curve (Figure 6.13). Aqueous carbon takes on three different forms depending on the acidic or basic nature of the water. At pH ~ 4.3, the concentration of bicarbonate ($HCO_3{}^-$) is 1% of the dissolved CO_2, and neutralisation of carbonate ($CO_3{}^{2-}$) is virtually complete. Alkalinity is, thus, related to

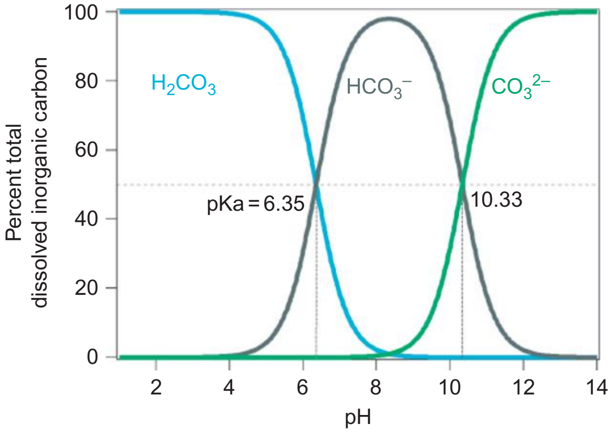


Figure 6.13 Carbonate speciation curve. Aqueous carbon takes on three forms depending on the acidic or basic nature (pH) of water.

carbonate hardness, specifically to HCO_3^- concentration. It is controlled or destroyed by the addition of acid with simultaneous generation of CO_2:

$$Ca(HCO_3) + 2HCl = CaCl_2 + H_2O + 2CO_2 \tag{6.8}$$

Acidification is followed by aeration (decarbonation) to remove excess CO_2. This is a common pre-treatment step in desalination plants to prevent carbonate scaling and reduce hardness. LSI and S&DSI should be less than 2.0–2.5 to reduce acid treatment.

Desalinated water is soft and acidic regardless of the process used. Soft waters are aggressive (corrosive). For example, RO permeate (desalinated water) is virtually devoid of hardness-producing ions (essentially Ca^{2+} and Mg^{2+}), resulting in CO_2-enriched RO permeate (CO_2 is not rejected by the membrane) and softened water (enriched in monovalent ions), whereas distilled water is virtually ion-free, devoid of all saline constituents. Decarbonation after acidification, therefore, is necessary to remove any excess dissolved CO_2 beyond required to keep Ca^{2+} and other hardness ions in solution because excess CO_2 acts like a mineral acid (carbonic acid), particularly in the presence of oxygen and corrodes ferrous pipes and equipment. Excess CO_2 also destroys the beneficial effects of the corrosion-protective mineral layer formed on steel pipes. The protective layer consists of crystalline $CaCO_3$ and $FeCO_3$. Hence, raising the pH value and remineralisation are essential. For example, desalinated water for drinking requires raising the pH to 8.0 and remineralisation with lime to up to 150 mg/l $CaCO_3$. The minimum remineralisation requirement for bulk transport of desalinated seawater is 35 mg/l $CaCO_3$.

Remineralisation with $Ca(OH)_2$ or $CaCO_3$ is commonly practiced. Use of limestone "beads" in a packed bed is the simplest process; demineralised water flows through the bed from the top resulting in dissolution of the calcite. The pH, alkalinity (HCO_3^-) and hardness (Ca^{2+}) of the processed water are increased. The calcite dissolution process is given by:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \tag{6.9}$$

Limestone is a sedimentary rock primarily composed of calcite and sometimes aragonite. This calcite can be pure in composition ($CaCO_3$) or contain low levels of magnesium forming magnesium calcite (see Table 6.6).

6.14.3 Procedure for calculating LSI value

The scaling tendency of a given feed water is often evaluated using the Langelier Saturation Index (LSI) for brackish water and the Stiff and Davis Stability Index (S&DSI) for seawater (LSI is acceptable for seawater). LSI and S&DSI are defined below:

$$
\begin{aligned}
&\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_S}\ (\mathrm{TDS} < 10{,}000\,\mathrm{mg/l})\\
&\mathrm{pH_S} = \mathrm{pCa} + \mathrm{pAlk} + \mathrm{pK_2} - \mathrm{pK_S}\\
&\mathrm{S\&DSI} = \mathrm{pH} - \mathrm{pHs}\ (\mathrm{TDS} > 10{,}000\,\mathrm{mg/l})\\
&\mathrm{pH_S} = \mathrm{pCa} + \mathrm{pAlk} + K
\end{aligned}
$$

where pH_S = pH level at which the water is in equilibrium with calcium carbonate; pCa = $-\log_{10}$ of calcium concentration (mol/l); pAlk = $-\log_{10}$ of total alkalinity (mol/l); $pK_2 = -\log_{10}$ of ionisation constant of HCO_3; $pK_S = -\log_{10}$ of the solubility product of calcium carbonate; and K = the ionic strength constant at 25°C.

LSI value guidelines are:

- when LSI > 0, water is supersaturated with respect to $CaCO_3$.
- when LSI < 0, $CaCO_3$ scale does not deposit, or if present, it will dissolve.
- when LSI is 0, the water is at a saturation state. As a result no scale is anticipated while corrosion is negligible.

