MATHEMATICAL MODELING OF REVERSE OSMOSIS FOR ULTRAPURE WATER PRODUCTION

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PREFACE

This study involved addressing different areas of reverse osmosis processes. An extensive literature review is presented in this thesis. A mathematical model of the reverse osmosis unit, used in the ultrapure water production systems, has been developed in this work. The Kimura-Sourirajan Membrane mass transport model was extended for multicomponent systems with suitable assumptions. Corrections were made in the mass transfer term to include the effect of module geometry, turbulence promoter, and nature of the system, and ions. The membrane model was combined with system material balances, and appropriate empirical correlations, and numerical methods were suggested for solution of the model. The developed model can be extended to handle a number of ions as long as experimental data on different ions and membrane are available.

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NOMENCLATURE

A	Solvent Permeation Coefficient defined by equation (III-23) Pure Water Permeability Constant (gmol $H_2O / cm^2.atm$)(KSA model)
A_M	Surface Area of the Membrane (cm^2)
A_{ch}	Area of the feed channel (cm^2)
A_0	Reference Solvent Permeability Coefficient
B	Solute Permeability Coefficient defined by equation (II-24)
B_0	Reference solute permeability coefficient
c	solution density (cm^2 / sec)
C_{Si}	Concentration of solute i. (cm^2 / sec)
c_{WM}	Concentration of the solvent in the membrane (gmol/cm^3)
D_{SM}	Diffusivity of the solute in the membrane (cm^2 / sec)
$D_{SM}K/\delta$	Solute Transport Parameter (cm/sec)
D_{SW}	Diffusivity of the solute in the water or solvent (cm^2 / sec)
$D_{SW,Ref}$	Diffusivity of the reference soluteJ_W Volumetric Flux of the solvent or water (cm^2 / sec)
D_{WM}	Diffusivity of the solvent in the membrane (cm^2 / sec)
f	real valued function
$J(x)$	Jacobian Matrix
k	Solute mass transfer coefficient (cm/sec)
k_{ref}	Mass transfer coefficient of the reference solute
K_e	Mixing Efficiency of the Turbulent Promoter Nets
K	Interfacial Equilibrium Constant, Partition coefficient or Solubility
L	Length of the Module (cm)
m	mass fraction of the solute
$\dot{m}_{diff}$	Diffusive mass transfer rate (gms/sec)
$\dot{m}_{conv}$	Convective mass transfer rate (gms/sec)
M	Mesh Step of the Turbulent Promoter Nets
M_W	Molecular Weight of the solvent or water

out	value in the output stream

Subscripts

diff	diffusive
conv	convective
0	Standard or Reference value
T	Temperature
P	Pressure
i	Cations
j	Anions
1	Feed Phase
2	Boundary layer phase
3	Permeate Phase
M	Membrane Phase
S	Solute
W	Solvent or Water
ch	Channel
ref	Reference
av	average
NaCl	Sodium Chloride

Greek Letters

Δ	Difference
Ω	Defined by equation (III-26,27)
σ	Product of Mesh Step and Mixing Efficiency of the Turbulence Promoter
ϕ	Osmotic Coefficient defined by equation (II-3)
δ	Boundary layer or film thickness (cm)
η	Solution Kinematic Viscosity (cp)
π	Osmotic Pressure (Bar or Atm)
∂	Partial operator
α	Empirical coefficient for the solvent
β	Empirical coefficient for the solute
ξ	Defined by equation (B-5)

Abbreviations

DI	Deionized (Water)

exp	Exponential
IEX	Ion Exchange
KSA	Kimura-Sourirajan Analysis
MF	Microfiltration
MTC	Mass Transfer Coefficient
Re	Reynolds Number
RO	Reverse Osmosis
Sc	Schmidt Number
Sh	Sherwood Number
TOC	Total Organic Carbon
TDS	Total Dissolved Solids
UF	Ultrafiltration

CHAPTER I

INTRODUCTION

One of the major achievements of the modern technology is the ability to reliably produce large quantities of pure, very pure, and ultrapure water for essential utility, industrial, and medical purposes at low costs. This ability has been due almost entirely to the development of high rate, high capacity cationic and anionic resins. However as requirements for higher and higher quality water have developed, the relatively simple systems of dual- and mixed-bed ion exchange resins have evolved into complex trains, including several pre-treatment and post-treatment units. One of such units is a membrane process called reverse osmosis (RO). Since their introduction in the late 1950's and commercialization in the 1960's, RO membranes have become an integral part of many high-purity water production systems.

Ultrapure Water

A useful definition of water purity levels suggested by Calmon (1972) is presented in Table I.

Table I

Water purity	Resistivity at 25^0 C (MΩ.cm)	Approximate Equivalent of Extraneous Electrolytes (ppm)
Pure	0.1 or more	2 to 5
Very Pure	1.0 or more	0.2 to 0.5
Ultrapure	10.0 or more	0.01 to 0.02
Theoretical	18.28	0.00

According to Calmon (1972) the above conditions are not the only criteria of ultrapurity. Other factors are particulates (subcolloidal, colloidal, and larger), microorganisms, organic compounds, non-ionized inorganic substances, and often gases. Ultrapure water is of critical importance in such areas as (Sudak et al., 1973):

1. Manufacture of semiconductors and microcircuits - for rinsing,
2. Manufacture of other electronic components such as cathode ray tubes,
3. Fossil-fueled power plants with supercritical or once-through boilers,
4. Nuclear industry,
5. Pharmaceuticals,
6. Electroplating,
7. Some food processing, and
8. Medical, chemical, biochemical, and physical research.

Although each industry requires ultrapure water, the particulate contaminants of concern and their residual level varies according to the industry. Although ideally, contaminant-free water should be completely free from all contaminants in any quantity, it is impossible to produce water of this quality, for any length of time. This is primarily because as water is purified, it becomes more and more aggressive and will start to dissolve almost anything into which it comes into contact. For this reason, each industry has established realistic quality requirements for its 'ultrapure water' which constitute a compromise between performance and economic reality. The primary technologies used to produce ultrapure water include:

1. Microfiltration (MF),
2. Ultrafiltration (UF),
3. Reverse Osmosis (RO),
4. Carbon Adsorption,
5. Ultraviolet irradiation, and
6. Ion exchange (IEX)

Why Reverse Osmosis ?

