1

History of Nanofiltration Membranes from 1960 to 1990

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1.1 Overview

This chapter describes the developments in nanofiltration (NF) membranes from the 1960s to the early 1990s that brought NF technology to its current status. NF began as a spin-off of reverse osmosis (RO) and ultrafiltration (UF) and was thus originally known as open RO, loose RO, or tight UF. The origin of NF membranes – and indeed of most pressure-driven membranes – can be traced back to the late 1950s and the development of the Loeb–Sourirajan (L–S) anisotropic or asymmetric cellulose acetate (CA) membranes for seawater desalination. These membranes constituted the basis for modern membrane development in RO and UF. Within a few years, RO composites comprising a submicron coating of a selective film on an asymmetric UF support were developed. Progress in RO and UF technology gave birth to yet another discipline – NF. This R&D effort spanned a remarkably short period of time of about 15 years, starting in 1960. In addition, by the early 1970s, a full range of CA asymmetric (or anisotropic) membranes spanning the entire spectrum, from RO through NF to UF, were available. In the search for improved water treatment economics and for other commercial applications, the limitations of CA as a membrane material were, however, quickly revealed. These limitations restricted the range of applications and impeded efforts to expand NF into new areas. One approach to overcoming this problem was the development of integrally skinned asymmetric membranes from materials other than CA, such as polyamides, polyethersulfone (PES), polysulfones, chlorinated polyvinyl chloride (PVC), and polvinylidene fluoride (PVDF). Although open NF membranes could be made by this approach, the selectivity/flux combination needed for many applications could not be achieved. The breakthrough in NF took place with the invention of noncellulosic composites based on coating UF supports with a submicron selective barrier by various methods such as interfacial polymerization. The work on composites started in the 1970s, but composite NF membranes were not widely available until the second half of the 1980s. Another approach, which followed later, was

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the development of NF ceramic and inorganic membranes. Today, NF has the power to solve many separation problems, but such actual applications are small in number compared to the potential applications that still await improvements in membrane stability, flux, and selectivity. Ongoing developments in NF membrane preparation and materials are described in Chapter 2.

1.2 Introduction

Typically, separations of monovalent and divalent salts and organic solutes of molecular weights up to 1000 characterize membrane selectivity between the RO and UF regions. The range of membrane separation characteristics that are covered by this definition are currently known as NF. This term was not coined until the second half of 1980s, but in reality, such membranes already existed in the 1960s, being categorized as open RO, loose RO, intermediate RO/UF, selective RO, or tight UF membranes.

The beginnings of NF are intertwined with the early days of RO, which are vividly described by Loeb in his "Reminiscences and Recollections" [1]. Production of potable water from saline solutions was first demonstrated by Reid and Breton [2], working with Breton, at the University of Florida. They accomplished desalination at a low flux with a cellulose acetate (CA) membrane. The desalination program at UCLA arrived at the use of commercially available CA membranes from a different starting point: they had been looking for the manifestation of the negative salt adsorption near the water/air interface predicted by the Gibbs equation. In 1959, Loeb and Sourirajan experimented with porous CA membranes obtained from Schleicher and Schuell (S&S), which after being heated under water acted as desalination membranes only if installed in the experimentally determined "right direction." Loeb considered this behavior as "…the seminal feature leading to the success of RO desalination and (to the) surge of interest in…membrane separation processes." The big step forward was the dramatic increase in desalination flux with the development of the Loeb–Sourirajan (L–S) membranes. They developed casting solutions resulting in anisotropic RO membranes with fluxes 10 times higher than those of the S&S membranes, with equivalent desalination. This development was based on the 1936 work of Dobry, who cast CA membranes from an aqueous, saturated solution of magnesium perchlorate [3]. The mechanism of membrane formation was later termed by Kesting as phase inversion [4]. It was shown by the electron micrograph studies of Riley et al. [5, 6] that such membranes consisted of a thin (less than 1-μm) layer on top of a much thicker porous sublayer.

The degree of desalting obtained with CA membranes depended on the conditions of heat treatment used to anneal and further densify the top dense layer. It was realized that the limited rejection observed with partial annealing could be exploited in various applications, later to be called NF.

In the early 1970s, CA and other cellulose esters were the standard materials used for making NF membranes, but it rapidly became evident that their lack of chemical and biological stability severely limited the range of water and industrial applications. Thus, developments after 1975 concentrated on other materials and other membrane fabrication processes, resulting in a second generation of membranes based on noncellulosic NF composites.

In the second half of the 1980s, improvements in the stability, selectivity, and flux of NF membranes were reflected in a growing number of applications. NF was then being accepted as a useful unit operation for the water treatment, dairy, and chemical industries. At that time, the term nanofiltration (NF) was introduced by FilmTec; it was derived from the membrane's selectivity toward noncharged solutes of approximately 10 Å or 1 nm cutoff.

Today, NF membranes are produced in spiral wound, plate and frame, hollow fiber, capillary, and tubular configurations from a range of materials, including cellulose derivatives, synthetic polymers, inorganic materials, and organic/inorganic hybrids. A short history of the developments that have brought us to the present state of art follows. Emphasis is placed on membrane materials, chemistry, and separation mechanisms, with implicit, but full, recognition of the developments in module design and membrane fabrication and applications that have made commercial NF possible.

1.3 First-Generation NF Membranes

Remarkably, in the early 1970s, a whole range of membranes including what we now call NF were commercially available. A list of such commercially available membranes taken from a 1972 review chapter by Lonsdale [7] is given in Table 1.1, covering a range of selectivity between RO and UF. As implied by the Table and article, NF membranes were not a distinct group but rather classified as either open RO or tight UF. In addition, the membranes were either asymmetric (anisotropic) or symmetric (isotropic), and the RO or NF membranes were either based on cellulose or polyelectrolyte complex membranes.

1.3.1 Cellulose Acetate Asymmetric Membranes

The 1964 U.S. patent of Loeb and Sourirajan describes in addition to membranes with 95+% rejection, open RO membranes with rejections in the range of 20–80% [8]. As pointed out in these patents and others, a wide range of open RO selectivities could be achieved by variation of casting solution composition, evaporation period, and annealing (Table 1.2) [9]. Subsequently, other workers also found that, by incorporating additives into the casting solution, CA membranes could be formed over a wide range of molecular weight cutoffs (MWCOs) that extended from tight RO up to UF, including the intermediate NF range [7]. For example, Cohen and Loeb [10] showed how CA membranes could be cast and modified by heat treatment to form either membranes that retain sucrose and multivalent ions with sodium chloride passage or membranes that pass sucrose but retain multivalent inorganic or organic ions. A transmission electron micrograph of a Loeb–Sourirajan asymmetric cellulose acetate membrane shows the characteristic integrally skinned layered upper surface on a porous support

Table 1.1 Commercially available loose RO (NF) membranes in 1973.

Membrane:	**Manufacturer**	**Chemical**	**Net pressure**	**Water flux**	**Solute**	**Rejection**
Type		composition	psi	l/m^2 d		%
Loeb–Sourirajan: anisotropic, unannealed	Several	Cellulose acetate	150	20 gfd	NaCl	25
Gel cellophane	DuPont, Union Carbide	Homogeneous	100	1.5	Sucrose	15
Polyelectrolyte: anisotropic (Diaflo UM-3)	Amicon	Sodium polystyrene sulfonate-polyvinylbenzyl triethylammonium chloride	100	25	Sucrose	90
Polyelectrolyte: Anisotropic (Diaflo UM-2)	Amicon	Sodium polystyrene sulfonate-polyvinylbenzyl triethylammonium chloride	100	60	Sucrose	50
Anisotropic: Pellicon PSAC	Millipore	Cellulose ester	100	120	Sucrose	40–60

Source: From Lonsdale 1972 [7], Table 8, p. 160 with permission from the John Wiley and Sons.

Table 1.2 Influence of evaporation and annealing temperature on flux/rejection of Loeb–Sourirajan membranes.

