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The early history of reverse osmosis membrane development

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Abstract

The birth of pressure driven membrane desalination took place nearly 100 years ago. Early developments in this technology remain shrouded in some mystery, especially with respect to application of the osmotic phenomenon to desalination. Existing literature is also somewhat confused regarding first usage of the term "reverse osmosis". A comprehensive review of early literature is presented in this paper in an effort to resolve some of these interesting questions. The unique feature of this review, as contrasted to several others, is inclusion of previously unpublished reports and experimental data. These documents, dating back to 1950, will reveal surprising insights into the origin of present-day technology now known as reverse osmosis.

Keywords: History; Membranes; Reverse osmosis; Ultrafiltration

1. Introduction

Membrane science and technology have indeed "come of age". "When one inserts the word *membrane* in a search of *Chemical Abstracts* for the past 10 years, the result is over 100,000 hits." This quote taken from a 1995 paper by Humphrey [1] clearly demonstrates the rate at which this technological area has expanded over the past few decades. I would venture to guess that several thousand more citations could be generated since the appearance of this publication. Growth in the membrane field is closely tied in with developments in polymer science, which occurred at a rapid pace following World War II.

In addition to desalination, recent applications of membrane science in areas such as biochemistry, microbiology, industrial separations and environmental protection, to mention just a few, have also been expanding rapidly. The historical development presented in this paper will

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not attempt to review overall progress in membrane science. Numerous reviews, including the seminal paper by Lonsdale [2], have been presented elsewhere. Textbooks in the area of synthetic membranes with emphasis on desalination, beginning with the classic text by Merten [3], did not appear until the mid-1960s. More than a dozen texts in this field have subsequently been published. Journals accepting contributions in membrane science are also relatively new. *The Journal of Applied Polymer Science* first appeared in 1959, followed by *Desalination* in 1965 and more recently, *The Journal of Membrane Science* in 1976.

The following discussions will begin with early development and application of pressure driven membrane processes, ultimately leading to a membrane suitable for separation of electrolytes from aqueous solutions. This process, now known as reverse osmosis, provides the most promising technology for desalination of natural waters. A unique feature of this paper is the inclusion of information from previously unpublished reports, which, in the judgment of the author, played an integral part in development of reverse osmosis (RO) technology. Due to the vast amount of literature, it is not the author's intent to exhaustively cover all references in this rapidly developing field. Instead, this effort will focus on those "key events" which have shaped the technology as we know it today.

2. Early history of ultrafiltration

Two hundred fifty years have passed since the osmotic phenomenon was first observed by the French Cleric, Abbé Nollet [4] in 1748. During the following century, osmosis was of especial interest to practitioners in the biological and medical sciences. Experimental work was conducted primarily with membranes of animal and plant origin. It was not until 1867 that the first inorganic semi-permeable membrane was prepared by Traube [5]. This gelatinous film of copper ferrocyanide supported on a porous clay frit displayed remarkable selectivity to dilute solutions of electrolytes.

Development of this truly semi-permeable synthetic membrane attracted the attention of physical chemists during the latter third of the 19th century. The phenomenon of osmotic pressure was of especial interest and added to the list of colligative properties under investigation at that time. The extreme sensitivity of this measurement and its simulation of gas behavior provided an incentive for numerous investigators. A variety of techniques for measurement of osmotic pressure were developed during that period. The unique nature of this phenomenon generated an interest among theoretical as well as experimental investigators. Quantitative relationships, including the classic studies by van't Hoff [6] in 1887 rapidly followed.

In the course of this literature search, I have made an effort to determine the first application of pressure driven membrane processes. Development of this technology seems especially important since utilization of pressure as a driving force was a forerunner of what is known today as RO. In 1855, Fick [7] worked on dialysis of solutions through artificial membranes formed from collodion. This technique was also used by Graham [8] for isolation of bacteria and separation of "colloids from crystalloids". Graham is also credited with first use of the term dialysis to describe the selective diffusion process across semi-permeable membranes. It was not until the end of the 19th century, however, that references to pressure driven filtration appeared in the literature.

The most carefully documented use of pressure as a driving force for membrane filtration was published in 1907 by Bechold [9]. These "ultrafiltration" (UF) studies were carried out by forcing solutions at pressures up to several atmospheres through membranes prepared by impregnating filter paper with acetic acid collodion. Bechold

was successful in developing membranes with graded porosities and designing the first ultrafilter. He is also credited with coining the term "ultrafiltration". A most impressive in-depth review of early studies on UF theory and applications by Ferry [10] includes published works up to 1934

Prior to the 1930s, very few polymeric materials were known. With the exception of bakelite, developed in 1906, all of the available plastics and films were derived from the natural product, cellulose. They consisted of celluloid, collodion, cellophane and rayon. These materials were derived from cellulose nitrate, cellulose acetate or regenerated cellulose. Modern polymer science did not begin to emerge until 1937 when nylon, the first synthetic polyamide, was developed by Carothers [11]. The high-performance RO and nanofiltration (NF) membranes in production today are primarily condensation polymers whose origin began with the first synthesis of nylon. I have presented this very brief history of polymeric materials since early development of semi-permeable membranes was focused primarily on derivatives of cellulose.