The focus of this work is on the modeling of the RO unit. RO is a membrane separation process. In its ideal definition RO retains all components other than the solvent itself. However most ultrapure water systems are designed to remove >95% of the total dissolved ionic impurities. Some of the reasons for using RO are as follows:

1. The method is efficient at reducing the ionic concentration in the feedwater.
2. The load on the IEX unit is decreased. The life and performance of the IEX resins are extended. The time between regenerations for mixed bed units downstream increases from days to nearly a month.
3. Disposal of waste from the IEX resin regeneration is reduced considerably
4. A major reduction in the regenerant chemicals is achieved.
5. Available water resources generally considered unfavorable as a source for IEX deionization may be used.
6. RO achieves a high degree of silica removal (Ammerer et al., 1990). Silica is one of the many materials that severely foul the resins.
7. RO efficiently removes the organic content of the feedwater and minimizes the effect of these substances on the IEX resins.
8. Bacteria and other microbes in the feedwater are almost completely removed.
9. A high degree of particulates, colloids, macromolecules and molecules are also efficiently removed.

Principles of Osmosis and Reverse Osmosis

Osmosis is defined as the spontaneous flow of pure water into an aqueous solution, or from a less to a more concentrated aqueous solution, when separated by a semipermeable membrane. A semipermeable membrane is one which is permeable to water but not to salts or organic molecules. Water molecules have a stronger tendency to escape from pure water than from a solution. Water flows through the membrane from the dilute to the concentrated side in order to equalize the osmotic pressure of the two solutions.

When pressure is applied to the more concentrated side and exceeds the osmotic pressure, the direction of water flow is reversed and separation of water from the solution becomes possible. Consequently this latter process has been conveniently termed 'RO' or 'Hyperfiltration'. The latter term is used to distinguish the process from other membrane processes such as Ultrafiltration and Microfiltration. However neither 'Osmosis' nor 'RO' is an explanation of the mechanism of the process involved, and hence it is misleading to explain 'RO' as the reverse of 'Osmosis' (Sourirajan, 1970). The distinction between the two terms is entirely one of arbitrary convention and popular usage.

Reverse Osmosis Membrane Separation Process

RO is a pressure driven process widely used for separation, concentration or fractionation of substances in fluid solutions. It is the first membrane-based separation process to be widely commercialized, and consists of passing a pressurized feed solution over one surface of the membrane and withdrawing the membrane permeate generally at atmospheric pressure and surrounding temperature. The development of the process has been supported largely by the Office of Saline Water of the United States Department of Interior. They were primarily interested in the application of the process to water desalination, for which it is most widely used. Thus most of the experimental and theoretical studies and equipment development and testing have been concerned with water desalination, purification and renovation. However their application is no longer limited to desalination. RO is now widely used in various industries. This process is attractive for several reasons, namely:

1. The process is inherently simple,
2. The same principle can be applied to a variety of problems in many different fields such as desalination, high-purity water production, waste treatment, etc.
3. There is no phase change involved. This reduces the energy requirement. And,
4. The operation is essentially at ambient temperature which is very important in certain applications where temperature-sensitive substances are involved.

The last advantage is particularly important in biological, pharmaceutical, and food processing applications. Baker et al. (1991) lists industries and RO markets within that industry, grouped by their maturity status. The manufacture of ultrapure water is an increasing application. The first application for boiler feedwater was reported by Rowland (1971). Since then it has found wide acceptance among every user of ultrapure water due to a reputation of being economical and reliable. In a recent survey of the power industry, 89% replied that they would consider a membrane process during the next major upgrade (Slejko, 1994). RO has been widely used in the semiconductor industry in water treatment systems. Another new industry, cogeneration, which is a subsegment of power generation, also commonly uses RO for high purity water treatment.

Modeling of Reverse Osmosis

The knowledge of individual ionic rejection rates and flux are very important for any high purity water production system using RO since it determines the TDS (total dissolved solids) loading rate of the feedwater and the effective operational period without membrane cleaning. With RO 90% to 95% of the dissolved solids in the feedwater is normally removed. The ionized solutes are not all removed to the same degree. Divalent and multivalent ions, such as calcium, magnesium, sulfate, iron and manganese, can be rejected to greater than 99%. Sodium, potassium, and chlorine are normally rejected to the 90% to 95% level. In order to fully understand RO, a good mathematical description of the process is required. Much research has been dedicated to the understanding of transport in RO type membranes (Sourirajan, 1970; Kedem and Katchalsky, 1958; Lonsdale et al., 1965).

Most of these mass transport models are, however valid for aqueous solutions containing one solute only. Model extension to multicomponent systems is complicated by the general non-availability of the osmotic pressure data, and the possibility of ionic interactions. Most natural waters, and industrial aqueous solutions contain more than one solute. The application of RO for the separation and fractionation of such multicomponent systems is of practical interest. Hence the development of suitable methods for predicting membrane performance for such multicomponent systems, is an area of fundamental importance. However very few studies have been reported on the subject. Some of the earliest investigation with mixed solute systems were made by Sourirajan (1963c, 1964b). Rangarajan et al. (1976, 1978a, 1978b, 1979, 1984, 1985) and Matsuura et al. (1975, 1985) have also done extensive work on this area. However these researcher have not considered the geometry of the membrane modules. Also, most of these models are applicable only to a small membrane area. Industry needs models to describe the performance of large membrane systems such as a number of modules connected in parallel and/or series.

Objective

RO has advanced technologically, unfortunately detailed modeling trails technical application. In applying RO to high purity water production, predicting the rejection of ionic solutes in a mixed system is of fundamental interest. Although the process has been widely studied and modeled for single solute systems, and many design equations have been proposed, the issue of multicomponent system modeling has not been addressed properly. Few references discuss the theory, development, and modeling for multicomponent systems. The objective of this thesis is to model RO to predict multicomponent performance. The highlights of this work are as follows:

1. The effect of module geometry is considered in the model,
2. The effect of concentration polarization is also considered,
3. The system model approach is used,
4. Theoretical framework for the development of a flowsheet simulation software and design software is suggested. And,
5. The available literature in this area is systematized for further investigation.

