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## Separation & Purification Reviews

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

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**To cite this Article** Shaban, H. I.(1990) 'Reverse Osmosis Membranes for Seawater Desalination State-of-the-Art', Separation & Purification Reviews, 19: 2, 121 — 131

**To link to this Article: DOI:** 10.1080/03602549008050934

**URL:** http://dx.doi.org/10.1080/03602549008050934

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SEPARATION AND PURIFICATION METHODS, 19(2), 121-131 (1990)

# REVERSE OSMOSIS MEMBRANES
# FOR SEAWATER DESALINATION
# STATE-OF-THE-ART

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## Abstract

The field of membrane technology has developed very rapidly during the last three decades. In this study, the major technical and commercial developments that took place in the field of reverse osmosis membranes as applied to seawater desalination are investigated. A brief historical review for each membrane type is also presented.

## Introduction

Reverse Osmosis is basically a membrane diffusion process for separating dissolved substances from water or other liquids. The principal field for reverse osmosis application is the desalination of seawater (35,000 to 42,000 ppm total dissolved salts). A semipermeable membrane capable of separating salt molecules of size ranging from (0.1 to 1 nm) from water is used in the process [1].

A combination of high salt-rejection (>98%) and high water flow rates (6.93 to 9.25 micrometers/second) is desirable in a practical reverse osmosis membrane, however, difficult to achieve (the water permeability is inversely related to the salt rejection). In addition, durability, physical, chemical and biological resistance, and low cost are desirable membrane characteristics.

Many kinds of reverse osmosis membranes have been developed. In this study, membrane types that have proven successful both in the technical and commercial levels namely, asymmetric and thin film composite membranes are discussed in details. An overview of the dynamic, membranes is presented.

## Membrane Types:

### I. Asymmetric Membranes:

Early work on cellulose acetate started in the mid 1950's when Reid and Berton [2, 3] at the University of Florida, introduced - for the first time-a semipermeable membrane. They discovered that cellulose acetate was permeable to water and relatively impermeable to dissolved salts. The salt removal efficiency of these membranes was about (99%). However, these membranes were dense thick films, (~ 10 - 20 μm) to stand handling and operation at high pressure. The water flux was very low (0.06 - 0.34 micrometers/second).

The great breakthrough in the field of membrane technology occurred in the late 1950's when Loeb and Sourirajan [3, 4] prepared the asymmetric semipermeable cellulose acetate membranes. These membranes exhibited very high water fluxes, compared to Reid's type (about two orders of magnitude) and, they were of the same apparent thickness.

Loeb and Sourirajan prepared their membrane as follows:

(a) A homogeneous solution was prepared consisting of 29.2 weight% cellulose acetate (acetyl content 39.8%), 66.6 weight % acetone, 10.0 weight % water and 1.1 weight % magnesium perchlorate.

(b) The solution was cast on a glass plate as (0.2-0.5 mm) film at 0 to 10°C, and the acetone was allowed to evaporate for a period of 3-4 minutes. This step is referred to as the "evaporation" step. During the "evaporation step" the film partially hardened to a semi solid mass.

(c) The partially hardened film was then immersed into a water bath at 0°C for at least an hour. This step is generally referred to as the 'gelation' step and resulted in the solidification of the film.

(d) The solidified film was washed in streaming water for 24 hours and then, immersed into a (75-80°C) water bath for (1-2 minutes). This last step is known as the annealing step.

Riley and coworkers [5] used the electron microscope to examine the structure of Loeb-Sourirajan membranes, which were found to be consisting of a very thin skin and a porous support. The skin blends into the porous support through a region of graded porosity. The thickness of the skin is in the range of (0.15 - 0.25 μm) depending on the way the membrane is cast and the subsequent treatment. The support is a thick porous structure (> 50% void space) and contains more than (60%) by weight water [6, 7]. The desalination characteristics of the membrane is determined by the thin dense skin which is the salt rejecting layer of the membrane.

The structure and properties of solvent casting membranes, also referred to as phase inversion membranes, are influenced by the following factors [8]:

a) Rate of solvent evaporation.
b) Composition of polymer solvent mixture.
c) Composition of precipitation bath (gelation step).
d) annealing.

The structure of the membranes is determined by the choice of solvent and polymer concentration with casting solution. Different structures can be produced from the same polymer, by changing the polymer concentration or altering the solvent mixture composition. Altering the composition of the precipitation bath leads to the same structural changes. The high selectivity of the membranes is determined at the annealing stage, where the imperfections of the skin layer are closed. On the otherhand, the selectivity and permeability are determined by the polymer itself, as sorption and diffusion coefficients of the individual components of the mixture to be separated in the membrane phase are vital.