3. Hassler's reverse osmosis system

Following the close of World War II, population growth in California was increasing rapidly and this semi-arid region was facing diminishing supplies of fresh water. During this period, "saline water conversion" was a high-priority research area in the United States and especially at the University of California. In 1952, the US Department of Interior established The Office of Saline Water which launched a comprehensive desalination research and development program. Even before this Federal program emerged, the University of California was actively involved in desalination. A UCLA report by Hassler [12] in 1949 marked the beginning of membrane research at the university. In this report, entitled *The Sea as a Source of Fresh Water*, Hassler mentions the possibility of vapor transfer through sheets of cellophane.

In a subsequent report [13], Hassler describes "salt repelling osmotic membranes" and "permselective films". I believe that this historic unpublished document, dated August, 1950, introduces the first concept of membrane desalination. Original ideas presented in this work draw from the literature of cell physiology and physical chemistry. Hassler proposed a synthetic multilayer film (Fig. 1), which would simulate cellular membranes involved in biological water transport. This type of film never became a reality. Instead, his experimental plan involving an air film bounded by cellophane membranes was designed and later carried out. The remainder of this report was concerned with thermodynamic arguments favoring membrane processes over conventional distillation concepts available at that time.

By 1954, equipment had been constructed for the experimental verification of "Hassler's reverse osmosis principle". Design of this system was based on a device for osmotic pressure measurements by Townsend [14] in which a porous plate separated solution from solvent. According to this concept, the very thin layer at the solution surface was assumed to be a "perfect" semi-permeable membrane. Hassler proposed the use of two membranes separated by an air gap and assumed that osmosis takes place via evaporation at one membrane surface and passage through the membrane as vapor. This was followed by condensation on the opposing membrane surface and transport of solvent through this film. According to this mechanism, the narrow air gap or vapor space would function as a semipermeable membrane.

Work on the narrow gap membrane project continued at UCLA for approximately 5 years. Progress was marked by refinements in equipment design and theoretical studies on liquid and vapor transport. These studies are documented in UCLA Department of Engineering reports [15–17] and in a later publication by Hassler and McCutchan

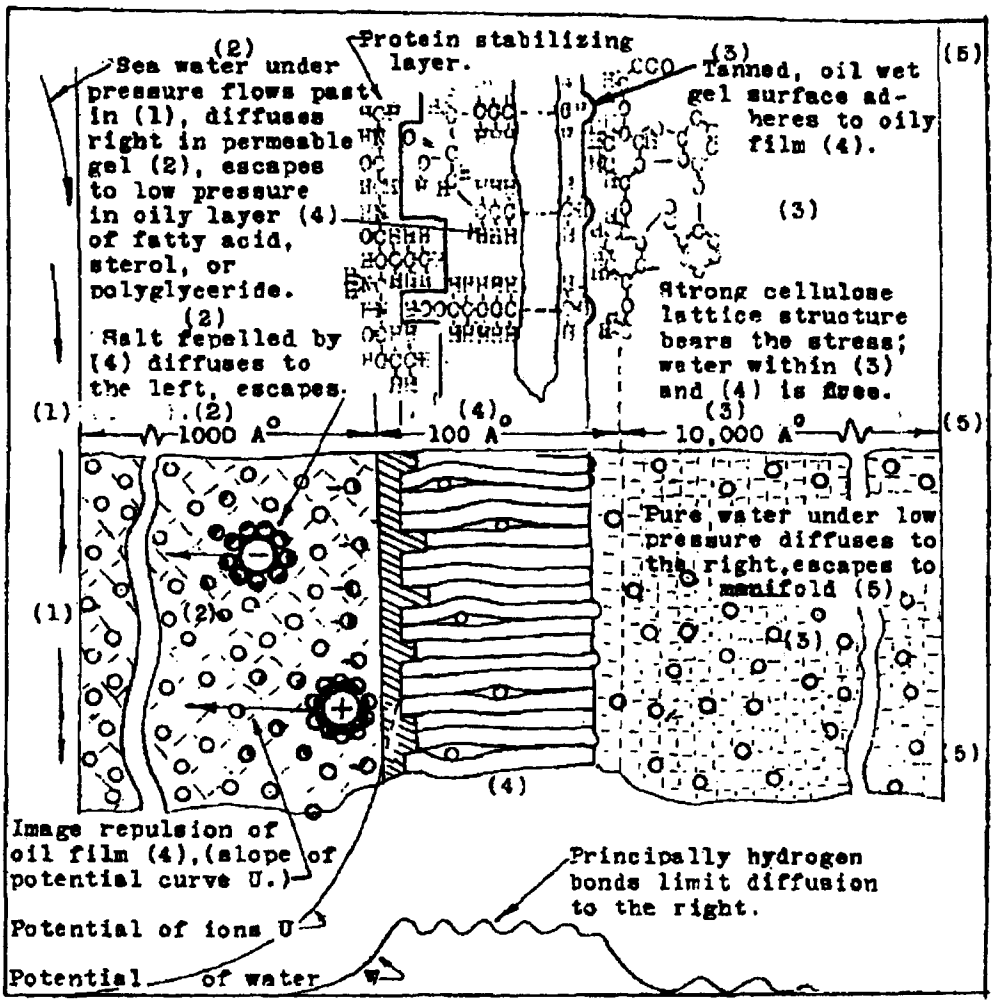

Fig. 1. Oriented molecular oil film.