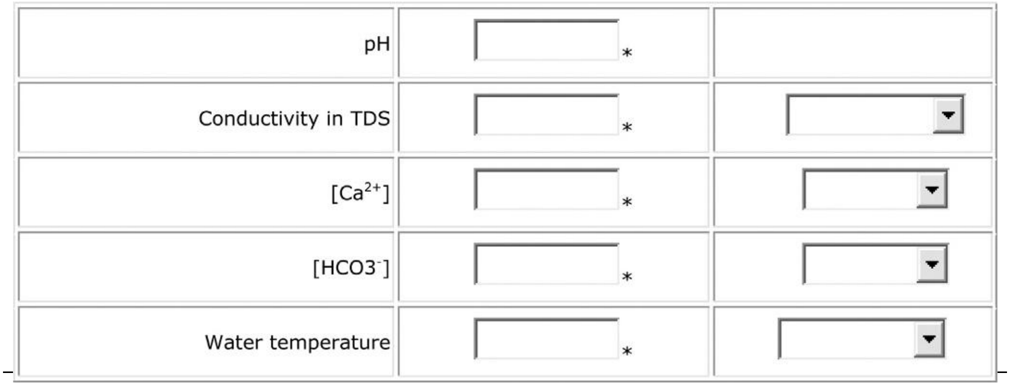
A quick and ready way to determine the LSI of water in the field is to access the following web site: http://www.lenntech.com/calculators/Langelier/index/Langelier.htm. Plug the following values – pH, temperature, TDS (or conductivity), calcium ion General loan assistance (800) 243-7552 and bicarbonate ion – into the Lennentech data input Table 6.3, and the programme will calculate the LSI value. Conversion from ion to $CaCO_3$ basis is as follows:

- Bicarbonate alkalinity as $CaCO_3 = HCO_3$ as ion × 0.82. Thus, when the HCO_3 value is 100 mg/l as ion, bicarbonate alkalinity is 82 mg/l as $CaCO_3$.
- Calcium as $CaCO_3$ = Ca as ion × 2.5. Thus, when the Ca value is 100 mg/l as ion, Ca hardness is 250 mg/l as $CaCO_3$.
- Magnesium as $CaCO_3$ = Mg as ion × 4.1. Thus, when the Mg value is 100 mg/l as ion, Mg hardness is 410 mg/l as $CaCO_3$.

6.14.4 Silica and boron removal

Weak acids and undissociated compounds such as silica and boron are poorly rejected by RO membranes at pH < 8.0. For example, boron exists as a weakly dissociated boric acid, H_3BO_3 at pH < 8.2. Silica dissolves in water forming weakly ionised silicic acid, which in

Table 6.3 Lennentech data input table for LSI value[a]



pH	☐ *	
Conductivity in TDS	☐ *	☐ ▾
$[Ca^{2+}]$	☐ *	☐ ▾
$[HCO3^{-}]$	☐ *	☐ ▾
Water temperature	☐ *	☐ ▾

[a] http://www.lenntech.com/calculators/Langelier/index/Langelier.htm.

alkaline conditions dissociates from silicates. At pH > 9.0 silica and boron get ionised with substantial increase in solubility resulting in higher rejection:

$$SiO_2 + H_2O \Leftrightarrow H_2SiO_3 \Leftrightarrow H^+ + HSiO_3 \Leftrightarrow 2H^+ + SiO_3{}^-$$
$$H_3BO_3 + H_2O \Leftrightarrow H^+ + B(OH)_4{}^-$$

At high pH values silica rejection also increases due to the molecule structure changing from silicic acid to orthosilicate, which is associated with six water molecules making a larger molecule resulting in higher rejection. Similarly, boron rejection levels are enhanced at high pH levels when the boron changes from boric acid to its salt; %rejection changes from approximately <30% to >90%. When a double-pass RO system is used, silica can be reduced from 10 ppm to <1 ppb, boron from 12 ppb to <100 ppt and TOC from 2 ppm to <5 ppb [29].

The high efficiency reverse osmosis (HERO™) process is used for enhanced rejection of silica and boron in SWRO and HPW applications [30]. The process is capable of high rejection of silica, TOC and boron with RO. Further, organic cleaning is minimised at high pH levels, akin to operating the RO unit in a continuous cleaning mode.

The central premise of the HERO process is the removal of all hardness in RO feed water so that RO can be operated at a high pH where silica is highly soluble. Opex is, however, 60–70% higher than RO alone. The HERO™ technology consists of three basic processes operating in series:

- Weak acid cation (WAC) ion exchange for removing hardness associated with alkalinity;

- Degasification for removing CO_2 resulting from alkalinity removal as a result of acid addition to lower the pH;
- RO operation at high pH (10.0–11.0) with caustic soda General loan assistance (800) 243-7552 which results in increasing the silica solubility to 1500 ppm.

6.15 WASTEWATER TREATMENT

6.15.1 Common constituents in wastewater

The most common constituents of wastewaters and their treatment methods are listed below:

1. Oil and grease – induced gas flotation (IGF), dissolved air flotation (DAF), membrane filtration
2. Suspended solids (turbidity) – IGF, DAF, coagulation + media filtration, membrane filtration
3. Hardness – chemical softening, IX, NF softening, scale inhibitors
4. Alkalinity – chemical softening, acidification, IX
5. Silica – chemical softening, IX, scale inhibitors
6. Iron/manganese – oxidation, greensand filtration, iron filter, aeration
7. Organic compounds – activated carbon, UV irradiation, chemical oxidation, biological treatment, NF
8. Ammonia – aeration, biological treatment
9. Hydrogen sulphide – chemical oxidation, biological treatment, aeration
10. Dissolved gases – aeration, membrane contactors (decarbonation)
11. VOCs – activated carbon, air stripping
12. Dissolved salts – thermal desalination, RO

Treatment of produced and flowback wastewaters is extremely challenging because of its composition and toxicity. The salinity range is 8000–200,000 ppm [31].