CHAPTER II

LITERATURE REVIEW

A brief description of RO is presented here. The first detailed textbook on the subject was written by Sourirajan (1970), who is also credited for many major developments in this area. Some other excellent material on the general description and theoretical details of RO can be found in Merten (1966), Spiegler (1966), Harris et al. (1969), Kesting (1971), Lonsdale and Podall (1972), Lacey & Loeb (1972), Meares (1976), Keller (1976), Sourirajan (1977), Guy (1980), Spiegler & Laird (1980), Turbak (1981), Lonsdale (1982), Hwang and Kammermeyer (1984), Belfort (1984), Sourirajan and Matsuura (1985a, 1985b), Bakish (1985), Bungay et al. (1986), Gutman (1987), Parekh (1988), Rautenbach and Albrecht (1989), Porter (1988, 1989), Mulder (1991), and Baker et al. (1991). The material in this section is common among the above mentioned textbooks and many RO articles.

Six major topics will be presented here. These topics include historical background, RO fundamentals, transport models, design methods, multicomponent system modeling, and high purity water applications. The first section reviews the historical development of RO. Basic definitions and principles of RO is covered in the second section. The third section reviews the membrane mass transport models used to describe the solute and solvent transfer across the membrane. These models are the basis of any design methods which are discussed in the fourth section. The fifth section discusses the status of multicomponent system modeling. The application of RO in high purity water industries is covered in section six.

Historical Development

Systematic studies of membrane phenomena started in late eighteenth century. In 1748 Abbe Nolet first coined the word osmosis to describe water permeation through a diaphragm. For the next two centuries, membranes were used as tools to develop physical and chemical theories. Traube (1867) and Pfeffer (1877) used membranes for measurements of solution osmotic pressure. Van't Hoff (1887) based his limit law on the experiments of Traube and Pfeffer. Early investigators used mostly diaphragm made from animal gut. Bechhold (1906) first devised a technique to prepare nitrocellulose membranes of graded pore size. By early 1930's microporous collodion membranes were commercially available. The practical use of these artificial membranes as separation media was not possible for the following reasons (Dresner and Johnson, 1975):

1. Lack of artificial polymeric membranes which could withstand pressure, and be chemically resistant to the solution to be separated,
2. Low rejection and low volume flux through the membranes made them commercially unfeasible, and
3. Lack of fabrication techniques to provide systems with large membrane area per volume ratio.

During the next 20 years this early technology was expanded to other polymers, particularly cellulose acetate. At the end of world war II, membranes would found their first major applications in the filtration of drinking water.

RO as a process emerged from the well known Gibbs adsorption equation (Sourirajan, 1970). Yuster et al. (1958) gave the first conceptual model for recovering fresh water from aqueous salt solutions. This led to the development of RO process and a search for appropriate membranes. Reid and Breton (1959a,b) first discovered the semipermeable properties of cellulose acetate membranes. But the seminal discovery that made RO practicable was the development of the Loeb-Sourirajan process for making defect-free, high-flux, ultrathin RO membranes in late 1950's (Loeb and Sourirajan, 1962). Loeb & Sourirajan developed a method of phase inversion for the preparation of cellulose acetate membranes. The work of Loeb and Sourirajan and the financial support of Office of Saline Water (OSW), United States Department of Interior, resulted in RO commercialization. The next 20-years period from 1960 to 1980 produced a tremendous change in the status of RO. Building on the original Loeb-Sourirajan membrane technology, other processes were developed for making ultrathin, high performance membranes. Membranes are now possible as thin as 0.1 μm or less. Methods of packaging membranes into spiral-wound, hollow-fine-fiber, capillary and plate-and-frame modules were also developed and advances were made in improving membrane stability. As a result RO is today a well established process. Historical details can be found in Ferry (1936), Merten (1966), and Lacy & Loeb (1972). Table II traces some milestones in the development of RO.

Table II

1867	Traube	Performed successful experiments with artificially prepared membranes.
1950s	Reid and Breton, university of Florida	Discovered selective desalination properties of cellulose acetate membranes.
1960	Loeb, Sourirajan, and co-workers, University of California, Los Angles	Developed processes for preparation of asymmetric membranes.
1961	Havens, Clark, and Guy, Havens Industries	Invented and developed porous fiberglass tubes containing asymmetric membranes.
	McMohan and Brown, Dow Chemical	Developed Cellulose Triacetate (CTA) hollow fibers and 'ball of twine' membrane element.
	Office of Saline Water, Department of Interior	Began large-scale funding of development of membranes, modules, systems, etc.
1964	Havens, Clark, and Guy, Havens Industries	Demonstrated two-stage sea water conversion plant at south bay plant of San-Diego Gas and Electric

	Keilin, Aerojet General	Investigation of role of membrane salt as a swelling agent in the cellulose diacetate (CDA) membrane.
1964	Francis	Developed the concept of Cellulose acetate thin film composite membrane
1965	Manjikian, University of California, Los Angles	Introduced an all-organic casting solution consisting of cellulose acetate, formamide, and acetone.
	Merten, Lonsdale, and Riley, General Atomic	Advanced the solution-diffusion model of membrane transport.
	Lonsdale, General Atomic	Investigations by electron microscope of a modified membrane confirmed predicted asymmetry.
	Sherwood and Brian, Massachusetts Institute of Technology	Determined the magnitude of boundary layer effect.
1966	Merten, Vos, and Hatcher, General Atomic	Importance of pH effect on CA membrane life.
	Westmoreland and Bray, General Atomic	Developed spiral-wound membrane module.
1967	DuPont	Developed B-15 polyamide hollow fiber permeator.
1968	Merten, Lonsdale, Riley, and Vos, General Atomic	pH effect on membrane life supported by additional research. Membrane dehydration.
	DuPont	Application of nylon hollow fiber modules to brackish water commercialized.
1970	King et al.	Developed Cellulose Acetate blend membrane.
	DuPont	Developed B-9 Polyamide hollow fiber permeator.
1972	Cadotte and Rozzell, North Star Research	Developed the NS-1 composite membrane using condensation polymerization.
	DuPont	Developed B-10 Polyamide hollow fiber.
1974	Dow	Developed Cellulose Triacetate hollow fiber permeator.
1976	Fluid Systems	Commercialized aryl-alkyl polyetherurea thi film composite membrane.
1977	Riley, Fluid Systems	Developed TFC membrane spiral - wound modules.
1978	Cadotte	Developed FT30 fully aromatic polyamide thin film composite membrane.