For membrane casting, it is essential for the polymer used to have a reasonable degree of solubility in some suitable solvents and such solvent soluble polymers are typically linear and can be assumed to have a cross linking density at or near zero [9]. A requirement for water transport in the active layer is the presence of hydrogen bonding groups such as hydroxyl, amino, carboxyl and amido and such highly polar groups as nitrile [10].

Asymmetric membranes are commonly cast from cellulose acetate, and polyamides and polyacrylonitrile [11]. In case of polyacrylonitrile membranes must be treated by means of cold plasma the resulting membrane must be subjected to plasma treatment [12]. The solvent casting approach has been applied successfully to produce asymmetric reverse osmosis membranes, however it has certain limitations. For some polymers it is difficult to identify suitable organic solvents. In addition, the complex procedures involved to induce the formation of a microporous structure may reduce the salt removal efficiency of the final membrane. In practice, the development of a process to manufacture membranes from a particular polymer is extremely complex, because the number of manufacturing parameters is large, and their influence on the membrane formation process is not completely understood [13].

Kitano and Co-workers [14] have found that burying a porous sheet in the gel layer of Loeb's membrane can improve the water flux without decreasing the salt rejection.

Loeb-Sourirajan cellulose acetate membranes, were the first to be used commercially for reverse osmosis separations and it is now widely used. Companies as Desal, DDS, Celanese and PCI produce asymmetric cellulose acetate membranes. They are available in various configurations as flat sheets, spirally wound sheets, tubes or hollow fibers. The main deficiencies of cellulose acetate membranes are their hydrolysis with time and susceptibility to biological degradation. Sumitomo chemical manufacture asymmetric, surface treated polyacrylonitrile membranes in spiral wound configuration. [10].

In the late 1960's, DuPont introduced another successful asymmetric membrane. The hollow fibre membrane was made from a class

Table I

Properties of Some Permsep$^{(R)}$ Permeator Product Line [17]

| Membrane | Operating Range (Tds/mg/l) | Minimum NaCl rejection (%) | Water flux (Micrometers/ sec.) | pH range | Temp range (°C) |
|---|---|---|---|---|---|
| B-9 | 150-10,000 | 90.0 | 1.16 | 4-11 | 0-40 |
| B-10 | 10,000-60,000 | 98.5 | 1.16 | 4-9 | 0-40 |
| B-15 | 200-15,000 | 95.0 - 96.0 | - | 4-11 | 0-40 |

of compounds described by Richter and Hohen [15] as "Synthetic, organic, nitrogen-linked, aromatic, substantially linear, condensation polymers". These compounds are represented by the general formula $-(LR)_n-$ where L represents linkage containing divalent nitrogen (e.g. amide, urea) and R represents divalent aromatic group. Amides, hydrazides, acylhydrazides are examples of these compounds.

Of these compounds, the aromatic polyamide was selected for the development of DuPont commercial permeators known as Permsep$^{(R)}$ [16, 17].

The finished fibers have approximately the diameter of a human hair (nominally 85 μm o.d. by 42 μm i.d.), with ultra thin skin of 0.1 to 1.0 μm supported by the porous spongy substructure [18].

Some of the Permsep(R) permeators (B-9, B-10 and B-15) alongwith their desalination characteristics are shown in Table I.

Aromatic polamide hollow fiber membranes possess two main advantages; durability and high surface-to-volume ratio [19-21]. On the other hand, the aromatic permeators have very little tolerance for the presence of free chlorine [13].

## II. Thin Film Composite Membranes:

In 1965, experimental work on thin film composite membranes started [22]. Cellulose acetate was first considered to form the thin dense film, but later a series of nitrogen containing aromatic backbone polymers were used. These polymers exhibit water and salt permeability characteristics, along with biological and chemical properties, better than those of cellulose acetates.

Cadotte and Riley [5] independently, developed the preparation technique of the thin film composite membranes. This technique is based on the work of P.W. Morgan [23] on the chemistry of interfacial polymerization.

Cadotte [24] developed a nonpolysaccharide membrane for single stage sea water desalination. The membrane, designated NS-1, was formed *in-situ* onto a microporous support material.

Cadotte also [9] reported that reverse osmosis membranes with excellent characteristics are obtained from cross linked interfacially polymerized aromatic polyamides, where a porous support layer is coated with polyamine component (as aqueous solution of phenylene diamine) and the coated support is contacted with the polyacylhalide component (as trimesoyl chloride). An interfacial polymerization *in-situ* on the support is initiated. When the resulting product is dried a composite membrane comprising of polyamide laminated to the porous support is obtained.