- *Organic compounds*: Aliphatic, aromatic, polar compounds, e.g. fatty acids, oil, grease, benzene, phenol, napthenic acids
- *Inorganic compounds:* Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}, silicates, borates, selenium, heavy metals
- *Production chemicals:* Emulsion breakers to improve oil/water separation, surfactants, corrosion inhibitors
- Ammonia, hydrogen sulphide, iron reducing bacteria and sulphur-reducing bacteria.

SAGD (steam-assisted gravity drainage) produced water has a high level of silica (200–300 mg/l), and soluble organics, mostly humic acid and asphaltenes. The TDS is typically <20,000 mg/l.

6.15.2 Trace contaminants in wastewater

Trace contaminants are chemicals that can be harmful to human health and the biotic environment because of their physicochemical toxicological properties, and are, hence, undesirable in water bodies [32]. In the aquatic environment, they are present at trace levels, usually in the μg/l (ppb) range or less. While coagulants preferentially remove larger molecular weight compounds, which tend to be more hydrophobic, it is more difficult to remove the smaller and more hydrophilic compounds by chemical means. Increasing demand for water leads to the exploitation of resources of lower water quality that are not suitable for conventional treatment. Membrane technologies offer a more reliable solution, e.g. NF is being increasingly used to retain organics and treat coloured or tainted waters.

Most trace contaminants are of anthropogenic origin. A variety of synthetic organics are produced in a substantial quantity such as pesticides, pigments, dye carriers, preservatives, pharmaceuticals, refrigerants, propellants, heat transfer media, dielectric fluids, degreasers, lubricants, etc. These compounds are collectively known as synthetic organic compounds. The production of such chemicals may entail the introduction of byproducts and their metabolites, some of which are far more detrimental to human health and the environment than the parent compounds. The majority of wastewater organic compounds are the remnants of biological treatment and tend to be lower in molecular weight and aromaticity than organics found in natural waters. These compounds are also referred to as effluent organic matter (EfOM). Further, such compounds may be less biologically degradable partly due to their binding capacity to organic matter and contain a large number of trace organics.

Some trace organics such as pesticides, trihalomethanes (THMs), polychlorinated biphenols (PCBs) and polyaromatic hydrocarbons (PAHs) are regulated. That is their maximum contamination levels are enforceable by a regulatory authority. However, many compounds have not yet been regulated. Treatment processes for removing trace amounts of arsenic and nitrates in ground waters are discussed in Chapter 3. Carbon filtration is used to remove metal ions, particularly cadmium, hexavalent chromium, silver and selenium as well as uncharged species such as arsenic and antimony from acidic streams. It is also used to remove any traces of hydrocarbons and chloramines. Biological methods are used to remove methanol, which is not rejected well by RO. Methanol is a highly miscible solvent in water, and it is virtually impossible to remove it to <10 ppm even with steam stripping.

6.16 CONVERSION FACTORS

Area:

$1\ \text{ft}^2 = 0.0929\ \text{m}^2 = 929\ \text{cm}^2$
$1\ \text{m}^2 = 10^4\ \text{cm}^2 = 10.764\ \text{ft}^2$
$1\ \text{cm}^2 = 0.0011\ \text{ft}^2 = 0.1550\ \text{in.}^2$

Density:

$1\ \text{lb(mass)}/\text{ft}^3 = 16.0185\ \text{g/l}$

Diffusivity:

$1\ \text{ft}^2/\text{h} = 2.581 \times 10^{-5}\ \text{m}^2/\text{s}$
$1\ \text{m}^2/\text{s} = 3.875 \times 10^{4}\ \text{ft}^2/\text{h}$

Flux:

$1\ \text{gal}/\text{ft}^2/\text{day} = 1.7\ \text{l}/\text{m}^2/\text{h}$ (lmh)

Force and pressure:

$1\ \text{dyne} = 1\ \text{g cm}/\text{s}^2$
$1\ \text{kg m}/\text{s}^2 = 1\ \text{N}$
$1\ \text{bar} = 10^5\ \text{Pa} = 10^5\ \text{N}/\text{m}^2 = 14.5\ \text{psi}\ (\text{lb}/\text{in.}^2)$
$1\ \text{psi}\ (\text{lb}_\text{f}/\text{in.}^2) = 6.8947\ \text{kPa} = 6.8947 \times 10^3\ \text{N}/\text{m}^2$
$1\ \text{psi} = 2.036\ \text{in. Hg} = 51.715\ \text{mm Hg}$
$1\ \text{psi} = 6.8947 \times 10^4\ \text{g}/\text{cm}/\text{s}^2 = 6.8947 \times 10^4\ \text{dyne}/\text{cm}^2$
$1\ \text{atm} = 14.696\ \text{psi} = 1.01325\ \text{bar} = 101.3251\ \text{kPa} = 760\ \text{mm Hg} = 33.9\ \text{ft water}$
$1\ \text{dyne}/\text{cm}^2 = 2.0886 \times 10^{-3}\ \text{lb}_\text{f}/\text{ft}^2$
$1\ \text{kPa} = 0.1450383\ \text{psi}$
$1\ \text{kg}_\text{f}/\text{cm}^2 = 14.2234\ \text{psi}$

Length:

$1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-4}\ \mu\text{m} = 0.1\ \text{nm}$
$1\ \text{in.} = 2.54\ \text{cm}$
$1\ \text{m} = 39.37\ \text{in.}$
$1\ \mu\text{m} = 10^{-6}\ \text{m} = 10^{-4}\ \text{cm}$
$1\ \text{mil} = 0.001\ \text{in.} = 25.4\ \mu\text{m}$
$1\ \text{nm} = 10\ \text{Å} = 10^{-9}\ \text{m}$

Mass:

1 lb = 16 oz = 453.59 g
1 lb = 8.3454 gal (US)
1 ton, short (US) = 2000 lb
1 ton, long = 2240 lb
1 kg = 2.2046 lb
1 ton, metric = 1000 kg
1 grain (gr) = 17.1 ppm per gallon
1 lb of any substance dissolved in 1000 gal ~ 120 ppm
1 quart of any substance dissolved in 1000 barrels ~ 6 ppm

Mass transfer coefficient:

$1\ \text{cm}/\text{s} = 0.01\ \text{m}/\text{s}$
$1\ \text{ft}/\text{h} = 8.4668 \times 10^{-5}\ \text{m}/\text{s}$

Power, work, and energy:

1 hp = 0.7457 kW = 550 ft lb/s = 0.7068 Btu/s
1 W = 14.3 cal/min
1 J/s = 1 W
1 Btu = 1055.06 J
1 kcal = 4.1840 kJ
1 hp h = 0.7457 kWh = 2544 Btu
1 ft $\mathrm{lb_f}$ = 1.35582 J
1 kWh/$\mathrm{m^3}$ = 3.788 kWh/kgal

Temperature:

T (°F) = [T (°C) × 1.8] + 32
T (°C) = [T (°F) − 32]/1.8

Velocity:

1 ft/s = 0.3048 m/s
1 m/s = 3.281 ft/s

Viscosity:

1 cP = 0.01 poise = 10^{-3} Pa s = 10^{-3} N s/$\mathrm{m^2}$
1 lb/ft/s = 1488.16 cP
1 cP = 2.4191 lb/ft/h = 6.72×10^{-4} lb/ft/s

Volume:

1 gal (US) = 4 quarts (qt) = 3.78541 l
1 gal (Imperial) = 1.20094 US gal
1 barrel = 42 US gal
1000 barrel/day = 29.2 gpm
1 acre-foot = 325,853 US gal
1 acre-foot = 1233.5 $\mathrm{m^3}$
1 $\mathrm{m^3}$ = 1000 l = 264.17 US gal
1 $\mathrm{m^3}$/h = 4.4 gpm
1 $\mathrm{in.^3}$ = 16.387 $\mathrm{cm^3}$
1 $\mathrm{ft^3}$ = 28.317 l
1 l = 1000 $\mathrm{cm^3}$

Molar concentration – TDS – conductivity chart (NaCl, 25°C):

- Conductivity <5000 μS/cm: TDS = conductivity × 0.5
- Conductivity 5000–40,000 μS/cm: TDS = conductivity × 0.64

- Conductivity >40,000 μS/cm: TDS = conductivity × 0.79
- Seawater: 500 mM ≃ 30,000 mg/l
- Brackish water: 170 mM ≃ 10,000 mg/l
- Potable water: 10 mM ≃ 600 mg/l
- Drinking water: 3 mM ≃ 180 mg/l

6.17 PHYSICAL AND CHEMICAL DATA

Table 6.4 Viscosity and density data

Fluid	Viscosity, μ (kg/m/s)	Density, ρ (kg/m^3)
Air	0.00002	1.3
Water	0.001	1000
Glycerine	1.8	1000
Golden syrup	120	1000

Table 6.5 Standard cleaning solutions for water treatment heat exchangers

Foulant type	Cleaning solution
Encrustation – scaling	
Calcium carbonate; calcium sulphate, silicates	Nitric acid, sulphamic acid, citric acid, phosphoric acid, complexing agents (EDTA, NTA), or sodium polyphosphates (<4% by wt; <60°C)
Sediment	
Corrosion products; metal oxides; silt; alumina; diatomic organisms and their excrement of various colours	Nitric acid, sulphamic acid, citric acid, phosphoric acid, complexing agents (EDTA, NTA), or sodium polyphosphates (<4% by wt; <60°C)
Biological growth	
Bacteria; nematodes; protozoa	Sodium hydroxide, or sodium carbonate plus surfactants (<4% by wt; <80°C)
Hydrocarbons	
Oil residue; asphalt; fats	Paraffin- or naphtha-based solvent (e.g. kerosene)[a]

[a] Note natural, butyl and EPDM gaskets swell in these solvents.

Table 6.6 Common chemicals used to treat water

Chemical	Common name	Typical specifications	Equivalent weight	Bulk density (lb/ft^3 or lb/gal)	Approx. pH (1% solution)	Solubility
Aluminium sulphate $Al_2(SO_4)_3 \cdot 14H_2O$	Alum	Lump – 17% Al_2O_3	100[a]	60	3.4	4.2 lb/gal at 60°F
		Liquid – 8.5% Al_2O_3		11		
Bentonitic clay	Bentonite	–	–	60	–	Insoluble
Calcium carbonate $CaCO_3$	Limestone	96% $CaCO_3$	50	80	9	Insoluble
Calcium hydroxide $Ca(OH)_2$	Hydrated lime Slaked lime	96% $Ca(OH)_2$	40[a]	40	12	Insoluble
Calcium hypochlorite $Ca(OCl)_2 \cdot 4H_2O$	HTH	70% Cl_2	103	55	6–8	3% at 60°F
Calcium oxide CaO	Burned lime	96% CaO	30[a]	60	12	Slake at 10–20%
	Quicklime					
Calcium sulphate $CaSO_4 \cdot 2H_2O$	Gypsum	98% Gypsum	86[a]	55	5–6	Insoluble
Chlorine(Cl_2)	Chlorine	Gas – 99.8% Cl_2	35.5	gas	–	0.07 lb/gal at 60°F
Copper sulphate $CuSO_4 \cdot 5H_2O$	Blue vitriol	98% Pure	121	75	5–6	2 lb/gal at 60°F
Dolomitic lime $Ca(OH)_2 \cdot MgO$	Dolomitic lime	36–40% MgO	67[b]	40	12.4	Insoluble
Ferric chloride $FeCl_3 \cdot 6H_2O$	Iron chloride	Lump – 20% Fe	91[a]	70	3–4	45% at 60°F
		Liquid – 20% Fe		13		