1985	Clark, Dow Chemical	Developed the quantum module. A 50 to 10 M gpd 'perfect' configuration for brackish water.
1986	DuPont	Developed B-15 polyamide thin film composite membrane.
	Fluid Systems, Nitto-Denko, FilmTech, Hydranautics	Modified the membrane lines for low pressure operation.
	Toray	Developed fully aromatic polyamide thin film composite membrane.
1990-2000	? (Research Continuation)	Development of oxidation resistant membrane required.

Source : (Harris et al., 1969; Guy, 1980 ; Baker et al. , 1991).

Fundamentals of Reverse Osmosis

The literature in this area is vast but rarely presented in a systematic manner. Here, an attempt is made to briefly review and discuss RO fundamentals. An exhaustive analysis of RO can be found in Sourirajan (1970, 1977), and Sourirajan and Matsuura (1985a). Parekh (1988) has also covered most of the fundamental aspects of RO, including its applications. Mathematical description of RO, as a membrane process, can be found in Rautenbach and Albrecht (1989), Mulder (1991), Hwang and Kammermeyer (1984), Belfort (1984).

Reverse Osmosis Membranes

A review of RO membranes can be found in Sourirajan (1977), Belfort (1984), Cadotte (1985), Allegrezza (1988), Petersen and Cadotte(1990), Bhattacharyya et al. (1992), and Petersen (1993). Due to the competition among membrane manufacturers, very little information on the preparation and composition of the membranes is available in the open literature. However some good sources are Kesting (1971), Riley et al. (1972), Strathman et al. (1975), Strathman (1986), and Wijman & Smolders (1986).

Petersen (1993) has reviewed the field of thin film composite RO membranes while emphasizing on the chemistry and composition of these membranes. Cadotte (1985) has written a review on this field covering activity from the beginning of composite RO membranes up through 1985. Allegrezza (1988) has summarized the field of commercial RO membranes and has listed commercial membrane products offered by manufacturers as of 1988. A relatively new listing of commercially available RO membranes and membrane manufacturers or suppliers can be found in Gutman (1987), Rautenbach and Albrecht (1989), and Bhattacharyya (1992). Samon (1984) has analyzed the effect of internal and external factors on the RO membranes, on their stability and life. Howell (1990) has listed different materials that have been used as membranes.

The flux through the membrane is as important as its selectivity towards various kinds of solute. When a given material have been selected on the basis of its intrinsic separation properties, the flux through the membrane prepared from this material can be improved by reducing its thickness. The flux is approximately inversely proportional to the membrane thickness and for this reason most RO membranes have an asymmetric structure with a thin dense top layer (thickness $\leq 1\ \mu m$) supported by a porous sublayer (thickness $\approx 50\text{-}150\ \mu m$), the resistance towards transport being determined mainly by the dense top layer. Salt rejection takes place at the surface of the top skin layer with the permeate passing into the porous sublayer. Commercially used RO membranes with asymmetric structures are of basically two types: integral asymmetric and thin-film composite. In integral asymmetric membranes, both the top layer and the sublayer consist of the same material. These membranes are prepared using phase inversion techniques. For this reason it is essential that the polymeric material from which the membrane is to be prepared is soluble in a solvent or a solvent mixture. Because most polymer are soluble in one or more solvents, asymmetric membranes can be prepared from almost any materials. However other restrictions limit the use of all these membranes for RO applications.

Common polymers used in asymmetric membranes are cellulose acetate, cellulose triacetate, and polyamide. The cellulose acetates that are used to make RO membranes generally have 100-200 polymer units and are mostly diacetates or triacetates. These materials have high permeability towards water. However the stability of these membranes against chemicals, temperature and bacteria is very poor. Typical operating condition of these membranes are over the pH range 5 to 7 and at temperature below 80° F, thus avoiding hydrolysis of the polymer. The extent of this hydrolysis decreases as the degree of acetylation increases, and for this reason cellulose diacetate is less resistant than cellulose triacetate. Biological degradation is also a severe problem whilst another limitation of cellulose acetate membranes is their rather poor selectivity towards small organic molecules other than carbohydrates.

In thin-film composite membranes, the surface skin and microporous sublayer are formed from two different polymers. Aromatic polyamide is mostly used for the surface skin with a graded polysulfonate resin used in the sublayer. Thin-film composites are also made from aryl-alkyl polyetherurea and other polymers. The first composite RO membrane was introduced commercially in 1977 by UOP under the codename PA300 (Riley et al., 1977). Since then a number of composite membranes have been introduced commercially. The two most widely used composite membrane in the market are FT 30 membrane, manufactured by FilmTec and PEC 1000 membrane produced by Toray. The technology of composite membranes is developing rapidly and advances in properties is expected in the near future. Riley (1991) has summarized the properties of two main types of commercial polyamide and polysulfonate composite membranes. These materials show high selectivities towards salts, but the water flux is somewhat lower. Polyamides can be used over a wider pH range, approximately from 5-9. The single greatest disadvantage of these membranes is their susceptibility to oxidants and free chlorine in particular. This is because of the structure of the polyamide which contains residual diamines. It is these residual linkages that cause its sensitivity to chlorine. Thin-film composite membranes are resistant to consumption by organisms, and offers the highest flux of any RO membrane. Cellulosic membranes cost less than thin-film composite membranes.

In addition to the composite and asymmetric RO membranes, more specialized types of RO membranes have been developed. Some of these developments are as follows:

1. Composite membrane produced by plasma polymerization (Yasuda, 1977).
2. Dynamic RO membranes (Brandon et al., 1981).
3. Hollow fiber glass RO membranes

Mechanism of Reverse Osmosis

Many mechanisms have been advanced to explain the RO phenomenon. One hypotheses holds that molecules wet the polymeric surface by hydrogen bonding to its polar groups (Breton, 1957; Reid and Breton, 1959). Under the influence of the applied pressure, water manages a passage way through the interstitial polymeric spacings. Therefore the hydrophilic nature of the polymer is a factor. The more hydrophilic the polymer, the greater the density of its polar substituents; and therefore less pressure may be required to intrude water, as into the pores of the hydrophilic filters. The water molecules thus permeate the RO membrane. However the hydrated ions are too large to pass through the RO membrane pores.