Riley and Co-workers [25, 26] reported that thin film composite membranes designated RC-100 and PA-300 were formed by an *in-situ* interfacial polymerization technique. A thin layer of an aqueous solution of an epichlorohydrin-ethylene diamine condensate on the finely porous surface of the support and subsequently contacting the poly(ether/amine) layer with a water immiscible solution of diisocyanate to prepare the RC-100 and a diacid chloride to prepare the PA-300. Subsequently membranes are dried at elevated temperatures.

The support can be fabricated from various types of polymers to form a microporous support having high water permeability characteristics and resistance to compaction under pressure. Polysulfone is widely used as a microporous support where it is cast directly on a backing material-usually made from woven or nonwoven polyester fabrics with a thickness of about 50 μm, and having an asymmetric pore structure, where the coarse pores-fraction of micrometer in size - face the backing material and the fine pores-about 300°A-is bonded to the thin dense film [7]. The active layer of the composite membrane is formed *in-situ* onto the top of the microporous support by one of the following methods [11,12]:

(a) immersion of the support layer in polymer solution (e.g. PEC-1000).
(b) spraying the casting solution onto the support layer.
(c) cross linking surface polymerization.
(d) interfacial cross-linking reactions (e.g. NS-100, PA-300, RC-100, FT-30).

The physical stability of this type of membrane is strong, since the skin is bonded chemically to the support. The desalting layer can be formed independently from the support which provides an advantage over the asymmetric membranes.

Many groups in USA, Europe and Japan have commercially introduced the thin film composite membranes for seawater desalination utilizing reverse osmosis. Some of these along with desalination properties are shown in Table II.

UOP introduced commercially, the first composite membrane for reverse osmosis PA-300 in 1977 [10]. The support layer is made from polysulphone and the desalting layer is a polyamide formed *in-situ* on the top of the polysulphone support. The PA-300 is produced in the form of spiral elements. It possesses excellent characteristics as shown in Table 2, but it is extremely sensitive to the presence of free chlorine.

The FT-30 membrane developed by Cadotte and Co-workers and manufactured by Film Tec outperforms the conventional Loeb-Sourirajan cellulose acetate membrane in reverse osmosis by about 2 to 1 in water flux under comparable operating conditions of temperature, pressure and feed water salinity. It also, exhibits high salt rejection, making single-pass seawater desalination possible. In addition, FT-30 has some tolerance to free chlorine and stable performance has been observed for feeds containing upto 0.2 ppm chlorine [13].

The Toray PEC-1000 exhibits lower flux than FT-30 but its organic removal efficiency is higher-reported to be 97% for ethanol [13].

Table II

Properties of Thin Film Composite Seawater Reverse Osmosis Membranes for Seawater Desalination [7,8,13]

| Membrane(1)(2) | Manufacturer | NaCl refjection (%) | Water flux (micrometer/ sec.) |
|---|---|---|---|
| FT-30 (Polyamide) | Film Tec | 98.06 | 11.56 |
| PA-300 (Polyamide) | UOP | 91.35 | 9.25 |
| PEC-1000 (Polyether) | Toray | 99.48 | 4.62 |
| NTR-7197 | Nitto | 93.29 | - |

(1)The configuration used is test cell

(2)Test conditions: 56 bar, 3.5% NaCl and 25°C

## III. Dynamic Membranes:

A different type of membrane, discovered by Marcinkowsky and Co-workers [27] called dynamic membrane is formed, when colloidal particles in aqueous solution are passed under pressure across the surface of a finely porous solid. The colloidal particles forms some kind of a gel membrane which is highly hydrophilic and permeable.

The great advantage of this type of membrane is their suitability for high temperature applications. However, they are not adequate for practical desalination application since they are not stable and do not possess high salt-rejection ability. In addition, the water flux declines considerably with time. Now, two U.S.A. firms manufacture and market dynamic reverse osmosis systems for dye effluent treatment and sizeing materials in textile industry [5].

## Conclusion:

The developments that took place in the field of membrane technology over the past three decades is tremendous. The technology has developed from a laboratory scale work to an industry of great technical and commercial importance.

The asymmetric cellulose acetate membranes have dominated the reverse osmosis membrane market over the past twenty years, however the reverse osmosis membrane industry as a whole is moving now towards the composite membranes, which exhibit excellent desalination characteristics. The main drawback of the composite membrane is their sensitivity to the presence of free chlorine.

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