[18]. The initial design (Fig. 2) consisted of two porous ceramic plates separated by a very narrow adjustable air gap varying in thickness between 10 to 25 microns. The porous plate model was limited by the "bubbling pressure" of the ceramic plate and could not operate at pressures above approximately four atmospheres. In order to desalt seawater or concentrated solutions with higher osmotic pressures, both evaporating and condensing surfaces were covered with cellophane sheets. This material was chosen because of its very high bubbling pressure which enabled the system to operate at pressures in excess of fifty atmospheres.

Initially, the entire assembly was enclosed in a pressure vessel with a primitive wick-siphon system (Fig. 3) designed to provide saline water flow over the cellophane evaporating surface. Small volumes of fresh water were obtained with this apparatus and product water flux was found to be inversely related to air gap thickness. With seawater at a pressure of 1000 PSI, flux values of approximately 0.2 GFD were obtained. The next phase of this project involved design of a special pressure vessel (Fig. 4) to house the membrane unit and development of the pilot plant assembly shown in Fig. 5.

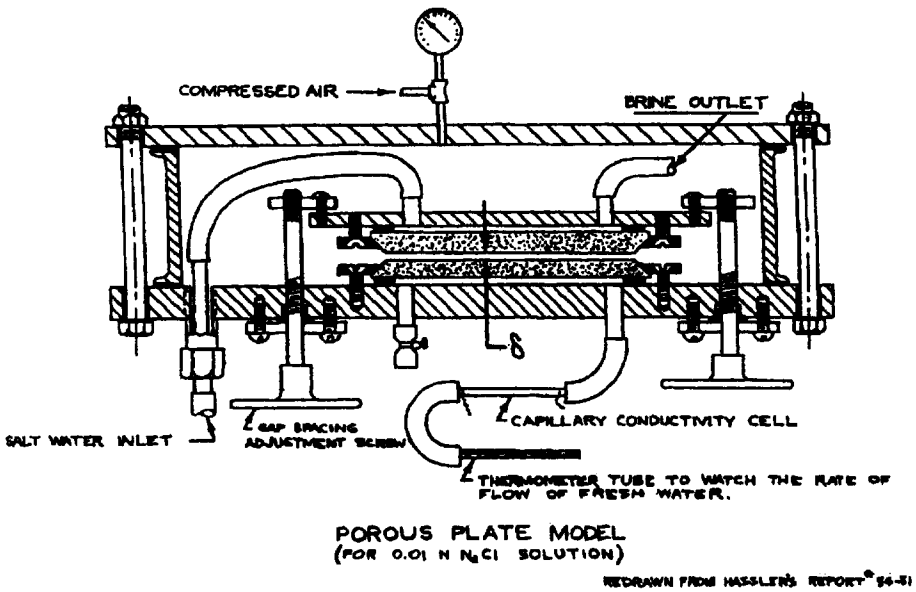

Fig. 2. Porous plate air gap apparatus.

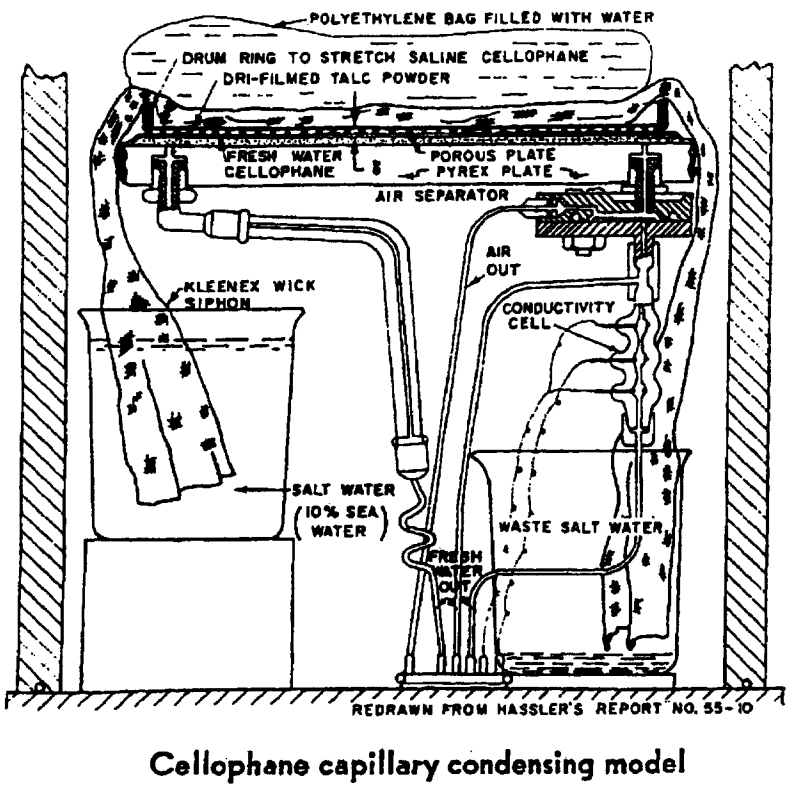

Fig. 3. Wick-syphon system.