Ferric sulphate $Fe_2(SO_4)_3\cdot 3H_2O$	Iron sulphate	18.5% Fe	51.5[a]	70	3–4	30% at 60°F
Ferrous sulphate $Fe(SO_4)_3\cdot 7H_2O$	Copperas	20% Fe	139[a]	70	3–4	1 lb/gal at 60°F
Hydrochloric acid HCl	Muriatic acid	30% HCl 20°Baume	120[a]	9.6	1–2	35% at 60°F
Sodium aluminate $NaAlO_2$	Aluminate	Flake – 46% Al_2O_3	100[a]	50	11–12	40% at 60°F
		Liquid 26% Al_2O_3	13			
Sodium chloride NaCl	Rock salt, salt	98% pure	58.5	60	6–8	2.6 lb/gal at 60°F
Sodium carbonate Na_2CO_3	Soda ash	98% pure 58% Na_2O	53	60	11	1.5 lb/gal at 60°F
Sodium hydroxide NaOH	Caustic, Lye	Flake – 99% NaOH		65	12.8	70% at 60°F
		Liquid – 50–70%	40	12		
Sodium phosphate Na_2HPO_4	Disodium phosphate	49% P_2O_5	47.3	55	9	20% at 60°F
Sodium metaphosphate $NaPO_3$	Hexametaphosphate	66% P_2O_5	34	47	5–6	1 lb/gal at 60°F
Sulphuric acid H_2SO_4	Oil of vitriol	94–96% 66° Baume	50[a]	15	1–2	Infinite

[a] Effective equivalent weight of commercial product.

[b] Effective equivalent weight based on $Ca(OH)_2$ content.

Table 6.7 Pre-treatment chemicals used in desalination plants

Chemical additive	Dosage (mg/l)
Chlorine	0.5–6
Sodium bisulphite	3–19
Ferric chloride	0.8–25
Polyelectrolyte	0.2–4
Sodium hexametaphosphate (SHMP)	2–10
Polyacrylic acid	2.9
Phosphonate	1.4
Sulphuric acid	6.6–100

Table 6.8 Properties of common coagulants

Coagulant	Advantages	Disadvantage
Alum, $Al_2(SO_4)_3 \cdot 18H_2O$	Easy to handle and apply; most common; produces less sludge than lime; pH range 6.5–7.5	Effective over a limited pH range; adds dissolved solids to water
Sodium aluminate, $Na_2Al_2O_4$	Effective in hard waters; small dosages typical	Often used with alum; high cost; ineffective in soft waters
Polyaluminium chloride (PAC), $Al_{13}(OH)_{20}(SO_4)_2 \cdot Cl_{15}$	Floc formed is more dense and faster settling than alum in some applications	Not often used
Ferric chloride, $FeCl_3 \cdot 6H_2O$	pH range 4–11	Adds dissolved solids to water; consumes 2 × alkalinity as alum
Ferric sulphate, $Fe_2(SO_4)_3$	pH range 4–6 and 8.8–9.2	Adds dissolved solids to water; usually need to add alkalinity
Ferrous sulphate (Copperas), $FeSO_4 \cdot 7H_2O$	Less pH sensitive than lime	Adds dissolved solids to water; usually need to add alkalinity
Lime, $Ca(OH)_2$	Very effective; commonly used; may not add dissolved solids to water	Very pH dependent; produces large qty. of sludge; overdose can result in poor effluent quality

Table 6.9 Calcium carbonate equivalent of common substances

	Formula	**Molecular weight**	**Equivalent weight**	**Substance to $CaCO_3$ equivalent (multiply by)**	**$CaCO_3$ equivalent to substance (multiply by)**
Aluminium	Al^{3+}	27.0	9.0	5.56	0.18
Ammonium	$NH_4{}^+$	18.0	18.0	2.78	0.36
Barium	Ba^{2+}	137.4	68.7	0.73	1.37
Calcium	Ca^{2+}	40.1	20.0	2.50	0.40
Copper	Cu^{2+}	63.6	31.8	1.57	0.64
Hydrogen	H^+	1.0	1.0	50.0	0.02
Ferric iron	Fe^{3+}	55.8	18.6	2.69	0.37
Ferrous iron	Fe^{2+}	55.8	27.9	1.79	0.56
Magnesium	Mg^{2+}	24.3	12.2	4.10	0.24
Manganese	Mn^{2+}	54.9	27.5	1.82	0.55
Potassium	K^+	39.1	39.1	1.28	0.78
Sodium	Na^+	23.0	23.0	2.18	0.46
Strontium	Sr^{2+}	87.6	43.8	1.14	0.88
Zinc	Zn^{2+}	65.4	32.7	1.53	0.65
Bicarbonate	$HCO_3{}^-$	61.0	61.0	0.82	1.22
Carbonate	$CO_3{}^{2-}$	60.0	30.0	1.67	0.60
Chloride	Cl^-	35.5	35.5	1.41	0.71
Chromate	$CrO_4{}^{2-}$	116.0	58.0	0.86	1.16
Fluoride	F^-	19.0	19.0	2.63	0.38
Iodide	I^-	126.9	126.9	0.39	2.54
Hydroxyl	OH^-	17.0	17.0	2.94	0.34
Nitrate	$NO_3{}^-$	62.0	62.0	0.81	1.24
Phosphate (tribasic)	$PO_4{}^{3-}$	95.0	31.7	1.58	0.63
Phosphate (dibasic)	$HPO_4{}^{2-}$	96.0	48.0	1.04	0.96
Phosphate (monobasic)	$H_2PO_4{}^-$	97.0	97.0	0.52	1.94
Sulphate	$SO_4{}^{2-}$	96.1	48.0	1.04	0.96
Bisulphate	$HSO_4{}^-$	97.1	97.1	0.52	1.94
Sulphite	$SO_3{}^{2-}$	80.1	40.0	1.25	0.80
Bisulphate	$HSO_3{}^-$	81.1	81.1	0.62	1.62
Sulphide	S^{2-}	32.1	16.0	3.13	0.32