Membrane casting solution	Evaporation time (min)	Annealing temperature (°C)	Flux (GFD)	Rejection (%)
Acetone 45%, formamide 30%, 25% CA	1	23	97	25.2
Acetone 45%, formamide 30%, 25% CA	1	68.5	44	79
Acetone 45%, formamide 30%, 25% CA	1	71	25.6	88
Acetone 45%, formamide 30%, 25% CA	1	74	30	92
DMF75%/CA 25%	8	87.2	55.6	63
DMF75%/CA 25%	8	93	10.8	97
Acetone 64%/ DMF 21% CA 14%	3.5	Unheated	12.4	89

Membrane casting and evaporation step are carried out under ambient conditions. Membrane testing: 600 psi, RT, and 5000 ppm NaCl.

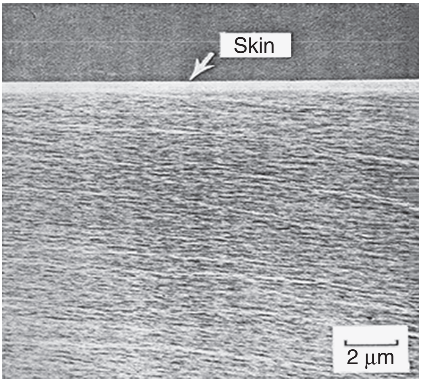


Figure 1.1 Transmission electron micrograph cross section of the skin and upper porous layer of a Loeb–Sourirajan cellulose acetate membrane. *Source:* McKinney and Rhode [11]. Reproduced with permission of ACS Publictions.

(Figure 1.1) [12]. This new method of phase inversion was found to be a very versatile tool for forming multilayered membrane structures with a controllable wide variety of morphologies and porosities [4].

Thus, in the early 1970s, membranes based on asymmetric CA, covering the NF range, became commercially available [13] from different suppliers, including Patterson Candy International Ltd. (PCI), Westinghouse Electric Corporation, Millipore, and De Danske Sukkerfabrikker (DDS), among others. These companies offered a range of asymmetric CA with cutoffs of, for example, 80%, 50%, 20%, and 0% rejection to NaCl and 95+% for 1000 MW dextran. The proposed uses were in water softening, fractionation of pharmaceutical fermentation liquors, whey desalting with lactose retention, skim milk concentration, fractionation of sugars, and concentration of antibiotics. One of the first applications was the treatment of drinking water sources with membranes that were relatively nonfouling and had some chorine resistance. In Florida, they were used for water softening as long ago as 1976 [14]. Commercial NF membranes based on CA, alone or in blends, were subsequently put into a variety of uses for water treatment, especially water softening and color removal from surface water. Although asymmetric CA had certain desirable characteristics, such as low fouling for some water sources, relative ease of cleaning, and chorine resistance, the limitations of this membrane material were quickly revealed when improved water treatment economics and other commercial applications were sought.

1.3.2 Deficiencies in Cellulosic Membranes

The limitations of cellulosic membranes were primarily their poor biological and chemical stability (e.g. hydrolysis of the acetate groups), resulting in continual changes in rejection and flux loss because of compaction. In addition, although it was possible to cast a membrane with any given rejection within the NF range, initial fluxes were often not sufficiently high for many applications. It was quickly realized that while NF had the potential for application in a large number of processes, especially in the chemical industry, fulfilling this potential would, however, require membranes other than CA or polyelectrolyte complexes. To realize the full market potential of NF, the development catch phrase of the second half of the 1970s became stable noncellulosic membranes (produced at least in part by the powerful tool of asymmetric casting). From 1975, membranes with the following characteristics were sought:

- Improved solvent, oxidant, pH, biological, and mechanical stability.
- Selectivities and fluxes that would facilitate economically favorable replacement of two or more processes with a single process, e.g. the simultaneous concentration and purification of product streams.
- Very high retention to organic solutes (e.g. 99+%), low rejections of inorganic salts, and high water flux.
- For water softening and purification, higher rejections of divalent salts and organic solutes, monovalent salt passage, high fluxes with good compaction resistance, and chlorine resistance.

1.3.3 Polyelectrolyte Complexes

During the heyday of CA membrane development, Amicon Co. offered, in the 1960s, NF-type anisotropic membranes of polyelectrolyte complexes made by electrostatic interaction between strongly acidic and basic polyanions and polycations, respectively [15]. Invented by Michaels, membranes covering the whole range between RO and UF could be made by this approach. A series of membranes with MWCOs of 1000, 500, and 380 (sucrose) were commercialized for use in the concentration and demineralization of proteins and organic solutes. These membranes never achieved the same widespread application as asymmetric CA NF membranes, possibly because of their relatively low mechanical strength, flux loss because of compaction, and variable separation characteristics in high ionic strength solutions [7].

1.3.4 Polyamide Membranes

Starting in the 1960s, DuPont and Monsanto began using their extensive fiber technology to develop asymmetric hollow fibers of aromatic polyamides for RO seawater desalination [11, 16]. These polyamide membranes could also be made in the NF range by adjustment of the properties of the casting solution [17]. Although relatively hydrophobic, polyamide membranes gave good rejection, but they could not achieve the fluxes needed for many applications, and their chlorine resistance was poor. When more hydrophilic polyamides were used, higher flux was achieved, but it declined steadily under pressure because of compaction. In addition, the selectivities of the more hydrophilic polyamides were often too low. The introduction of ionic groups into the polymeric structures, for making membranes from aromatic polyamides (which originally gave good selectivity but low flux), improved the permeability but lowered the rejection. In general, casting of asymmetric membranes from polyamides could not be optimized to compete with existing separation processes or with the new technology of composite membranes.

1.3.5 Polysulfones and Other Polymer Membranes

Many other polymeric materials were investigated to make asymmetric RO and NF with improved chemical stability. This effort was guided by the electron micrograph studies of Riley et al. [5, 6] on the ultrastructure of anisotropic membranes and by the extensive work carried out on the phase inversion process by Kesting et al. It was shown that almost any polymer that forms a homogeneous solution in a solvent and a homogeneous precipitate could form asymmetric skin structures [4, 18–21]. Asymmetric membranes could be made from polycarbonates, chlorinated PVC, polyamides, polysulfone, PES, polyphenylene oxide, PVDF, polyacrylonitrile (PAN), copolymers of PAN/PVC, polyacetals, polyacrylates, polyelectrolyte complexes, and cross-linked polyvinyl alcohol (PVA). To a certain extent, the performance of the above-mentioned polymers as membrane-forming materials could be correlated with their hydrophobic/hydrophilic balance. Based on this classification, it was rapidly discovered that for asymmetric NF membranes, many hydrophobic polymers had too low flux or lacked selectivity, while hydrophilic polymers lost flux because of compaction. Achieving the optimum degree of cross-linking to prevent the swelling of hydrophilic polymers was also difficult.

Open asymmetric NF membranes with a MWCO of 1000 could, however, be made with some hydrophobic polymers such as polysulfone and PES; these membranes demonstrated good chemical and mechanical stability and reasonable flux [22]. They could not, however, be cast into selective NF membranes with lower MWCOs, such as for sucrose, without losing flux. Increasing the hydrophilicity of polyarylether sulfones by sulfonation [23] to improve flux did not work because to achieve the desired flux, the degree of sulfonation had to be increased to the point that reduced rejection. Carboxylation of polysulfone was tried by Guiver et al. [24] as a substitute for sulfonation to give high flux and selectivity with limited swelling. Model et al. [25] used the hydrophilic polymer polybenzimidazole, which could be cast into NF asymmetric membranes with a range of MWCO as a function of casting solution and coagulation bath formulations. In a similar approach, Bayer developed from sulfonated polybenzoxazindione membranes with an MWCO of 300. These membranes were, however, not developed commercially for NF, possibly because of the high cost of polymeric materials and/or because membranes with sufficiently high flux could not be made due to compaction.