The most widely accepted mechanism is the solution-diffusion mechanism (Lonsdale et al., 1965; Lonsdale, 1966). According to this mechanism solvent and solute molecules dissolve into the membrane on the high-pressure side, diffuse through the homogeneous nonporous surface layer of the membrane independently, and emerge on the low-pressure side. A separation results because the solvent and solute diffusion rates are different. For such membranes called perfect membranes (membranes with completely nonporous surface layer), Riley et al. (1967) calculated definite theoretical levels of solute separations in RO from solubility measurements. According to the solution-diffusion mechanism, membranes giving less than such theoretical levels of solute separation are termed 'imperfect' and RO is limited only to perfect membranes.

Anderson et al. (1972) have explained the RO separations on the basis of partition coefficients of solutes between water and cellulose acetate material. Eisenman (1962) and Krasne and Eisenman (1973) have explained the selectivity of membranes for different ions on the basis of the relative free energy of interaction between water and membrane sites. Choi and Bennion (1973) have studied the membrane potential and relativemobilities of alkali and alkaline earth metal chlorides in cellulose acetate membranes. They showed that the relative mobilities of the ions are in the order:

$Li^+ < Na^+ < K^+ \geq Rb^+ > Cs^+$
and
$Be^{+2} > Mg^{+2} < Ca^{+2} < Sr^{+2} > Ba^{+2}$

They suggested that the hydrated radius controlled transport rate for small ions, and crystallographic radius controlled the transport rate for large ions.

Glueckauf (1965, 1970), Bean (1969, 1972) and Dytnerskii et al.(1972) have proposed theories for the RO separation of inorganic ions in aqueous solutions using cellulose acetate membranes. Ions are repelled in the close vicinity of materials of low dielectric constant; Consequently, water is preferentially adsorbed at the membrane-solution interface, and positive ion separations are obtainable for ionized solutes in RO. Glueckauf (1965) developed equations to express the repulsion of ions in the close vicinity of materials of low dielectric constant under RO operating conditions. Bean (1969, 1972) extensively analyzed the diffusion through pores and the electric forces which causes ions to avoid a region of low dielectric constant. His results confirmed explicitly with the predictions of Glueckauf analysis. The equations of Glueckauf and Bean are equally applicable for the separation of ionized organic solutes.

According to Dytnerskii et al. (1972), the surface of RO membrane is assumed to contain capillary pores of various sizes. When a hydrophilic RO membrane is in contact with an aqueous solution of an electrolyte, an equilibrium layer of bound water forms both the membrane surface and the walls of the capillaries. The hydrated ions, because of their size, are not transmitted through most of the capillaries. On application of pressure, liquid flows through the capillaries disrupting the initial equilibrium and decreasing the thickness of the bound water layer on the membrane surface; simultaneously, the bound water equilibrium is reestablished by the interaction of the membrane with the hydrated-envelopes of close-by ions which are thus partially dehydrated and reduced in size so as to be able to pass through the membrane capillaries. Consequently the extent of RO separation of ionic solutes depend on the degree of dehydration of the ions or the strength of the hydration envelope of ions. This strength is different for different ions depending on the ratio of the ion-solvent and membrane-solvent interactions. The strength of the hydration envelopes of ions, and consequently separation of ionic solutes in RO, increase with decrease in crystallographic radii of ions and with increase in their charge. The ion contained in water are of different sizes. The greater the ion's electric charge and the smaller the ions crystallographic size, the more water molecule it binds into its hydration shell, and the larger its actual overall dimension. Therefore, a calcium ion of atomic weight 40.1 with two charges is larger in its overall hydrated size than the hydrated sodium ion of atomic weight 23 with one charge. The hydrated ions militate against the pores of the RO membranes, and because of the size, the calcium ion is more easily excluded than is sodium ion.

More than size exclusion is involved in RO. A solubility influence, namely cohesive energy density also plays a role (Meltzer, 1991). When the cohesive energy densities of the polymer and organic compound are sufficiently close, they will form a solid solution. This permits the passage of one through the other. Thus certain organic molecules, such as phenol, formaldehyde, and acetic acid, are passed preferentially by cellulose acetate membranes.

Sourirajan (1970) has proposed the Preferential Sorption-Capillary flow mechanism. According to this mechanism, RO separation is governed by two distinct factors, namely :

1. An equilibrium effect which is concerned with the details of preferential sorption in the vicinity of the membrane surface, and
2. A kinetic effect which is concerned with the mobilities of solute and solvent through the membrane pores.

While the equilibrium effect is governed by repulsive and / or attractive potential gradients in the vicinity of the membrane surface, the mobility effect is governed both by the equilibrium effect and the stearic effects associated with the structure and size of molecules relative to those of the pores on the membrane surface. Consequently, an appropriate chemical nature of the membrane surface in contact with solution and the existence of pores of appropriate size and number on the area of the membrane at the interface together constitute the twin-requirement for the practical success of the RO process. The surface layer of a practically useful RO membrane must be as thin as possible in order to minimize resistance to fluid permeation through membrane pores, and consequently, the entire porous structure of the membrane must be asymmetric. Sourirajan concludes RO is governed by a surface phenomenon. Figure 1. shows the schematic representation of preferential sorption-capillary flow mechanism for RO separation of sodium chloride from aqueous solutions. Whatever the mechanism involved, in my personal opinion none of these mechanisms give a complete and satisfactory explanation of the process.

