

Reverse Osmosis

Design, Processes, and Applications for Engineers

Jane Kucera





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Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts Published simultaneously in Canada

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Cover design by Russell Richardson.

Library of Congress Cataloging-in-Publication Data:

ISBN 978-0-470-618431

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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

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Preface

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

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

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

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

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Acknowledgements

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

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

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

Thanks also go to Nalco Company, Naperville, IL, for supporting me in this endeavor. Individuals at Nalco who have provided technical and administrative support include: Ching Liang, Anne Arza, Anders Hallsby, Beth Meyers, Carl Rossow, Alice Korneffel, and Kevin O'Leary. Nalco-Crossbow LLC personnel who have provided support include Mark Sadus (contributor to Chapter 6), Scott Watkins, Mike Antenore, Jason Fues, and Dave Weygandt. Valuable technical support has been provided by Julius Glater—Professor Emeritus UCLA; Mark Wilf of Tetratech; Rajindar Singh—Consultant; Madalyn Epple of Toray Membrane USA; Scott Beardsley, Craig Granlund, of Dow Water and Process Solutions; Jonathan Wood and John Yen of Siemens Water Technologies— Ionpure Products; Bruce Tait of Layne Christensen; Jean Gucciardi of MarTech Systems; Rick Ide of AdEdge Technologies; and Lisa Fitzgerald of ITT—Goulds Pumps.

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

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

1 FUNDAMENTALS

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Introduction and History of Development

1.1 Introduction

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

1.1.1 Uses of Reverse Osmosis

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

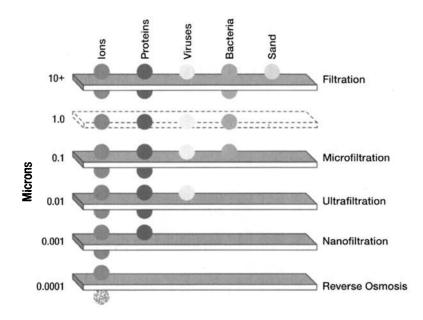


Figure 1.1 "Filtration Spectrum" comparing the rejection capabilities of reverse osmosis with other membrane technologies and with the separation afforded by conventional filtration.

the second RO may be used directly or is sometimes polished with mixed-bed ion exchange or continuous electrodeionization to achieve even higher product water purity (see Chapter 16.3).

Other common applications of RO include:

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

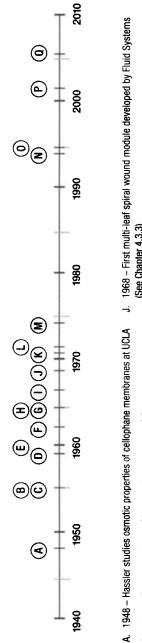
1.1.2 History of Reverse Osmosis Development

One of the earliest recorded documentation of semipermeable membranes was in 1748, when Abbe Nollet observed the phenomenon of osmosis.¹ Others, including Pfeffer and Traube studied osmotic phenomena using ceramic membranes in the 1850's. However, current technology dates back to the 1940's when Dr. Gerald Hassler at the Unitversity of California at Los Angeles (UCLA) began investigation of osmotic properties of cellophane in 1948.² He proposed an "air film" bounded by two cellophane membranes.³ Hassler assumed that osmosis takes place via evaporation at one membrane surface followed by passage through the air gap as a vapor, with condensation on the opposing membrane surface. Today, we know that osmosis does not involve evaporation, but most likely involves solution and diffusion of the solute in the membrane (see Chapter 4).

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

In 1959, C.E. Reid and E.J. Breton at University of Florida, demonstrated the desalination capabilities of cellulose acetate film.⁴ They evaluated candidate semipermeable membranes in a trial-anderror approach, focusing on polymer films containing hydrophilic groups. Materials tested included cellophane, rubber hydrochloride, polystyrene, and cellulose acetate. Many of these materials exhibited no permeate flow, under pressures as high at 800 psi, and had chloride rejections of less than 35%. Cellulose acetate (specifically the DuPont 88 CA-43), however, exhibited chloride rejections of greater than 96%, even at pressures as low as 400 psi. Fluxes ranged from about 2 gallons per square foot-day (gfd) for a 22-micron thick cellulose acetate film to greater than 14 gfd for a 3.7-micron thick film when tested at 600 psi on a 0.1M sodium chloride solution. Reid and Breton's conclusions were that cellulose acetate showed requisite semipermeability properties for practical application, but that improvements in flux and durability were required for commercial viability.