1.4 Early Studies of Charged Reverse Osmosis (Hyperfiltration) Membranes

1.4.1 Dynamic Membranes

An inexpensive route to producing membranes rejecting salt by Donnan exclusion was envisioned by Kraus and his group working at the Oak Ridge National Laboratory [26]. By depositing polyelectrolytes on a robust support, a charged membrane could be formed. If the membrane became damaged or clogged, it could be removed or regenerated, hence the term dynamic membrane. Salt rejections of 25–85% could be achieved by circulating low concentrations of polymeric electrolytes, such as vinylbenzyl trimethylammonium chloride or polystyrene sulfonic acid, and depositing the polymers on a porous support [26]. As a transport barrier, this type of membrane was classified as NF in terms of its specific water permeability and MWCO [27]. Dynamic membranes were used to recover dyes and sizing materials in the textile industry [28].

1.4.2 Polyelectrolyte Membranes

Salt exclusion by membranes carrying fixed charges and the general properties of such polyelectrolyte membranes have been well known to physiologists for many decades; such membranes have been discussed by Meyer and Sievers [29] in the 1930s and by Teorell [30] in 1953. The salt rejection expected in hyperfiltration through collodion membranes, chemically modified for carrying a fixed charge, was later calculated from the Teorell–Meyer–Siever model by Hoffer and Kedem [31, 32]. The expected dependence of rejection on fixed charge density, salt concentration, and valency of the ions was subsequently confirmed experimentally [33, 34]. It was thought that separation between ions of different salt valencies might be a useful concept for water treatment, but this idea was not carried out in practice for a long time. Instead, the development of charged porous membranes resulted in an early industrial application for NF [35].

1.5 Early Models of NF Selectivity

Models to interpret NF selectivity performance were proposed and analyzed from the very beginnings of NF applications covering processes where the rejection was dependent on charge/noncharged, molecular size, and concentration.

The models covered a range of selective processes for membranes with an MWCO of 150–1000 (in effect between RO and UF). Membrane selectivities have been interpreted by a number of models, each suited to a particular range. Some of the models were originally developed for RO, but in reality, they were more applicable and easily adapted to NF.

Water flow with retention of various solutes has been studied by generations of physiologists because it is a vital function in living organisms. Developed in the early 1950s, models for exclusion by size, such as that elaborated by the group of Renkin [36, 37], may be used for analysis of transport phenomena in synthetic membranes, including those in the upper limit of the NF range. In this type of model, an effective membrane area is defined, depending on the ratio between the molecular radius of the permeant and the pore radius. The size of the solutes limits both the probability of entrance into the pore – even if the pore radius is larger than the molecular radius – and the rate of movement through the pore.

Selective ion transport is another physiological function that is also an important NF characteristic. As already mentioned, Meyer and Sievers [29] and Teorell [30] sought to understand this phenomenon through their fixed charge model. It is clear today that this was a gross oversimplification for biomembranes, but in NF technology, salt exclusion from the membrane as a consequence of fixed charges, the well-known Donnan exclusion, is a basic mechanism of selectivity. The quantitatively predictable features of Donnan exclusion enabled the preparation of charged-ion-rejecting membranes in the early 1970s [34]. It was possible to relate the rejection of ions of different valencies to the known thermodynamic properties of polyelectrolyte solutions, assuming a homogeneous distribution of ions in the pore volume [32]. This assumption is justified for narrow pores having a pore radius smaller than the thickness of the diffuse double layer.

As long ago as 1965, Dresner [38] calculated nonhomogeneous ion distribution in wider charged pores. In 1973, Simons and Kedem [39] performed a detailed calculation of rejection in an assembly of rectangular slits in an ion exchange matrix, taking into consideration both the velocity profile and the ion distribution in the pore. Rejection of ions from a mixed electrolyte feed, which was different from the rejection of each salt separately – now a major application of NF – was predicted by Dresner [40].

A major source of basic ideas in membrane development was classic colloid and interfacial science. The surface tension of salt solutions is higher than that of pure water, and thus, the Gibbs equation relating the interfacial concentration to surface tension predicts a salt-poor region at the air/water interface [41]. With the aim of carrying out surface skimming, the UCLA group on seawater desalination initiated their research effort with the exploitation of this phenomenon in mind. In the 1977 book edited by Sourirajan [12], the performance of the L–S CA membrane and its interpretation are discussed in detail. The well-known preferential sorption capillary flow mechanism is described by Sourirajan in the first chapter (referring to his work of the 1960s): in this work-up, the surface membrane is microporous and heterogeneous; “pore” or “capillary” refers to any connecting void space, regardless of its origin or size; preferential sorption, positive or negative, takes place at the pore wall/fluid interface and the desalted layer is continually removed under pressure.

The Sourirajan concept was subsequently modified by Glueckauf [42], working together with Russel and coworker [43]. In a model calculation presented at the First International Symposium on Water Desalination in 1965, Glueckauf [42] showed that salt exclusion from the interface with a medium having a low dielectric constant is more pronounced in a narrow cylindrical pore than near a flat surface. There must then be an optimal pore size that is small enough to lead to dielectric exclusion of ions but large enough to allow water flow. His estimate of the optimal pore diameter was less than 6 Å. Water would enter such a narrow space only if the matrix was sufficiently hydrophilic. Glueckauf thus concluded that the special combination of properties of CA that makes it suitable for hyperfiltration is a low dielectric constant and sufficient hydrophilicity. Salt rejection by dielectric exclusion was further elaborated by Bean [44], and his overestimate of rejection was probably because of his neglecting of the screening by the salt itself.

Yet another approach was taken by Kraus et al. [45] who considered the membrane as a continuous organic phase that dissolves water but does not dissolve salt. To back up this idea, they measured salt and water distribution with solvents closely related to CA used to make L–S anisotropic RO membranes. In their paper of 1964, when the existence of a thin dense selective layer was "almost certain," they concluded from their data and theory that "the effective thickness of such a membrane is presumably of the order of 0.1 μm."

The models described above are basically related to one another far more closely than is apparent from their formal presentation. The phenomena of salt-free layers close to the polymer and of low solubility of salt in the membrane phase are both related to a low dielectric constant of the polymer. The distinction between the pore model and the solution/diffusion model becomes blurred if pores are of molecular dimensions [46, 47].

None of these models explain the unexpected specificity of seawater RO salt rejection. After all the intense efforts of polymer chemists, only very few polymers show the high salt rejection needed. NF membranes can, however, be prepared from a variety of materials. The nonspecific pore models developed for RO do, in fact, work for NF, and similarly, the Spiegler/Kedem flux equations developed for RO are applicable to NF [48]. Moreover, just as NF is a process lying between UF and RO, models from both these areas and their combinations can be used to represent NF performance. Early NF membranes used to separate salts from dyes were based on a combination of size exclusion and fixed charge exclusion (unlike the salts, the large charged dye ions cannot be drawn into the center of the pores). In thin layer polyamide NF membranes with partial salt rejection, dielectric exclusion is probably the major factor enabling separation. More porous NF relies on Donnan exclusion. The currently accepted theory for ion transport in NF membranes seeks to combine the effects of the dielectric constant of the medium and of fixed charges as a function of pore size (see Chapters 4–6 for a more extensive description of NF selectivity models and mechanisms).

1.6 Negative Salt Rejection

1.6.1 Solutions of One Electrolyte

As mentioned above, the salt rejection of charged membranes can be described by the model (TMS) based on Donnan exclusion. It was, however, realized that salt rejection depends not only on salt distribution but also on the ratios between the mobilities of the ions. For the extreme case of some acid filtered through positively charged membranes, negative rejection, i.e. enrichment in the product solution, was predicted and obtained experimentally [33]. Negative salt rejection is closely related to the so-called anomalous osmosis, leading to volume flow from the concentrate into the dilute solution in the absence of a pressure gradient. This was observed by the pioneers of membrane science, Sollner and coworker [49] and Schloegl [50].

Negative rejection of a single salt-comprising cations and anions of similar mobilities is obtained in “mosaic” membranes containing small regions of anion and cation elements. It was considered for some time that this effect could serve for desalting [51]. The considerable efforts devoted to these systems have been reviewed by Leitz [52].