Table 6.10 Solubility product of sparingly soluble salts

Substance	Formula	Temp. (°C)	Solubility product, K_{sp}
Aluminium hydroxide	$Al(OH)_3$	20	1.9×10^{-33}
Barium carbonate	$BaCO_3$	16	7×10^{-9}
Barium sulphate	$BaSO_4$	25	1.08×10^{-10}
Calcium carbonate	$CaCO_3$	25	8.7×10^{-9}
Calcium fluoride	CaF_2	26	3.95×10^{-11}
Calcium sulphate	$CaSO_4$	10	6.1×10^{-5}
Cupric sulphide	CuS	18	3.5×10^{-45}
Ferric hydroxide	$Fe(OH)_3$	18	1.1×10^{-36}
Ferrous hydroxide	$Fe(OH)_2$	18	1.64×10^{-14}
Magnesium ammonium phosphate	$MgNH_4PO_4$	25	2.5×10^{-13}
Magnesium carbonate	$MgCO_3$	12	2.6×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	18	1.2×10^{-11}
Manganese hydroxide	$Mn(OH)_2$	18	4×10^{-14}
Strontium carbonate	$SrCO_3$	25	1.6×10^{-9}
Strontium sulphate	$SrCO_4$	17.4	2.81×10^{-7}
Zinc hydroxide	$Zn(OH)_2$	20	1.8×10^{-14}

Table 6.11 Osmotic pressure of various solutions at 25°C

Compound	Concentration (mg/l)	Concentration (mol/l)	Osmotic pressure (psi)[a]
NaCl	2000	0.0342	23
NaCl	35,000	0.6	398
Brackish water	5000	–	40
Seawater	33,000	–	340
Sucrose	1000	0.00292	1.1
Dextrose	1000	0.0055	2.0

[a] 1 psi = 14.5 bar.

6.18 MEMBRANE DATA

Table 6.12 Pore size characteristics of UF membranes[a]

MW cutoff Nominal (Da)	Apparent pore dia (nm)	Water flux at 3.7 bar ($l/m^2/h$)	Rejection D-Alanin (%)	Rejection Sucrose (%)	Rejection Myoglobin (%)	Rejection IgM (%)
500	2.1	17	15	70	>95	>98
1000	2.4	34	0	50	>95	>98
10,000	3.0	102	0	25	95	>98
10,000	3.8	935	0	0	80	>98
30,000	4.7	850	–	0	35	>98
50,000	6.6	425	–	–	20	>98
100,000	11	1105	–	–	–	>98
300,000	48	2215	–	–	–	>98

Molecular weights: D-alanin, MW = 89 Da; Sucrose, MW = 342 Da; Myoglobin, MW = 17,500 Da; IgM (immunoglobin), MW > 900,000 Da.

[a] Water flux and %rejection as a function of pore size rating of membranes used in cross-flow systems.

Source: Amicon.

Table 6.13 Data for sample UF/MF ceramic membranes and modules

Characteristic	*Membrane Property*	
Substrate	α-Alumina	α-Alumina
Membrane	α-Alumina	α-Alumina
Pore size[a] (μm)	0.2, 0.45, 1.0	0.2, 0.45, 0.8, 1.2, 1.5, 3.5
Water permeability[b] ($m^3/h\ m^2$ bar)	4.0	3.0
Module		
Cross-section	Circular	Hexagonal
Length (cm)	88	85
Diameter (cm)	1.6	2.8
Number of lumens	19	19, 37
Lumen diameter (mm)	2.0, 2.7, 4.0, 6.0	3.0, 4.0, 6.0
Surface area (m^2)	0.14	0.20, 0.30
Pressure (bar)	21[c]	>100[d]

[a] Smaller-pore ultrafiltration ceramic membranes are also manufactured.

[b] Measured at 20°C for 0.2 μm pore membrane.

[c] Operating pressure.

[d] Burst pressure.

Table 6.14 Classification of commercial UF/MF membranes and dead-end modules

Manufacturer	Membrane						Module			Configuration	
	Polymer	UF/MF	MWCO (kDa)	Pore size (μm)	I.D. (mm)	O.D. (mm)	Diameter (mm)	L (cm)	Surface area (m^3)	PD	SUB
Aquasouce	CA	UF	35–100	0.01	0.93	–	450	132	125	PDI	–
Dow/Omexell	PVDF	UF	20	0.01	0.65	1.25	165	221	47.1	PDO	–
Hydranautics	PES	UF	100–150	0.02–0.025	0.8	1.3	225	168	46	PDI	–
Inge	PES	UF	100–150	0.01–0.025	0.9	4.2	250	168	50	PDI	–
Koch	PS	UF	100	–	0.89	1.4	273	183	80.9	PDI	–
Memcor	PVDF	MF/UF	–	0.04–0.1	0.5	0.8	150	119	27.9	PDO	SUBO
Memcor	PP	MF	–	0.2	0.3	0.6	150	–	3.5	PDO	SUBO
Norit	PES/PVP	UF	100–150	0.02–0.025	0.8	1.3	200	150	40	PDI	–
Pall/Asahi	PVDF	MF	–	0.1	0.7	1.3	165	234	50	PDO	–
Pall/Asahi	PAN	UF	80	0.01	0.8	1.4	140	223	41	PDO	–
Polymem	PS	UF	100	–	–	0.72	315	98	114	PDO	–
Toray	PVDF	MF	–	0.1	0.8	1.35	200	216	80	PDO	–
Toray	PAN	UF	001	–	–	–	100	–	10	PDO	–
Zenon	PVDF	MF	–	0.2–0.4	0.8	1.9	1750	2.54 × 2.11 m	31.6	–	SUBO
Zenon	PVDF	UF	–	0.02–0.025	0.4	0.7	890	2.6 × 1.82 m	37–56	–	SUBO