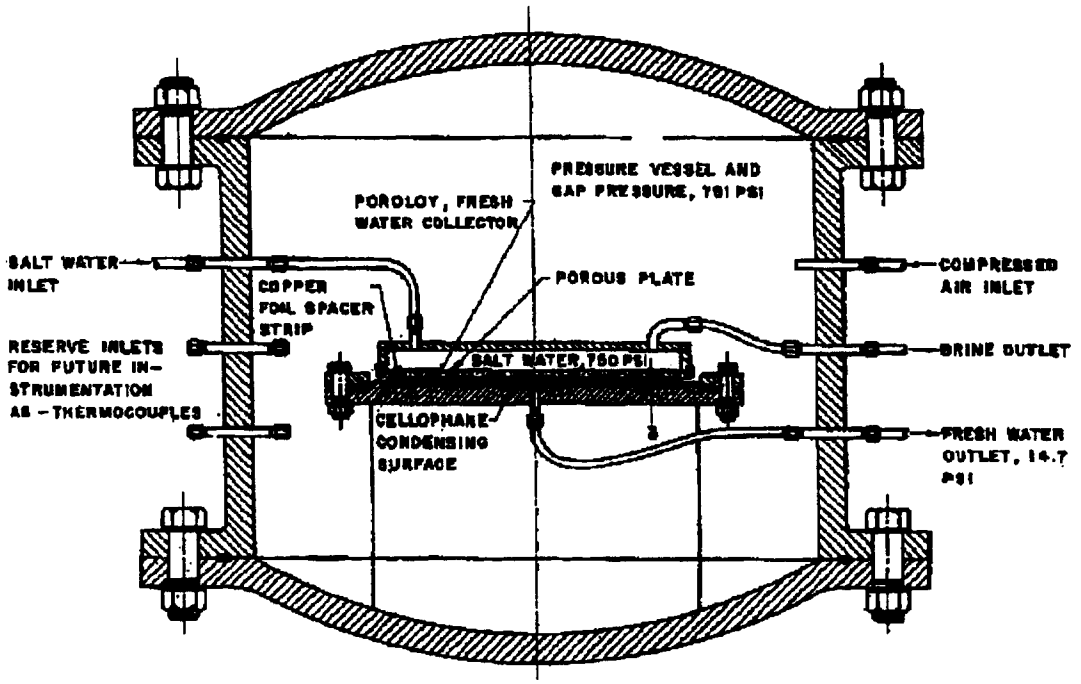

Fig. 4. Pressure vessel assembly.

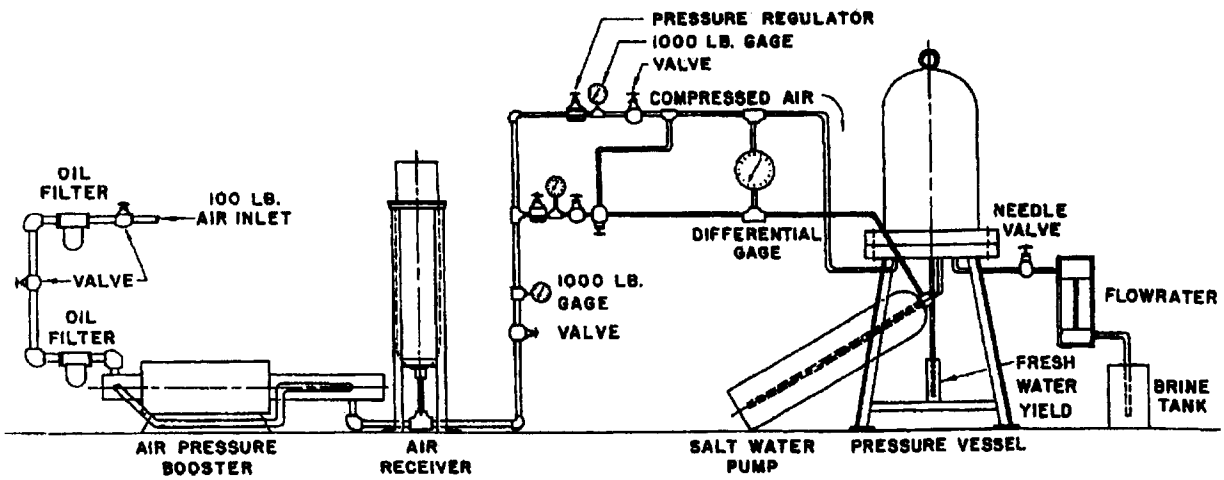

Fig. 5. Pilot plant desalination system.

High yields of product water were never accomplished by this technology, and the project was finally abandoned about 1960. Despite disappointing results, this research effort "set the stage" for further work on RO. Prior to this time, studies on UF and dialysis were primarily of interest to chemists and biologists. Gerald Hassler was indeed a visionary and, in my judgment, one

of the unsung heroes leading the way to development of present-day membrane desalination.