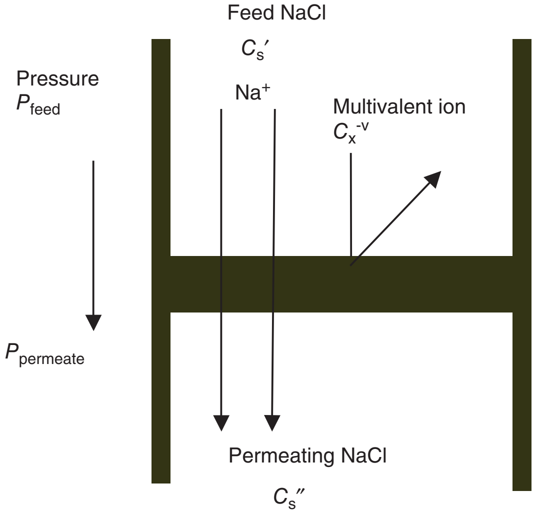
1.6.2 Separation by Negative Salt Rejection

The salt exclusion originally described by Donnan is obtained when a membrane separates a solution containing charged macromolecules and salt from a solution of salt only. At equilibrium, the salt concentration in the mixed “inside” solution is smaller than that in the outside. When the solutions are separate by an ultrafiltration membrane and pressure is applied, salt will be enriched in the product. Such negative salt rejection was predicted and observed by Lonsdale et al. [53] in the hyperfiltration of citrate and chloride and by Akred et al. [54] in the ultrafiltration of gelatin solutions containing calcium or sodium salts. The principle of negative rejection is illustrated in Figure 1.2.

The technically important negative salt rejection from mixtures containing charged molecules of medium molecular weight (200–1000 Da) can be achieved with nanofiltration membranes of suitable cutoff. This is feasible in principle with any type of NF membrane – charged or neutral.

1.7 Early Development of Industrial NF: Ionic Modification of Asymmetric Cellulose Acetate

By about 1972, ecological issues were beginning to become a cause for concern to industry, especially industrial entities in Europe that found themselves in heavily populated areas. In activities such as dye production, large quantities of salty dyed polluted water were being discharged into waterbeds and rivers. One solution to this problem was to apply the new membrane technology that was becoming successful in RO applications such as water desalination and in UF applications such as protein separations. However, many industrial waste



From Ref. [55], negative rejection of a permeating salt in the presence of a highly rejected ion, can be defined by the following equations:

For permeating salt alone:
$R_S = (1-F)\sigma/[(1-\sigma)F]$ (1)
$F = \exp(-J_v A)$,
$A = (1-\sigma)\,\Delta x/P_{av} = (1-\sigma)/P$

For permeating salt and highly rejected ions:
Define: $\beta = (1 + \nu C'_x/c'_s)^{0.5}$
Then,
$R_s = 1 - [(1-\sigma)\beta]/(1-\sigma F)$ (2)

When only permeating salt is present, then $C'_x = 0$, $\beta = 1$ and eqn (2) reduces to eqn (1)

R_S = NaCl salt rejection, σ = reflection coefficient, C'_x = concentration of multivalent ion, ν = number of charged groups, C'_S = salt concentration

Figure 1.2 Principle of negative salt rejection in the presence of highly rejected ions [55].

streams presented special problems for the new membrane technology: In RO, the salt concentrations were so high that any concentration effort was doomed by uneconomically low flux because of the osmotic forces of the rejected salt. UF was not efficient, as both the dye and the salt permeated through the membrane.

One of the efforts to overcome these difficulties led to the founding of a small company – known as RPR – in the early 1970s by Bloch and Kedem, which used open NF asymmetric cellulosic membranes modified with reactive dyes. This approach to membrane modification was an early example of how existing membranes could be chemically modified to achieve valuable separation characteristics. The modification in this case formed charged groups on the pore walls and at the same time stabilized the membrane structure by cross-linking. With these modified membranes, 99% dye rejection was achieved.

It was found that these membranes could be advantageously applied not only to wastewater treatment but also to dye production because of the then-amazingly effective purification effect by negative salt rejection. This was explained to be a consequence of Donnan equilibrium, as described in Section 1.6. The salt passed through the membrane easily and was, in practice, equilibrated between the feed and permeate. The feed contained the large impermeable dye anions, small sodium counterions, and a high concentration of salt, while the permeate contained only small ions, which had been pushed into the permeate by the highly rejected dye counterions.

Thus, in the late 1970s, a single-unit operation could be used for both concentration and purification. The first tubular pilot units based on modified cellulosic membranes very rapidly became the core of production machines that concentrated and desalted simultaneously, thus saving vast quantities of the salt need to precipitate the dye and solving the original development problem of reducing salty/dyed discharge. The membranes were used on an industrial scale by dye manufacturers to desalt and concentrate dye solutions. In one process, both a production and an ecology problem had been solved!

A formal description of this Donnan effect in dye solutions was published only much later (1989) after it had long been understood and put into practice [55]. The incorporation of a Donnan distribution term into the flux equations of Spiegler and Kedem [48] defined earlier could explain the strong negative salt rejection found in dye processing (shown schematically in Figure 1.2) and its concentration dependence. Negative salt rejection because of the Donnan effect may be observed for any type of NF membrane, whether charged or uncharged.

Cellulosic membranes were, however, not chemically stable and suffered from flux decline after short periods. As experience was gained, it was realized that there were still some significant drawbacks associated with the modified CA membranes: they allowed relatively large quantities of dye to pass through them, which constituted an economic loss, and membrane lifetime was not sufficiently long. It was also realized that tighter membranes, which could operate at higher and lower pH values, would have many other uses. Starting in late 1970s, tighter noncellulosic membranes were developed in RPR's manufacturing company, Membrane Products Kiryat Weizmann (MPW).

1.8 Early NF Composites

1.8.1 General

By 1975, it became apparent that asymmetric NF membranes from a single polymer or polymer mixtures could not give the characteristics of selectivity and flux needed to compete with standard technologies in many applications. Attempts to make asymmetric NF membranes by casting polymers with the hydrophilic/hydrophobic balance of CA did not produce membranes with sufficient flux or rejection if they were too hydrophobic or with flux stability if they were too hydrophilic.

Workers such as Rozelle, Cadotte, and Riley and their colleagues had resolved a similar dilemma for RO in the early 1970s with the development of composite membranes [56, 57]. They produced high-salt-rejecting membranes by placing a very thin selective layer over one surface of a finely porous asymmetric UF membrane. Such a composite membrane was produced either by coating the UF membrane with a thin CA film or by carrying out interfacial cross-linking of polyamines (for example, polyethyleneimine [PEI]) with isophthaloyl chloride (IPC), toluene diisocyanate (TDI), or other aromatic cross-linkers. The latter approach appeared to be the key breakthrough. These composite membranes exhibited important advantages over integrally skinned asymmetric membranes in that the selective barrier film and the support could be optimized independently. With this process, a variety of chemical combinations and methods could be used to form thin barrier coatings, including the use of linear and cross-linked polymers, whereas asymmetric membrane formation was limited to processable stiff linear polymers. In Cadotte's patent of 1977 [58] and NTIS report 1968 of Rozelle et al. [59] on composite membranes, comparison examples were given of other composites made by different cross-linking reagents, which showed significantly lower salt rejections compared to the claimed RO membranes. These more open membranes were, however, what we would now term composite NF.

In general, it may be said that the composite approach is applied to form a selective layer that is both thin and sufficiently hydrophilic to give high water flux but at the same time cross-linked to the extent required for NF selectivity. In addition to the original method of interfacial cross-linking of polymers for forming composites, other methods have included interfacial polymerization (Section 1.9), plasma polymerization (Section 1.8.2), polymer coating and curing, and surface modification (see Section 1.8.3).