Osmotic Pressure

Osmotic pressure is a very important quantity in RO. The phenomena of osmosis is already described in chapter I of this thesis. In osmosis, transport occurs due to the chemical potential driving force which is caused by the presence of the solute. The exact

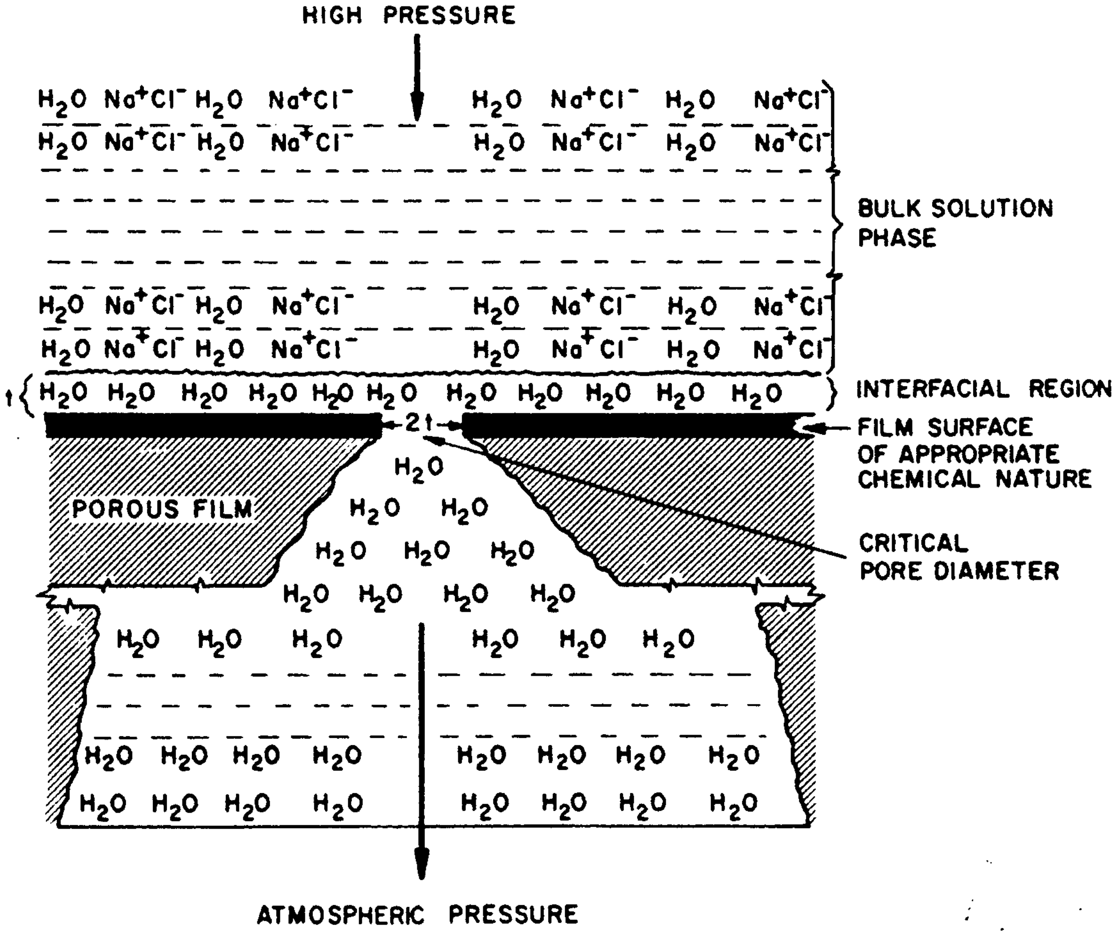

Figure 1: Schematic Representation of preferential sorption-capillary flow mechanism (Sourirajan, 1963a)

pressure that must be applied to stop the solvent flux is called Osmotic pressure. Osmotic pressure is a thermodynamic property of a solution. The osmotic Pressure of a solution, π_i, is related to the mole fraction of the solvent, X_{wi}, as (Castellan, 1971):

$$\pi_i = -(\frac{RT}{\breve{V}_W}) \ln X_{Wi} \qquad \text{(II-1)}$$

Where R is the universal gas constant, T is the temperature and $\breve{V}_W$ is the partial molar volume of the solvent. For dilute solutions the above equation simplifies to the Van't Hoff equation (Castellan, 1971) as:

$$\pi_i = C_{si} RT \qquad \text{(II-2)}$$

Where C_{Si} is the concentration of solute 'i'. Therefore, the osmotic pressure difference across a membrane, $\Delta\pi$, is related linearly to the concentration difference, $C_{S2} - C_{S3}$. Osmotic pressure can also be defined in terms of data on osmotic coefficients (ϕ) available in the literature (Robinson and Stokes, 1965), by the relation

$$\pi = \sum_i RTM_W m\phi / 1000\breve{V}_W \qquad \text{(II-3)}$$

where $\sum_i$ = total number of moles of ions given by one mole of an electrolytic solute or $\sum_i = 1$ for a non-ionized molecular species. Although the above three equations are useful, it is preferable to use experimental data on osmotic pressure if the information is available. Data on osmotic pressure is available in the literature for a number of aqueous solutions (Sourirajan, 1970; Weast, 1983). Most waters treated by RO have substantial osmotic pressure. For sea water, $\pi \approx 25$ atm, while for most brackish waters $\pi \approx 1$-4 atm. For tapwater containing 500 ppm of TDS, the osmotic pressure is about 0.4 atm. Also osmotic pressure increases as water is removed from the solutions. An useful rule of thumb for estimating the osmotic pressure of a natural water is 1 psi (pound per square inch) per 100 milligrams per liter of dissolved salts (Belfort, 1984b). For NaCl solutions,

π (atm) = 8.0 × wt% (at 25° C)

Driving Forces for Transport

In RO systems, the driving forces of interest are pressure and concentration. The cross-influence of solute concentration driving force on solvent flux is represented by the osmotic pressure term in the solvent flux equation. The cross-influence of pressure driving force on solute flux is often small, for high separation membranes, and is therefore neglected. The solvent flux equation indicates that flux is directly proportional to the effective pressure driving force (Sourirajan, 1970):

$$N_W = J_W C = A(P - \Delta\pi) \tag{II-4}$$

where J_W is the volume flux of the solvent, N_W is the molar flux of solvent, C is the molar density of the solution and A is the appropriate proportionality constant. The effective driving pressure ΔP is the driving force for solvent flow through the membrane and can be given as:

$$\Delta P = P - \Delta\pi \tag{II-5}$$

Where P is the operating gauge pressure on the high pressure side of the RO membrane, (the low pressure side of the membrane being at atmospheric pressure), and $\Delta\pi$ is the difference between the osmotic pressure of the solutions on the high pressure and low pressure sides of the membrane. The above equation implies that $\Delta\pi$ represents the chemical potential barrier for solvent transporting RO. This is strictly true only when there is no solute in the membrane pores, and hence solute separation is 100%. When there is solute in the membrane pores, the osmotic pressure of the solution in the pores has to be taken into consideration. Therefore, in actual RO process, the net chemical potential barrier is not $\Delta\pi$, but a factor times $\Delta\pi$. This factor may be equal to or less than unity, or even a negative number, depending on the magnitude of the interfacial forces involved, and the average pore size on the membrane surface. Therefore the above equation is not always strictly true. However in most practical systems the above factor is very little less than unity. For this reason equation (II-4) is practically valid for such systems.