4. Contributions of Reid and Breton

Beginning about 1955 Professor Charles Reid, at the University of Florida, proposed a study entitled *Osmotic Membranes for Demineralization of Saline Water*. This effort, supported by The Office of Saline Water, also involved application of pressure to reverse the normal osmotic tendency through a variety of polymeric materials. Unlike the Hassler narrow air gap concept, apparatus designed for this study was similar to UF equipment described at that time. This RO system, shown in Fig. 6, was driven by compressed air and the feed solution was stirred convectively.

Several publications arising from this work [19–21] provide experimental details on the performance of a variety of commercial polymeric films available in the 1950s. The most promising of these membrane materials was cellulose acetate which displayed very high salt rejection but disappointing levels of product water flux. Techniques were also developed for preparation of hand-cast ultra-thin membranes from acetone solutions of cellulose acetate. At pressures up to 850 psi, salt rejection values of approximately 98% were reported with 0.10M sodium chloride. Product water flux was inversely related to membrane thickness, but even the very thin films (less than 10 microns) provided such small product water volumes that flux levels were reported in units of $\mu L/cm^2$ h.

Reid and Breton [21] also proposed an interesting mechanism for membrane transport. It was postulated that passage of water took place via hydrogen bonding to carbonyl oxygens in cellulose acetate thereby filling membrane voids with bound water. Ions and molecules, not capable of hydrogen bonding, could then pass through the membrane by "hole type diffusion" only. Resistance to ion transport would occur when such

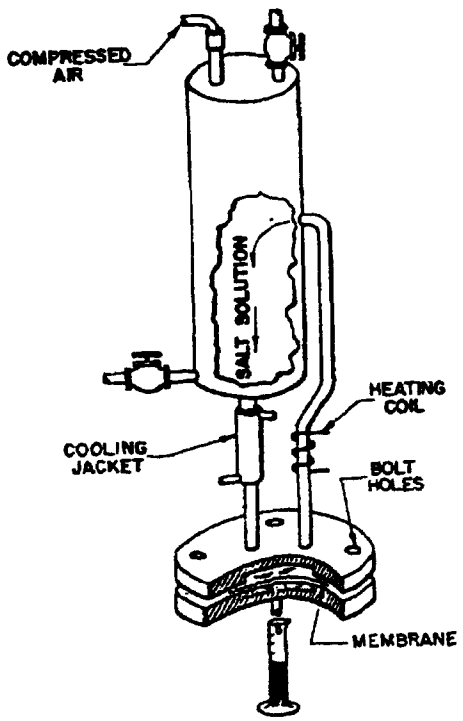

Fig. 6. Apparatus for determining the semi-permeability of imperfect osmotic membranes. (From Reid and Breton [21]).

holes became filled with bound water. These postulates are indeed innovative and among the first proposed models for membrane permselectivity. In an effort to support these ideas, cellulose acetate membrane samples were subjected to a variety of physical measurements including electrical resistance and dielectric constant.

Despite performance limitations of membranes tested, the Florida work provided an experimental and theoretical framework for the next "chapter" in the on-going search for a practical and economical method of membrane desalination. These studies represent a superb application of physical chemistry to the osmotic phenomenon and to the properties of polymeric materials. It seems quite remarkable that two research groups working on membrane desalination on opposite sides of the United States were completely unaware of each

other's contributions until November 1957. At that time, Professor Reid was invited to make a presentation at a Saline Water Symposium sponsored by the United States National Academy of Sciences–National Research Council [20]. This conference was attended by Gerald Hassler and Joseph McCutchan of UCLA.

Over the years this author has been most curious regarding origin of the term "reverse osmosis". I believe that first usage of this term appeared in a UCLA Engineering Report [15] dated August 1956 and should be credited to Gerald Hassler. It is also worth noting that RO was mentioned in the Office of Saline Water R&D Progress Report [19] dated April 1957 which was generated by the Florida research group. Initial usage of this term is still not completely clear since each research group was working independently. I expect, however, that it was coined by a physical chemist since the concept of reversibility is a cornerstone of chemical and engineering thermodynamics. Both Gerald Hassler and Charles Reid were trained in physical chemistry.

5. The Loeb-Sourirajan membrane

In 1958 two desalination projects at UCLA were still in progress. One involved Hassler's work on the narrow gap osmotic process. The other, under the direction of Professor Samuel Yuster, was exploring the possibility of skimming the monomolecular surface layer of fresh water at the air interface of saline water solutions. Although theoretically possible, "surface skimming" in the laboratory with fine capillaries or bubble generation met with little success. At that time a new approach was attempted. This consisted of pressurizing the solution directly against a flat plastic film. Small quantities of fresh water resulted from this experiment. In the summer of 1958, Sidney Loeb joined the Yuster group working jointly with S. Sourirajan who was already involved in this project. It seems quite remarkable that neither of these researchers was aware, at that time, of publications by Reid and Breton.