The first composites – RO composites – were based on cellulose nitrate UF supports, but they suffered from the same lack of biological, chemical, and mechanical stability that had limited CA in RO and UF applications. Very early in the 1970s, polysulfone was recognized as the material of choice for UF porous supports because such membranes combined high surface porosity with minimal pore diameter and high chemical and mechanical stability. They could be readily cast and optimized (high degree of porosity and controlled pore size distribution) to give the asymmetric structures for commercially valuable RO or NF composites [56, 57]. A number of other polymeric materials were also investigated [58], such as polycarbonate, chlorinated PVC [56], polyamide, PVDF, PAN and styrene/acrylonitrile copolymers, polyacetals, and polyacrylates. From these investigations, it was found that polymer molecules making stable compaction-resistant supports are inherently stiff chains capable of hydrogen bonding or polar and hydrophobic bonding, giving networks with low chain mobility. UF membranes based on chemically stable aromatic engineering plastics, such as polysulfone or PES, have currently become the standard supports for composite RO and NF membranes. Different UF membrane morphologies could be used for making composites; however, a typical asymmetric polysulfone is shown in Figure 1.3. The membrane comprises an integral "tight" skin layer of about 0.1–0.7 μm, a larger pore intermediate sponge layer of 1–5 μm, and a 80–100 plus μm thick, open support layer with large finger-like pores. Other UF supports have a sponge-like structure instead of fingers in the porous layer.

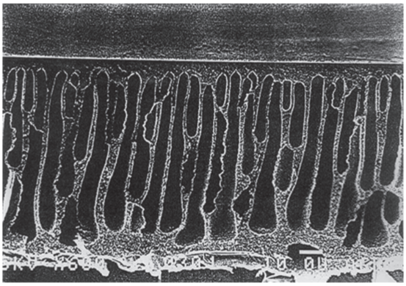


Figure 1.3 Scanning electron micrograph of UF PES membrane used for making NF composites.

If 1960 marked the beginning of the development of asymmetric membranes, then about 1969 marked the beginning of the use of asymmetric UF membranes for making composites. From 1969, Cadotte and Rozelle [58, 60] and then Wrasildo, Riley, and coworkers [61, 62] showed that high-rejection RO composites could be made by interfacial cross-linking of coated hydrophilic polymers such as PEI or polyepiamine with IPC or TDI on polysulfone or chlorinated PVC UF membranes. As a spin-off of this development on single-pass water desalination membranes, Cadotte and others also described open RO or NF membranes. For example, in 1972, open RO (NF) composite membranes were made from the interfacial reaction of low molecular weight polyamines and teraphthaloyl chloride (Figure 1.4) [60]. Similar membranes were also made from mixtures of PEI with different cross-linkers, as described in a 1977 patent (Figure 1.5) [58]. These membranes were not, however, commercially viable and were superseded by the piperazineamide composites described below.

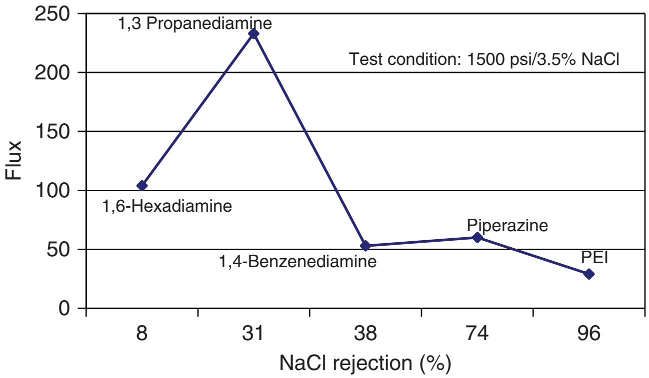


Figure 1.4 Flux (gallons/ft^2 d) vs. salt rejection (%) for early open RO membranes (NF) prepared by interfacial polymerization of teraphthaloyl chloride with different polyamines (NTIS report No. PB-229337, November 1972) [60].

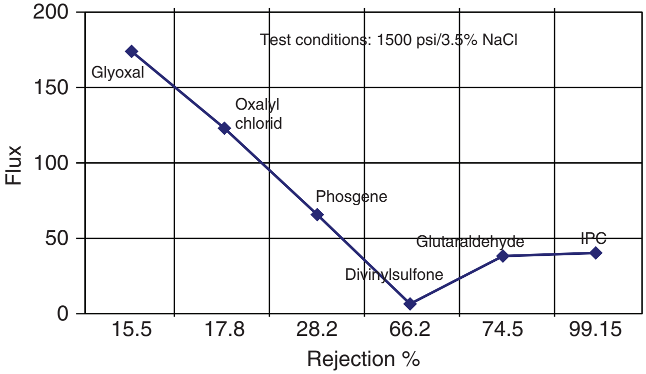


Figure 1.5 Flux (gallons/ft^2-d) vs rejection (%NaCl) for different interfacial membranes from US Patent 4, 039, 440 (1977) [58].

1.8.2 Plasma Polymerization

Another approach to the preparation of composites, which first appeared in the 1960s, was plasma polymerization of coated films on a microporous support. In his 1977 review of the subject, Yasuda [63] reported the use of plasma polymerization of different monomers (e.g. 4-vinylpyridine, *N*-vinyl pyrrolidinone, pyridine 1-methyl-2-pyrrolidinone, thiophene, and thiazole) on polysulfone supports to produce very thin selective membranes. Although the main goal was the production of RO membranes, NF membranes produced from a variety of monomers were also prepared.

Plasma processes were also used to modify the surfaces of UF membranes to bring them into the NF range. For example, Sano [64] used plasma polymerization with He and H_2 on UF PAN to produce commercial RO membranes by sealing and hydrophilizing the membrane surface. This method can be adapted to give NF membranes; for example, Lai and Chao [65] modified Nylon 4 microporous membranes with gas plasma to produce membranes with 74% rejection to NaCl. Polyarylsulfone UF membranes were also plasma-treated by Sano and his coworkers to give 96.3% rejection, where the original membrane had exhibited 0% rejection. Such membranes could also be expected to give NF under different preparation conditions.

1.8.3 Graft Polymerization

Graft polymerization of nonionic or ionic vinyl monomers by a variety of methods, i.e. with ionizing radiation such as gamma rays from ^{60}Co, by photochemical means, or by chemical initiation on asymmetric membranes has been carried out in an effort to improve RO performance. In the 1960s and 1970s, Stannett et al. [66] grafted styrene on CA membranes. Although the results were not encouraging for RO, they did give, in some cases, membranes with NF properties. The fluxes were, however, too low for the membranes to be of commercial value. In another study, Kesting and Stannett [67] showed that the attachment of acrylic monomers could be used to increase the starting membrane permeability to salt and possibly to bring RO membranes into the NF range. In yet another study, double grafting of PVC films with 2-vinylpyridine and acrylic acid gave membranes with a high flux per unit thickness with NF salt rejections of 65% [68]. However, the absolute flux in the dense films was low, and only by casting asymmetric membranes could this approach be of practical value.

1.9 NF Composites of the 1980s

1.9.1 Piperazineamide Membranes

Commercial NF composites were not generally available until the second half of the 1980s, even though their development began in the late 1970s [28]. One of the first successful approaches was based on the interfacial polymerization of an aqueous piperazine film on a polysulfone UF support by hydrophobic aromatic

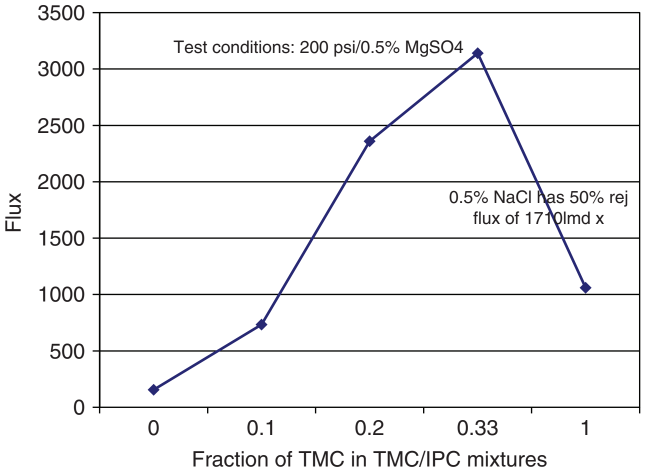


Figure 1.6 Flux (l/m^2 d) vs TMC/IPC ratio of piperazineamide interfacial membranes with 99 + % rejection to $MgSO_4$ (US Patent 4, 259, 183 (1981)) [69].

cross-linkers. Many such NF products were made by a number of different companies. Polypiperazineamide NF composites were prepared when Cadotte et al. [69] replaced IPC with trimesoyl chloride (TMC), making NF membranes with high $MgSO_4$ rejection (99%) and low NaCl retention (<60%) (Figure 1.6).