PDI, pressure driven inside feed; PDO, pressure driven outside feed; SUBO, submerged vacuum driven; CA, cellulose acetate; PAN, polyacrylonitrile; PS, polysulphone; PES, polyether sulphone; PVP, polyvinyl pyrrolidone; PVDF, polyvinylidene fluoride; PP, polypropylene.

Source: Adapted from Graeme Pearce, Filtration + Separation, October 2007.

Table 6.15 Hydrophilic/hydrophobic surface characteristics of various commercial NF membranes based on contact angle

Membrane	Polymer	Contact angle (°)	Hydrophilicity	Manufacturer
PVD-1	Polyvinyl alcohol	20[a]	Most hydrophilic	Nitto Denko – Hydranautics
Desal-5 DK	Polyamide	31[a]		GE Osmonics
SR1	–	32[a]		Koch
UTC-20	Polypiperazineamide	36[b]		Toray
ATF-60	–	38[a]		Parker-Hannifan
Desal-5 DL	Cross-linked aromatic polyamide	42[a] 44[b]		GE Osmonics
XN-40	Polyamide	46[a]		Tri-Sep
Desal-51 HL	Cross-linked aromatic polyamide	47[b]		GE Osmonics
NF-PES-10	Polyethersulphone	54[a] 72[b]		Nadir GmbH
NTR-7450	Sulphonated polyether sulphone	58[a] 70[b]		Nitto Denko – Hydranautics
N30-F	Polyethersulphone	88[b]	Most hydrophobic	Nadir GmbH

[a] *Source*: Mantarri et al., Desalination 149 (2002) 131–136.
[b] *Source*: Boussu et al., Desalination 191 (2006) 245–253.

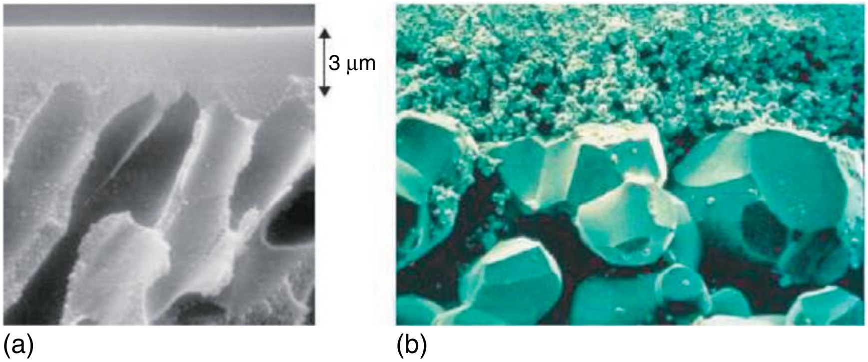


Figure 6.14 Anisotropic UF membranes: (a) polymeric (thickness of "skin" shown) and (b) ceramic. *Source: Judd, The MBR Book, Elsevier, 2006.*

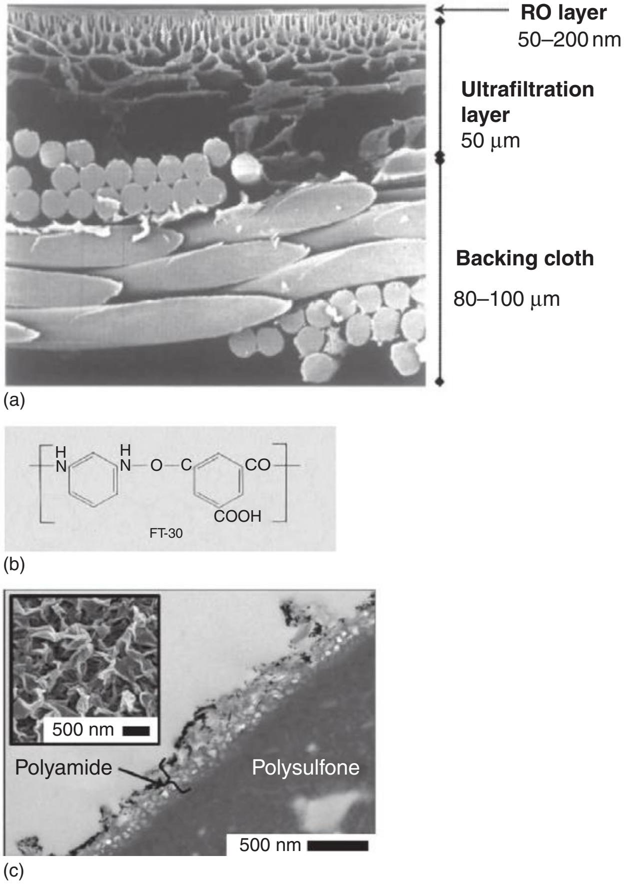


Figure 6.15 (a) Cross-section of a thin-film composite polyamide RO membrane (FT-30), (b) chemical structure of FT-30 polymer, and (c) Micrograph of a thin-film composite membrane–polyamide layer on polysulphone support. *Source: P.A. Pacheo et al., J. Memb. Sci. 358 (2010), 51-59. Copyright® (2010), with permission from Elsevier.*