Resulting from this discovery, Loeb and Sourirajan were motivated to develop a membrane capable of providing practical levels of water flux while maintaining high levels of salt rejection. Early efforts were directed toward modification of commercial cellulose acetate UF membranes marketed by Schleicher & Schuell. Results obtained with these films showed some promise, but performance was still inadequate for economical water production. Among the findings from this effort, it was learned that membranes must be stored in water and that performance alteration could be achieved by heat treatment. The most significant discovery, however, was the fact that these films were asymmetric. By trial and error, it was found that one side of the membrane provided an active desalination layer. Salt rejection resulted only when feed solution contacted this layer.

In an effort to significantly improve performance, Loeb and Sourirajan decided to hand-cast membranes from cellulose acetate polymers obtained from Eastman Chemical Products. Polymer samples differed in degree of acetylation and polymer chain length. Casting solutions were then prepared by dissolving polymer samples in acetone and evenly spreading the resulting viscous material on a glass plate by use of a doctor blade. The resulting film was first air dried for a brief period followed by immersion in ice water. A unique feature of this casting solution was the addition of aqueous magnesium perchlorate which evidently acted as a swelling agent or pore former. These hand-cast membranes were chemically homogeneous but physically asymmetric. The dense active layer formed on the side exposed to air and was supported by an underlying porous substrate. This structure was later confirmed by electron microscopy [22]. An early desalination cell and solution circulation system are displayed in Figs. 7 and 8.

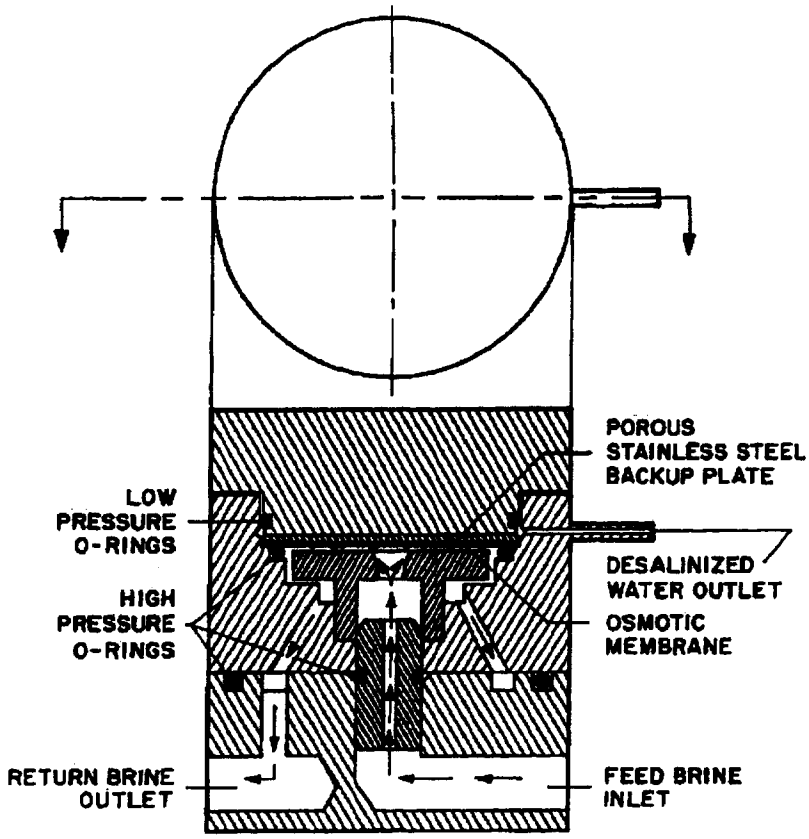

Fig. 7. Early UCLA desalination cell.

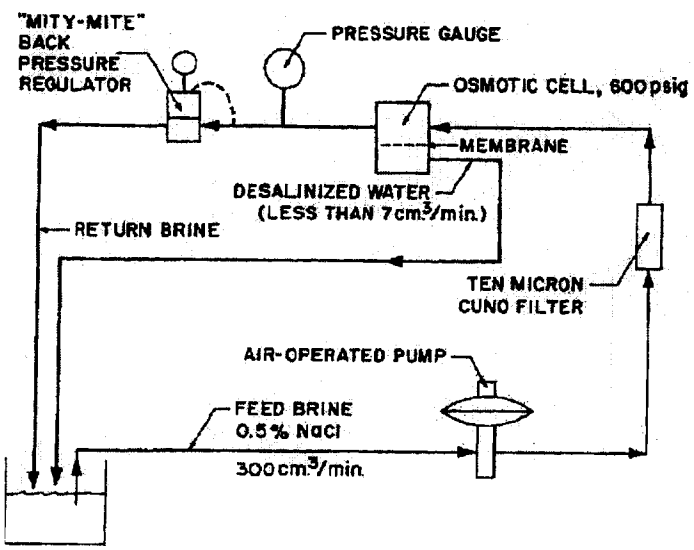

Fig. 8. Early UCLA pressurized desalination flow system

Months of painstaking effort resulted in the first practical RO membrane which, according to Loeb and Sourirajan [23] and Loeb [24], provided performance levels an order of magnitude greater than the modified Schleicher and Schuell products. This breakthrough heralded production of a membrane with promise of application to economical desalination. In 1980, Loeb and Sourirajan were honored at a special American Chemical Society symposium marking the 20th anniversary of this important discovery. In his plenary lecture, Sidney Loeb [25], in a very personal way, recounted the story of "How it Came About".