Starting in the 1980s, FilmTec marketed variations of these membranes with 40–50% NaCl rejections [70]. Other companies also developed and commercialized NF composite membranes based on the interfacial polymerization of piperazine and its derivatives on UF PES and polysulfone supports. Examples of these membranes are (i) PCI's polypiperazineamide membranes in tubular form [71] having 30–70% NaCl passage and a MWCO to organics of 350 and (ii) Toray also commercialized NF polypiperazineamide-based barrier layer membranes [72]. These membranes found application in the desalting of whey, water softening, removal of organics from surface waters, removal of sulfate from seawater, recycling of waste dye streams, recycling of melamine-based anionic electrophoretic paints for aluminum surface finishing, removal of color from bleach effluents, wood pulping, and removal of radium from well waters [73].

An important commercial variation of polypiperazineamide membranes is the inclusion of a polymer that simultaneously undergoes interfacial cross-linking during the interfacial polymerization of piperazine. Because the polymer cannot readily diffuse into the interfacial layer, the piperazine monomer accumulates on the surface to form a thin polypiperazineamide layer on the cross-linked polymer, which is supported by the UF membrane. For example, Nitto Denko NTR 7199 is a polyamide [74] formed by the interfacial reaction of TMC with an aqueous solution containing both piperazine and PVA with subsequent curing at 110 °C. Their process produces a selective bilayer consisting of cross-linked PVA covered with a surface layer of polypiperazineamide, which is supported by an asymmetric UF membrane. In this membrane, chlorine stability is supposedly improved because of the presence of PVA.

In another type of commercial product, a thin coating of one polymer is first placed on a UF support, followed by interfacial polymerization of piperazine. It is thought that Desalination Engineers' Desal 5 membranes (now Osmonics Corporation) comprise a polysulfone UF support coated with a layer of sulfonated polysulfone upon which is an ultrathin layer of polypiperazineamide [75]. This type of membrane can be made to give glucose rejections of 82–98% and a sucrose rejection of 99%. Although the Desal 5 membrane is negatively charged, its characteristics are different from those of other negatively charged sulfonated polysulfone membranes and are more similar to those of piperazine composites of FilmTec (e.g. NF40).

1.9.2 Other NF Interfacially Produced Composites

Commercial NF membranes have also been prepared via interfacial polymerization with monomers other than piperazine. In 1985, FilmTec introduced fully aromatic cross-linked polyamide NF membranes, NF70 (70% rejection to NaCl), with an MWCO of 400 [75]. These membranes are typical of NF membranes used in drinking water purification and softening. McCray et al. [75–77], at Bend Research, developed chlorine-resistant membranes, with 20% and 60% salt rejection, respectively; these membranes were made by the interfacial polymerization of tetrakis-(*N*-methyl-amino-methyl) methane with IPC and TMC, respectively.

Multilayered NF membranes have been prepared by Linder et al. by the interfacial polymerization/cross-linking of PEI and diaminobenzene sulfonic acid with TMC [78]. In this interfacial reaction, the monomeric amine diffuses through a PEI layer that has previously undergone thermal cross-linking, reacts with TMC, and deposits a layer of diaminobenzene sulfonic acid polymer on the cross-linked PEI. According to the patent literature, these membranes have 95+% rejection to glucose and sucrose, low NaCl rejection, and sodium sulfate rejections of 90+%.

1.9.3 Modification of RO Membrane Composites to Bring Them into the NF Range

In the 1980s and early 1990s, patents were taken out on processes to produce NF membranes by modification treatment of RO polyamide composites with various reagents, such as acids, bases, and oxidants, with the aim of lowering rejection and increasing fluxes. For example, Strantz and Brehm [79] described a process for treating polyamide RO membranes to make NF membranes with acidic solutions of permanganate salts to open the selective barrier, followed by sodium bisulfite or hydrogen peroxide treatment to chemically stabilize the new membrane. In another example, Cadotte and Walker [80] used hot phosphoric acid/sulfuric acid mixtures to open up a polyamide composite to decrease salt rejection and increase flux. The resultant open membrane was further modified to increase $MgSO_4$ rejection to 90+%. These rejection-enhancing agents may be colloids such as tannic acid or water-dispersible polymers.

1.10 Composites Produced by Noninterfacial Cross-linking

In the latter half of the 1970s, work started on developing composites by noninterfacial cross-linking methods. This resulted in the production of a class of commercial NF membranes formed by coating and curing thin selective films on asymmetric UF supports. There are two possible methods of preparation:

1. Coating of a polymer solution on a UF support, followed by a curing step to activate cross-linking via self-condensation or by a latent cross-linker in the coating solution;
2. Coating the UF support with a polymer solution, washing and/or draining the support, and then immersing it in another bath containing cross-linker(s) that diffuse into the wet film, followed by a curing step.

The curing steps may comprise a temperature increase, a change of pH, or ionizing radiation. Commonly used coating polymers are PVA, PEI, polyallylamines, and sulfonated engineering plastics such as polysulfone, PES, and polyetheretherketone.

1.10.1 Polyvinyl Alcohol Composites

Because of its hydrophilicity, water solubility, and ready availability in different molecular weights, PVA has always been an attractive candidate for making composites. It has generally been found that NF PVA composites made by thermal cross-linking exhibit low flux and tend to compact under high pressure. This is due to chain flexibility and hydrogen bonding, resulting in tight packing and crystallization before cross-linking, and a nonuniform distribution of cross-links, all of which give a film that compacts under pressure [81]. To make membranes with sufficiently high flux, tight packing and crystallization should be avoided.

NF composites have been made by coating a mixture of PVA with a reactive dye on microporous supports (such as microporous polypropylene), followed by cross-linking by immersion of the membrane in hot sodium sulfate, according to the 1980 patent of Linder et al. [82]. These membranes have basic pH stability to pH 12 at 60 °C and give typical rejections and fluxes of 98% to ionic dyes with an MWCO of 700+ at 20–30 bars. They can be used in various industrial applications, such as the desalting of dye solutions. Cadotte [83] developed PVA membranes from thin PVA films cross-linked on a porous support by acetylation with a dialdehyde catalyzed by phosphoric acid at 110 °C. Phosphoric acid was used both as a cross-linking catalyst and a pore former. The membrane (XP20) had 20% rejection to NaCl, 85% to $MgSO_4$, 99% to ETDA, and pH stability up to pH 13. This membrane found use in the concentration of copper EDTA, for which it had 99% rejection, in an alkaline electroless plating bath. Other NF composites have been developed on the basis of films made with PVA and different cross-linkers such as hexahydroxycyclohexane [84] and divinylsulfone [85].

1.10.2 Sulfonated Engineering Plastics as Selective Barriers

Asymmetric membranes cast from solutions of sulfonated polysulfones or other engineering polymers were not successful because the degree of sulfonation needed for sufficient flux resulted in low rejection and in compaction under pressure and hence in flux loss. Sulfonated aromatic polymers were, however, used to make commercial composites by coating the polymer on a UF support, generally followed by a curing and cross-linking step.

In the second half of the 1980s, Nitto Denko commercialized NF composite membranes based on sulfonated polysulfone membranes. This series of membranes, designated NTR-7400, exhibits high flux and low salt rejection with excellent chlorine resistance [86, 87]. Their performance depends on the degree of sulfonation; for example, a membrane with a 3000-Å thick film (Figure 1.7) having a capacity of 1.92 meq./g gave 35–50% rejection to NaCl and 35% to sucrose, with lower capacity films giving higher rejections and lower fluxes. A phenomenon observed with loose-charged membranes of this type was the production of a permeate enriched in a particular anion relative to the feed [88], giving a negative rejection of an ion with mixed salt solutions.