Operational Considerations

(A) Pressure: As mentioned before, RO is a pressure driven separation process. The pressure imposed on the feedwater in RO operation has two components:

1. That required to overcome the osmotic pressure if the solution to liberate the pure water, and
2. That required to overcome the resistance to flow posed by the membrane.

A salt containing water can have an osmotic pressure of 350 to 500 psig. However, many RO systems in the high purity water industry is operated on municipally treated waters. These generally have osmotic pressures of about 1 psig per 100 ppm of total dissolved solids. A feedwater of 100 ppm of TDS would require only 1 psig of pressure to overcome its osmotic pressure; the remainder of the applied pump pressure would drive the water flow and determine its rate of permeation. In most actual plant operations, the applied external pressure serves virtually to drive the water. Applied pressure is usually from 200 to 500 psig. The feed water entering an RO unit emerges in two sections: the permeate stream and the reject stream or the concentrated stream. A schematic diagram of the process is given below in Figure 2. Water flux through the membranes varies directly with the applied external pressure. Higher pressure forces flow through pores that are too small to be involved at low pressures. At higher pressures, the water tension at the smaller pores are broken, bringing them into production (Comb, 1991). Above 30 psig there is no practical effect on the rejection of the ions. However a certain minimum pressure is required in any RO operation to keep the rejected stream turbulent in order to enable it to clean the membrane surface free of polarizing contaminants. The effect of pressure on RO performance is shown in Figure 3.

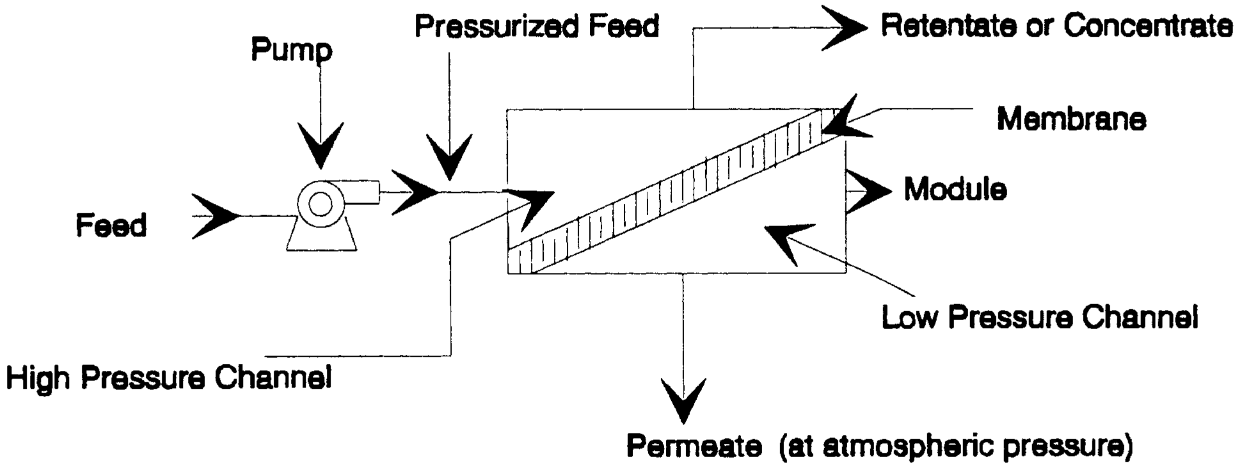

Figure 2: Schematic Diagram of RO.

(B) Temperature : The effect of temperature on rejection can be approximated to be linear. As the operating temperature of a RO unit increases, both the solute and the solvent permeabilities increases. However the ion rejection decreases with increase in temperature, since the apparent activation energy for salt is greater than that of water. Temperature is an important factor in the design of RO units. The increase in temperature of the feed water reduces feed viscosity thereby facilitating its flow through the membranes. In practice the membranes are rated at 25° C. However this does not imply that the membranes are to be operated at this temperature. RO operations become practical at a feed water temperature of 10° C. The effect of temperature on the performance of RO systems is shown in Fig 3. A high temperature generally enhances the membrane compaction and deterioration, and therefore shortens the life of the membrane. There is a 3% increase in flux for every 1 C temperature rise near room temperature, and salt rejection declines slightly with increasing temperature.

(C) pH: As mentioned earlier cellulosic membranes are normally operated in the pH range of 5-7. This usually requires an acid feed. At an increased pH degradation of the membranes take place. But the thin-film composite membranes can be operated at a wider pH range of 5-9. The pH of the feedwater does not contribute importantly to the RO performance as regards sodium chloride, but it does affect bicarbonate and carbon dioxide. pH control is practiced to minimize hydrolytic degradation, but pH adjustment is generally recommended in RO processing to minimize membrane fouling.

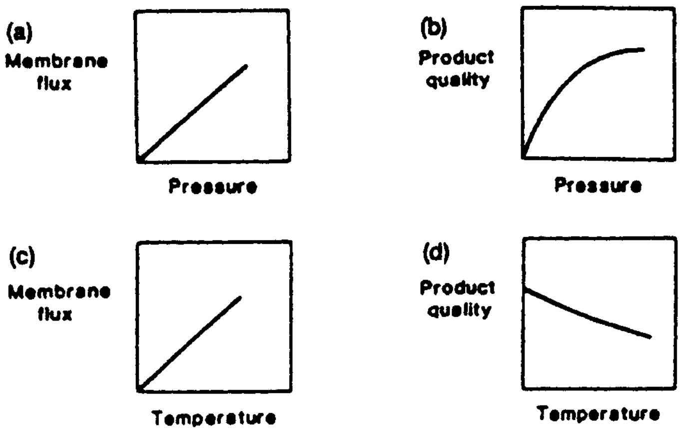

Figure 3: Effect of Pressure and Temperature on the performance of RO (Source: Riley, 1991)

RO Membrane Performance

A number of different expressions are used to represent the performance of RO membranes.