Research in membrane casting solution optimization continued at UCLA in an effort to develop an all-organic formulation. The major change reported by Manjikian [26] involved the use of formamide ($HCONH_2$) as a swelling agent in place of magnesium perchlorate. Reproducible membrane fabrication could then be easily accomplished with this completely organic casting solution. A ternary diagram for membrane optimization is shown in Fig. 9. This author is not completely clear about the source of information leading to the use of formamide. A wide variety of other organic compounds as swelling agents for cellulose acetate is presently employed by commercial membrane manufacturers.

Progress in membrane science and technology at UCLA did not end with development of the first practical RO membrane. This discovery was followed by novel innovations in hardware and pilot plant design. Contributions involved a multistage 16" plate-and-frame configuration [27] and development of methods for casting tubular membranes [28]. The most significant event resulting from early work was establishment of the first commercial membrane desalination plant at Coalinga, California. This historic facility [29] provided 5,000 gal/d of additional drinking water needed to augment diminishing water supplies for this small mountain community. A review of early

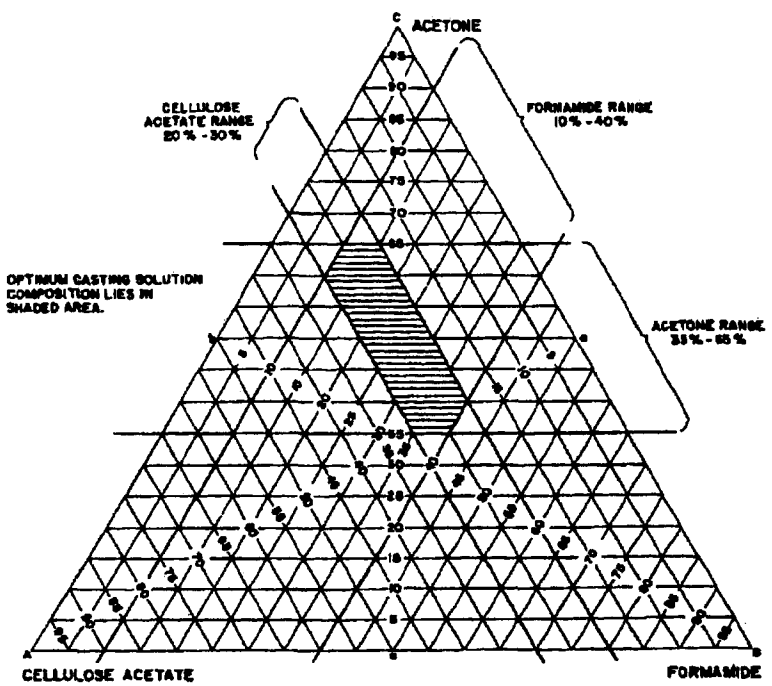

Fig. 9. Organic casting solution optimization.

pilot plant studies at UCLA is presented by Glater [30] and Sieveka [31].

6. Early industrial developments

By 1961, the Loeb-Sourirajan membrane entered the public domain via patents, publications and technical presentations. The potential for development of low-cost desalination equipment aroused the interest of several industrial firms in southern California. Havens Industries, a manufacturer of fiberglass products, was the first company to apply the new technology. A method was developed for casting membranes on the inside wall of cylindrical un-cured fiberglass tubes (Fig. 10). In this novel desalination system, marketed as "osmotic processing" [32], tubes served the dual role of membrane support and pressure vessel. This tubular casting method, later modified by Loeb [33] and shown in Fig. 11, provided the design concept from which the Coalinga desalination plant was constructed.

Another industry to become involved in membrane desalination during the early 1960s was the Aerojet-General Corporation. A 14" multistage plate-and-frame unit fitted with flat sheet Loeb-Sourirajan membranes was put into operation. The initial design [34], followed by additional modified units, provided pilot plant operation at seawater and brackish water sites. These efforts represent the first industrial on-site performance data with the newly developed desalination membranes. Some studies on membrane modification and feed water additives were also reported by the Aerojet group. This project was relatively short-lived, however, and finally abandoned due to unfavorable economic projections, especially for seawater.

The next, and most significant, industrial development took place in San Diego at the General Atomics Company. This firm, known today as Fluid Systems, remains actively engaged in the business of membrane manufacturing. The "climate" at General Atomics during the 1960s was geared to innovative research, and the