1.10.3 Polyethyleneimine

NF membranes based on a cross-linked coating of PEI on UF polysulfone were described as part of the original work of Cadotte in the early 1970s [58], but these membranes were never commercialized. Linder, Nemas, and their coworkers, citing the use of hydrophilic polymers such as PEI, also extensively patented NF membranes, starting from 1980. The patents describe processes of immersing a UF membrane in a sequence of different solutions containing polymers and cross-linkers. According to the patent literature, this process comprises the following steps: the support is coated by immersion in a polymer solution; drained and immersed in an aqueous suspension or solution of cross-linkers, such as polyepoxides, reactive dyes, divinylsulfones, and polyaldehyde; drained; and finally cured in solution or by drying. Different supports have been modified by this procedure to give a range of NF membranes with different acid/base stabilities. According to the patents, the UF supports may be cellulosic [89], PAN, [90], or polysulfone [91]. These membranes have varying degrees of stability, depending on the support and the polymer cross-linking reaction. For example,

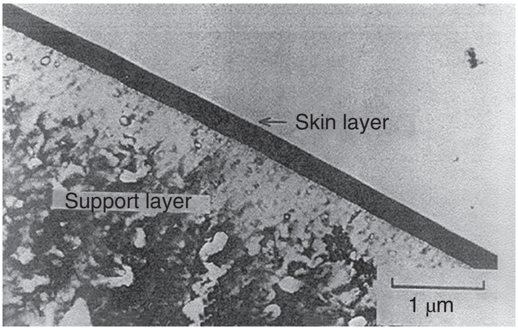


Figure 1.7 Scanning electron micrograph cross section of a cross-linked sulfonated polyethersulfone skin on a UF polysulfone support. *Source:* Taken from Figure 1 of Ikeda et al. 1986 [86] with permission from the Elsevier .

the CA NF is limited to pH 4.0–8.0, while membranes based on polysulfone can be used between pH 2 and 12 at 60 °C. Depending on the degree of cross-linking, the membranes can have rejections to glucose that vary from 20% to 95+%, and pure salt rejection of 0–75% as a function of the selective barrier and the salt concentration. Fluxes at 20 bars can vary from 50 to 150 l/m^2 h as a function of the membrane type. Other membranes having rejections to organic molecules such as glucose of 95+% and ionic dye molecules of 99+% with salt passage have also been patented. In mixtures of monovalent salt, and highly rejected organic ions, large negative salt rejections were reported by Perry and Linder [55].

1.11 Chemically Stable NF Membranes

1.11.1 Chemically Stable Polymeric Asymmetric Membranes

By the early 1980s, asymmetric chemically stable NF (in effect acid-, base-, and chlorine-resistant) could be made by casting polysulfone or polyether sulfone into asymmetric membranes with an MWCO of 1000–2000. These membranes have a pH stability of 0–14 at temperatures up to 60 or 80 °C and good chlorine stability. In some cases, however, the nonwoven and module materials rather than the membrane limited performance. Asymmetric membranes with lower MWCO selectivity and good flux cannot, however, be readily made by this approach. Such relatively open membranes cannot be used effectively for applications needing high rejections to low molecular weight solutes such as sucrose. Experience in different industrial applications has shown that these membranes compacted and fouled easily, with loss of flux. To overcome fouling and to increase flux, the surfaces of these asymmetric membranes were hydrophilized by various methods [92, 93]. One procedure was to cast the membrane with a compatible hydrophilic polymer, such as polyvinylpyrrolidone, which was subsequently cross-linked by heating.

1.11.2 Oxidant and pH-Stable Composite Membranes

In the early development of noncellulosic NF membranes with hydrolytic stability, good selectivity, and high flux, polyamide and polyurea composites were made. The stability of these membranes to chlorine was, however, found to be lower than that of CA membranes. The chlorine tolerance of the Desal 5 membrane is about 1000 ppm-h, while other polypiperazineamide membranes can typically operate at constant chlorine exposure levels of 0.1< ppm. Dechlorination is, however, generally recommended for most polypiperazineamide and polyaromatic amide membranes. In comparison, PVA and CA NF membranes can operate continuously at 0.5 ppm of chlorine (up to a maximum of 1.0 ppm). High chlorine stability can be achieved in sulfonated polysulfone composites; for example, the NTR-7400 series, having high flux and low salt rejection (50%), are stable in 10 000 ppm chlorine for at least 30 days. These oxidant-stable membranes are, however, open NF membranes, and as such cannot be used for many of the applications requiring better selectivity. NF membranes with a combination of high flux, selectivity to low molecular weight solutes, and chlorine resistance are still to be developed.

One of the first goals of membrane development in the 1970s was improvement of the pH stability of CA membranes, which were limited to a pH range of 4–8. Polyamide and polyurea composite membranes offered by many companies such as Desalination Engineers (now Osmonics) (Desal 5) and Dow FilmTec (NF40, 45, 50, and 70) can be operated continuously at room temperature at pH values between 1 and 11, but under more acidic or basic conditions or at high temperatures, they lose rejection ability. Asymmetric membranes cast from sulfonated polybenzoxazindione with an MWCO of 300 stable from pH 2 to 12 were developed by Bayer but were never commercialized [94]. The Nitto membrane of sulfonated polyether sulfone on a polysulfone support (NTR-7400 series) showed stability in the pH range of 0.5 –13 in immersion tests at 80 °C [86]. This class of membranes has a high MWCO, with sucrose rejections of 50% in the tightest membrane.

There are many potential applications for NF at the pH extremes of 0–14 and at elevated temperatures that require selectivities to low molecular weight solutes, such as glucose, sucrose, aluminates, and sodium carbonate, while freely passing acids and bases. For example, aqueous acid and base streams are used on a large scale as reaction media, as catalysts in fine chemicals, in the mining, petrochemical, and pharmaceutical industries and for daily cleaning in the dairy, food, beverage, and pharmaceutical industries. The ability to carry out selective separations of acids, bases and solvents from low molecular weight organics (150+) and salts (e.g. carbonates) present in production and waste stream would enable these recycling chemicals, the concentration and purification of products, and the recovery of valuable materials from waste streams.

During the 1980s, a series of patents by Linder et al. [91, 95, 96] described acid/base-stable NF membranes with good selectivity based on the chemical modification of polysulfone. It is claimed in these patents that the membranes are stable in the pH range from 2 to 12 at temperatures up to 80 °C and that the membranes can be made with an MWCO of 200 with fluxes from 50 to 150 l/m^2 h at 20 bars. According to the patent literature, the modification was carried by a sequence of immersion steps, which, for example, resulted in a cross-linked selective layer of PEI on a polysulfone or PES UF support. In 1989, Perry and Linder described NF membranes with 95+% rejection to sucrose and stability at pH 0.5–12 [55], and in 1991, Perry and Linder described NF membranes with an MWCO of 200 and pH stability from 0 to 14 at 80 °C [97, 98].

1.11.3 Solvent-Stable NF Composites

The use of solvents is particularly prevalent in the fine chemical, pharmaceutical, food, and petrochemical industries as described in Chapters 12 and 20.

The ability to carry out selective separations with solvent-containing solutions would enable the recycling of solvents, the concentration and purification of products, and the recovery of valuable materials. Many such applications require the rejection of low molecular weight solutes (down to 150) and the free passage of the solvents. There are, however, a number of problems in developing solvent-stable NF membranes for solvent applications, i.e. the need to provide (i) support stability, (ii) economically favorable fluxes by optimizing a different membrane for each solvent class, and (iii) membrane selectivities that vary from one solvent to another and in solvent mixtures. The origin of the flux/selectivity problems lies in solvent/support interactions, the solution–diffusion transport mechanism, and the many different solvents with a wide range of hydrophobicity/hydrophilicity balances, viscosities, and surface tensions. Solvent stability can be measured as a function of the degree of swelling of a membrane in a particular solvent. For constant performance in a particular application, the membrane, including the support, should be essentially nonswelling in that application's solvent. Many claimed solvent-resistant supports are nonswelling for one category of solvents but swell in others. A general solvent-stable UF support is one that is nonswelling in many solvent categories.