A decade after Dr. Hassler's efforts, Sidney Loeb and Srinivasa Sourirajan at UCLA attempted an approach to osmosis and reverse osmosis that differed from that of Dr. Hassler. Their approach consisted of pressurizing a solution directly against a flat, plastic film.³ Their work led to the development of the first asymmetric cellulose acetate membrane in 1960 (see Chapter 4.2.1).² This membrane made RO a commercial viability due to the significantly



- B. 1955 First reported use of the term "reverse osmosis"
- 1955 Reid begins study of membranes of demineralization at University of Florida ن
- 1959 Breton and Reid demonstrate desalination capability of cellulose acetate film
- 1960 Loeb and Sourirajan develop asymmetric cellulose acetate membrane at UCLA ய
- F. 1963 First practical spiral wound module developed by General Atomics (see Chapter 4.3.3)
- 1965 First commercial brackish water R0 facility at Coalinga, CA G
- H. 1965 Solution-Diffusion transport model described by Lonsdale, et. al See Chapter 4.1.1)
- 1967 First commercially successful hollow fiber module developed by DuPont (see Chapter 4.3.4)

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

- (See Chapter 4.3.3)
- 1971 Richter-Hoehn at DuPont patents aromatic polyamide membrane (see Chapter 4.2.2) ÷
- 1972 Cadotte develops interfacial composite membrane (See Chapter 4.2.2) <u>ن</u>ــ
- M. 1974 First commercial seawater R0 facility at Bermuda
- 1994 TriSep introduces first "low fouling" membrane (see Chapter 4.4.2.3) ż
- 0. 1995 Hydranautics introduces first 'energy saving' polyamide membrane see Chapter 4.4.2.1)
- 2002 Koch Membrane Systems introduces first 18-inch diameter MegaMagnum" module ۵.:
- 2006 Thin-film nanocomposite membrane developed at UCLA đ

improved flux, which was 10 times that of other known membrane materials at the time (such as Reid and Breton's membranes).⁵ These membranes were first cast by hand as flat sheets. Continued development in this area led to casting of tubular membranes. Figure 1.3 is a schematic of the tubular casting equipment used by Loeb and Sourirajan. Figure 1.4 shows the capped, in-floor immersion well that was used by Loeb and students and is still located in Boelter Hall at UCLA.

Following the lead of Loeb and Sourirajan, researchers in the 1960's and early 1970's made rapid progress in the development of commercially-viable RO membranes. Harry Lonsdale, U. Merten, and Robert Riley formulated the "solution-diffusion" model of mass transport through RO membranes (see Chapter 4.1).⁶ Although most membranes at the time were cellulose acetate, this model

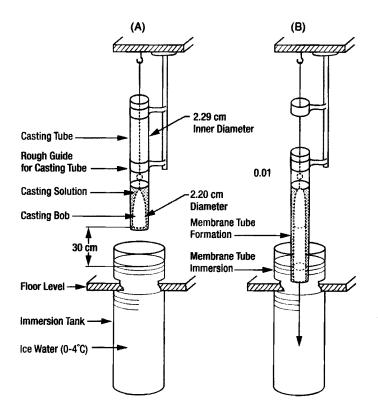


Figure 1.3 Schematic on tubular casting equipment used by Loeb. *Courtesy of Julius Glater, UCLA.*



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

represented empirical data very well, even with respect to presentday polyamide membranes.⁷ Understanding transport mechanisms was important to the development of membranes that exhibit improved performance (flux and rejection).

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

Cellulose acetate and linear aromatic polyamide membranes were the industry standard until 1972, when John Cadotte, then at North Star Research, prepared the first interfacial composite polyamide membrane.⁸ This new membrane exhibited both higher throughput and rejection of solutes at lower operating pressure than the here-to-date cellulose acetate and linear aromatic polyamide membranes. Later, Cadotte developed a fully aromatic interfacial composite membrane based on the reaction of phenylene diamine and trimesoyl chloride. This membrane became the new industry standard and is known today as FT30, and it is the basis for the majority