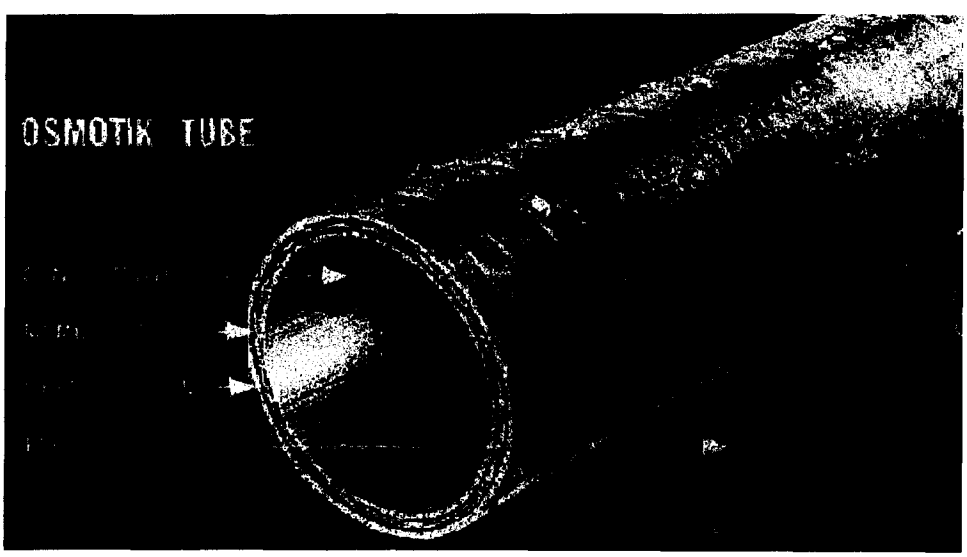

Fig. 10. Fiberglass tubular concept (after Havens).

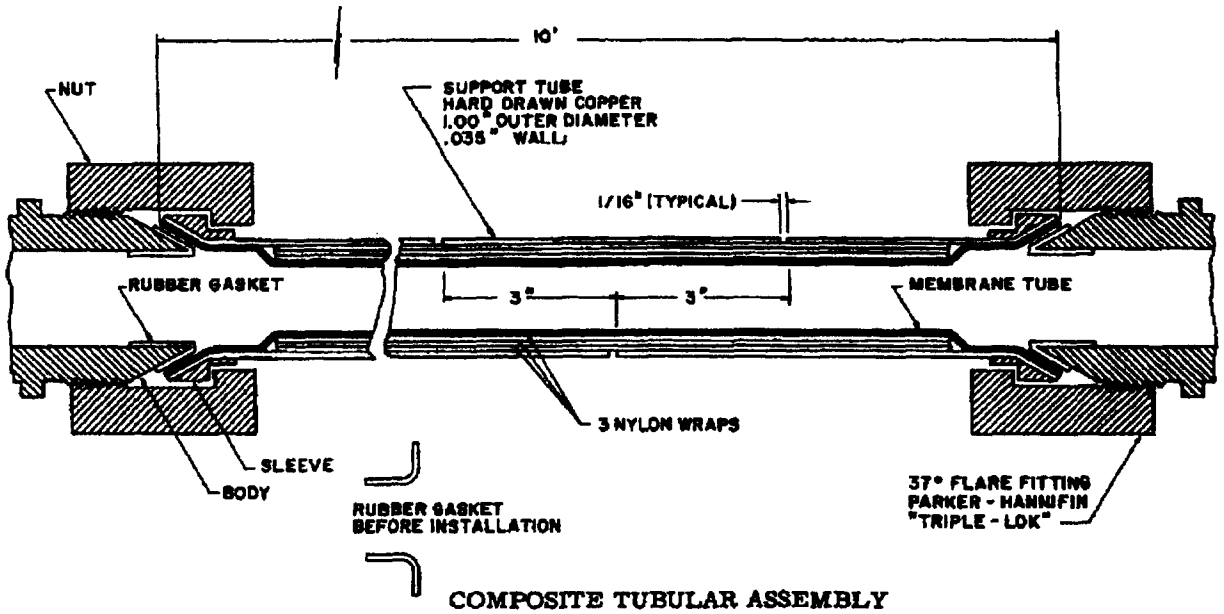

Fig. 11. Composite tubular assembly.

possible commercial membrane desalination whetted the appetites of several young investigators. Theoretical and practical contributions by Merten, Riley, Lonsdale and Bray are succinctly reviewed by Lonsdale [2]. These studies were concerned with structure, equilibria and transport properties of the "new" Loeb-Sourirajan membrane. Fundamental relationships derived by this group continue to be useful to practitioners in membrane science. Also included in developments arising from this period is the now familiar spiral-wound membrane module invented by Bray [35].

By the mid-1960s, two major chemical companies, Dow Chemical and DuPont, recognized the potential for large-scale membrane desalination. Both firms embarked in R&D efforts which resulted in development of hollow fiber desalination modules. The Dow concept involved cellulose acetate fibers [36] while DuPont focused on polyamides. Initial work on aliphatics was followed by development of successful aromatic polyamide hollow fibers [37]. Both Dow and DuPont are actively engaged in membrane desalination; however, the hollow fiber "Permasep" process developed by DuPont is capable of the very high salt rejection necessary for one-pass seawater desalination.

Since this paper is dedicated to "early history" only, this author did not plan to review developments beyond the 1960s. Hopefully one of my successors, in the future, will document the many important contributions which have followed such an incredible period of discovery. Surely, all of us in this dynamic field of membrane desalination should be indebted to the early investigators who "opened the door" to this remarkable advancement in technology.

Acknowledgments

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