The potential of the new membrane technology for solvent applications was recognized in the 1960s by Sourirajan [99] and others on a condition that both the necessary selectivity and stability could be developed. The membranes used in early studies were based on CA and cross-linked rubbery materials [100]. NF membranes based on CA or polyamide composites on polysulfone supports could be used with solvents that do not swell the support (e.g. hexane) [101]. Most commercial NF membranes, including CA and polyamides, swell or dissolve in many solvent classes and are therefore not considered to have general solvent stability.

Most work on solvent separations involves pervaporation. There are, however, patents on pressure-driven processes for treating solutions of organic solvents. For example, Black [102] prepared composite membranes formed on solvent-stable supports (e.g. nylon, cellulose, polyester, Teflon, and polypropylene) by the interfacial polymerization and cross-linking of polyamines with polyfunctional agents. The proposed use was the separation of aromatic extraction solvents, such as 1-methyl-2-pyrrolidinone (NMP), furfural, phenols, and ketones, from oils and aromatic hydrocarbons under RO conditions. Composites on a microporous nylon support (0.04 μm) with oil rejections of 98% and NMP fluxes of 103 l/m^2 d were achieved at 500 psig. It does not appear that the membranes or the applications have been developed into commercial processes, possibly because of the lack of long-term stability or uneconomically low fluxes.

In another approach to NF operating at 20–80 bars, Bitter et al. developed membranes, which retained the solvents but passed the hydrocarbon oil [103]. Their membranes were based on dense selective silicone layers (1–10 μm thick), coated onto microporous supports (e.g. polypropylene with rectangular 0.2 by 0.02 μm pores). Apparently, the oil was transported by a solution diffusion mechanism through the silicone barrier while the more polar solvent was rejected. These membranes were not, however, applied in actual practice. The thickness of the selective layer and support size are quite different from the thin selective barriers placed on UF supports for most NF membranes.

In the 1980s and early 1990s, MPW commercialized general solvent-stable NF membrane composites, designated as MPT 42, MPT 50, and MPT 60, which had MWCOs of 200, 700, and 400, respectively, and were stable to pH values of 2–10 and nonswelling in a broad range of solvents [97]. The patent literature cites

Table 1.3 SelRO™ acid/base/solvent-resistant membranes.

			Typical % rejections					
Membrane	**Acid/base stability**	**Solvent stability**	**MWCO**	**NaCl 5% (MW 58)**	**Ampicillin (MW 349)**	**Murexide (MW 284)**	**Remazole Blue (510)**	**Lactose (360)**
MPT-11	Yes			31	99	95	99.9	99.5
MPT 20		Yes	600	0		90	99.9	97
MPT 30	Yes		500	10	98	90	99.9	96
MPT 40		Yes	300	15		95	99.9	90
					Glucose (MW 186)	Sucrose (MW 342)	Raffinose MW 504)	Aspartame MW 294)
MPT 42		Yes	150		93	98	99	99

Source: Adapted from Ref. [98].

stable NF membranes prepared by Linder et al. [104–106] based on cross-linked PAN and polysulfone, with the composites being made by coating and curing or interfacial polymerization. To achieve sufficient flux, the selective layer was optimized for a particular solvent category. The patent literature shows that hydrophobic solvents, such as hexane, were treated with solvent-stable composites with polysiloxane layers, giving good fluxes. For polar solvents, such as ethanol, esters, dimethyl formamide, and NMP, more hydrophilic composites with selective layers of polyamines or polyphenyleneoxide derivatives are required. The membranes cited in the above-described patents have MWCOs down to 150 and solvent fluxes that vary according to the particular membrane and solvent (Table 1.3).

A more detailed account of NF membranes in solvent applications is given in Chapter 20.

1.11.4 Chemically Stable Inorganic NF and Polymeric/Inorganic Hybrids

The development of inorganic NF membranes, which are generally ceramic materials, is motivated by superior thermal and solvent stability characteristics compared to organic polymers. Typically, the porous support for the selective NF layer is composed of Al_2O_3, carbon, SiC, or a metal made by sintering large particles of these materials. The substrate is then coated with a thin layer of small particles of zirconia, alumina, or titania to form a microporous membrane. A third layer of still finer particles or a colloidal dispersion is then applied to form a UF membrane. On these UF membranes, an NF film is coated. Each stage of the ceramic membrane composite is formed by sintering particles or by a sol–gel technique.

In the early 1990s, ceramic NF membranes were developed by two different approaches: (i) All-inorganic membranes were made by coating a ceramic UF membrane with nanoparticles, followed by sintering or by a sol–gel process, or (ii) hybrid NF membranes were produced by coating the ceramic UF membrane with organic polymers or organic–inorganic polymers.

NF ceramic membranes can be made with high rejection to charged organic solutes with molecular weights as low as 400. For example, Larbot et al. [107] prepared α-alumina NF membranes having rejections to NaCl of 10% and to sucrose of 70%. The ceramic route to NF has not yet been able to produce NF membranes with selective separations of noncharged solutes such as glucose and sucrose from salt. There are also indications of changing rejection characteristics under pressure because of fusion of the nanosized particles that make up the selective layer. In the early 1990s, NF membranes comprising a porous ceramic support coated with a thin polymeric layer were developed. For example, Guizard and his group [108, 109] coated a porous ceramic support with polyphosphazenes or heteropolysiloxanes to give NF membranes with 50% rejection to sucrose and low rejections (10%) to NaCl. Bardot et al. [110] coated other polymeric barriers, such as sulfonated polysulfone, polybenzimidazolone-grafted PVDF, or Nafion, on inorganic supports to make RO and NF membranes.

1.12 Conclusions

CA membranes were the first membranes to be used for NF applications. They demonstrated the potential of selective separations within the molecular weight range up to 1000. One of the major drawbacks of these membranes was their lack of stability, which resulted in a rapid loss of rejection ability and/or of flux in many industrial applications. With each successive improvement in stability, there was a widening of the range of applications. The first improvements were made in pH stability and then in stability to solvents and oxidants. Improvements in selectivity and flux were made together with improvements in stability. The number of NF applications could be greatly widened if stability and selectivity could be refined further. This chapter covered NF developments of the first three decades (1960–1990). Improvements in NF performance continued in the 1990s, until the present, and are described in subsequent chapters (Chapters 2 and 3).

In the fine chemical and pharmaceutical industries, there is still a need for improved solvent stability with better selectivity in the molecular weight range below 500. In the mining and sugar industries, there is a need for high-flux selective membranes with improved acid stability at values as low as pH 0. In other industries, improved flux together with better stability and selectivity would open many new applications; in particular, base stability at concentrations of 10–50% at temperatures up to 80 °C with 150–200 MWCO would have many applications. In the petrochemical industry, solvent separations and purifications are extremely important but require solvent-stable membranes with selectivity properties optimized for each solvent class. Work in this area has only just begun with ceramic and solvent-stable polymeric membranes.

Another important industrial application relates to the widespread use of sulfuric acid as a solvent catalyst and pH adjuster. This results in the production of waste streams with high concentrations of sodium sulfate. NF membranes that could selectively pass sulfate with less than 20% rejection while retaining low molecular weight organics, such as sucrose and glucose, would find many applications.

Separation between molecules with molecular weights up to 1000 is needed in many aspects of water and industrial activity. Achieving such separations economically is becoming important in terms of ecological and energy considerations. NF membranes have made significant contributions to this activity, and as progress is made in stability, selectivity, and flux, even more applications will be found.

Abbreviations

CA	Cellulose acetate
IPC	Isophthaloyl chloride
L–S	Loeb–Sourirajan
MPW	Products Kiryat Weizmann
MWCO	Molecular weight cutoffs
NF	Nanofiltration
PAN	Polyacrylonitrile
PCI	Patterson Candy International Ltd.
PEI	Polyethyleneimine
PES	Polyethersulfone
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
S&S	Schleicher and Schuell
TMC	Trimesoyl chloride
UF	Ultrafiltration

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