REFERENCES

[1] R. Singh, Characteristics of a chlorine resistant reverse osmosis membrane, Desalination 95 (1994) 27–37.
[2] H.K. Lonsdale, U. Merten, R.L. Riley, Transport properties of cellulose acetate osmotic membranes, J. Appl. Poly. Sci. 9 (1965) 1341–1362.
[3] R.E. Kesting, Synthetic Polymeric Membranes, John Wiley & Sons, New York, NY, 1985.
[4] V.L. Punzi, K.B. Hunt, G.P. Muldowney, Ind. Eng. Chem. Res. 29 (1990) 259.
[5] K. Ghosal, R.T. Chern, B.D. Freeman, AIChE Reprints, (1992).
[6] S. Chowdhury, P. Kumar, P.K. Bhattacharya, A. Kumar, Separation characteristics of modified polysulfone ultrafiltration membranes using NO_x, Sep. Purif. Technol. 24 (2001) 271–282.
[7] R. Singh, Polyamide polymer solution behaviour under chlorination conditions, J. Memb. Sci. 88 (1994) 285–287.

[8] J. Glater, M.R. Zachariah, S.B. McCray, J.W. McCutchen, Reverse osmosis membrane sensitivity to ozone and halogen disinfectants, Desalination 48 (1983) 1.
[9] D.B. Guy, R. Singh, On-site regeneration of reverse osmosis membranes, WSIA J. 9 (1) (1982) 35–43.
[10] T. Matsuura, Future trends in reverse osmosis membrane research and technology, in: Z. Amjad (Ed.), Reverse Osmosis, Van Nostrand Reinhold, New York, NY, 1993, pp. 37–75.
[11] J.P. Kohler, An investigation of laminar flow through a porous-walled channel, Ph.D. Dissertation University of Massachusetts, Amherst, 1973.
[12] R. Singh, R.L. Laurence, Influence of slip velocity at a membrane surface on ultrafiltration performance – I. Channel flow system, Int. J. Heat Mass Transfer 22 (1979) 721–729.
[13] R. Singh, R.L. Laurence, Influence of slip velocity at a membrane surface on ultrafiltration performance – II. Tube flow system, Int. J. Heat Mass Transfer 22 (1979) 731–737.
[14] S. Chellam, M.R. Wiesner, C. Dawson, Laminar flow in porous ducts, Rev. Chem. Eng. 11 (1) (1995) 53–98.
[15] P. Dulal, N. Rudraiah, R. Devanathan, The effects of slip velocity at a membrane surface on blood flow in the microcirculation, J. Math. Biol. 28 (1988) 705–712.
[16] H.M. Yeh, T.W. Cheng, Analysis of the slip effect on the permeate flux in membrane ultrafiltration, J. Memb. Sci. 154 (1) (1999) 41–51.
[17] M.C. Porter, Concentration polarization with membrane ultrafiltration, Ind. Eng. Chem. Product Res. Dev. 11 (1972) 234–248.
[18] R. Singh, Removal of volatile organic compounds by ultrafiltration, Desalination 104 (1996) 203–214.
[19] R. Singh, Investigation of ultrafiltration rejection of surfactant micelles by dynamic light scattering, Sep. Sci. Technol. 31 (9) (1996) 1351–1356.
[20] S. Siverns, C. Wilson, J. d'Ailly, Process water treatment: navigating the options, Chem. Eng. 107 (6) (2000) 64–71.
[21] S.B. Applebaum, Demineralization by Ion Exchange, Academic Press, New York, NY, 1968.
[22] N.P. Chopey, T.G. Hicks, Handbook of Chemical Engineering Calculations, McGraw-Hill, New York, NY, 1984 (Section 14).
[23] K. Fernandez, B. Pyzdrowski, D.W. Schiller, M.B. Smith, Understanding the basics of centrifugal pumps, CEP 98 (6) (2002) 52–56.
[24] T. Bishop, M. Chapeaux, L. Jaffer, K. Nair, S. Patel, Ease control valve selection, CEP 98 (11) (2002) 52–56.
[25] I.D.A. Desalination Yearbook 2010–2011, Media Analytics Ltd, Oxford, UK, 2011.
[26] R. Greene, Choose your material, CEP 98 (6) (2002) 15–17.
[27] C.J. Gabelich, M.D. Williams, A. Rahardianto, J.C. Franklin, Y. Cohen, High-recovery reverse osmosis desalination using intermediate chemical demineralization, J. Memb. Sci. 301 (2007) 131–141.
[28] T. Waly, M.D. Kennedy, G.-J. Witkamp, G. Amy, J.C. Schippers, The role of inorganic ions in the calcium carbonate scaling of seawater reverse osmosis systems, Desalination 284 (2012) 279–287.
[29] D. Mukhopadhyay, S. Whipple, RO system that reduces membrane scaling and fouling tendencies, Ultrapure Water 14 (7) (1997) 21–27.
[30] The HERO™ process, Desal, Water Reuse 18 (1) (2008) 43–44.
[31] S.A. Holditch, Getting the gas out of the ground, CEP 108 (8) (2012) 41–48.
[32] L.D. Nghiem, A.I. Schafer, Trace contaminant removal with nanofiltration, in: A.J. Schafer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration, Elsevier, Oxford, UK, 2004, pp. 480–520.

INDEX

Note: Page numbers followed by *f* indicate figures and *t* indicate tables.