Recovery

Recovery is defined as the percentage of the feedwater flow that is converted into permeate or product water. Typically for large systems it is about 75% to 80%. The other 20% to 25% of the treated feedwater is usually rejected. It is a costly waste. The more concentrated the feedwater the less is recovery. It is good practice from economic standpoint to somehow utilize the reject stream. Usually it is used as makeup for cooling towers, for compressor cooling, and even for watering the grass. The reject stream comes off from the RO unit under pressure. Therefore, the costs of storage and repumping can be avoided. For these reasons its volume is best minimized. Recovery also influences rejection. Mathematically,

$$Y = \frac{Q_3}{Q_1} \times 100 \qquad \text{(II-6)}$$

where Q_3 is the permeate flow rate, Q_1 is the feed flow rate and Y is the recovery.

Rejection

The rejection of ions and soluble organics varies from membrane to membrane. Higher rejection rates is always accompanied by lower recovery rates. However performance data are not easily obtained and compared due to conflicting claims of competitive market and different interpretation of data and operating conditions. Not all ions are equally rejected. Divalents are generally rejected to upward of 99% by polyamide. But the monovalent ions are rejected to about 97%. For this reason, sodium and chloride ions, being comparatively difficult to reject, are used to characterize RO membrane rejection qualities. A typical ion rejection by RO is presented in Table III below. Sourirajan (1963, 1964) showed that for cellulose acetate membranes, anions could be arranged in the following decreasing order of rejection: citrate, tartrate, sulfate, acetate, chloride, bromide, nitrate, iodide, and thiocyanide; and cations in a like order: magnesium, barium, strontium, calcium, lithium, sodium, and potassium.

RO units reject organics rather well if these organics are larger than 200 in molecular weight for cellulosic membranes and over 100 for thin-film composite membranes. Generally, TOC reductions of a high order are effected by RO.

According to the Glueckauf model (1965), the rejection increases with valence and the unhydrated ionic radius. Blunk (1964) found that, when a monovalent anion is associated with hydrogen or ammonium, the tendency is reversed as follows: HI > HBr >

Table III : Ion rejection by RO (Rickli and Zurcher, 1980)

Cations	Maximum salt rejection %	Maximum attainable conc. in the concentrate %	Anions	Maximum salt rejection %	Maximum attainable conc. in the concentrate %
Na^+	94-96	3-4	Cl^-	94-95	3-4
NH_4^+	88-95	3-4	F^-	94-96	3-4
Ag^+	94-96	-	NO_3^-	93-96	3-4
Ca^{2+}	96-98	-	CN^-	90-95	4-12*
Mg^{2+}	96-98	-	SO_4^{2-}	99	8-12
Cd^{2+}	95-98	8-10	SiO_3^{2-}	95-97	-

Fe^{2+}	98-99	-	CrO_4^{2-}	90-98	8-12
Ni^{2+}	97-99	10-12	PO_4^{3-}	99	10-14
Zn^{2+}	97-99	-	$[Fe(CN)_6]^{3-}$	99	8-14
Cu^{2+}	96-99	8-10			
Al^{3+}	99	5-10			

* dependent upon pH-value

$HCl > HF$; $NaClO_4 > NH_4ClO_4 > HClO_4$, and $NaNO_3 > NH_4NO_3 > HNO_3$. On the other hand , most divalent and trivalent electrolytes are relatively well rejected. The rejection increases with the molecular weight of the oragnic solutes, in the homologue series, and for isomers, tertiary > iso- > secondary > primary. For polar substances of low molecular weights, aldehyde > alcohol > amine > acid.

Rejection is usually expressed as percentage and is defined in terms of feed and permeate molal concentrations, C_{S1} and C_{S3}, respectively:

$$R = \frac{C_{S1} - C_{S3}}{C_{S1}} \times 100 = 1 - \frac{C_{S3}}{C_{S1}} \qquad \text{(II-7)}$$

Where R is the rejection. Since concentration polarization causes a high solute concentration at the membrane wall, the rejection coefficient based on the bulk solution concentration will be lower than expected. The separation based on the boundary layer concentration, R', can be written as:

$$R' = \frac{C_{S2} - C_{S3}}{C_{S2}} \qquad \text{(II-8)}$$

where C_{S2} is the concentration at the membrane surface. The separation calculated in this manner represents the separation that would be measured with perfect mixing on the high pressure side of the membrane. The observed rejection can be related to the actual rejection by a mass transfer model.

Tangential Flow or Cross-Flow filtration

In RO separation, the conventional mode of filtration is inappropriate. It requires, what is called "Crossflow Filtration". Crossflow (also called tangential flow) filtration is the pressurized flow of the feed water, or influent, across a membrane, with a portion of the permeating the membrane and the balance of the feed sweeping tangentially along the membrane to exit the system without being filtered. Because the feed and the concentrate flow parallel to the membrane instead of perpendicular to it, the process is called "crossflow" or "tangential flow".

Figure 4 shows a schematic diagram of crossflow filtration. This serves to remove or at least reduce the polarized layer of particles whose accumulation on the membrane surface would otherwise prematurely shorten the useful service life of the RO device. Crossflow velocity is the average of the feed and concentrate or reject flows. Its practical measure may be made in terms of the feed flow rate. The economic considerations of tangential flow filtration were investigated by Korin (1990). Because of the crossflow, RO separate fluids into two product streams. These are the permeate which is depleted of certain solutes and, the concentrate or the retentate, which is enriched in these solutes.

Concentration Polarization

In RO some of the ions or solutes in the solution are rejected by the membrane. Before steady state the convective flow of these components to the membrane surface is greater than that due to diffusion backflow to the bulk solution. Because of this an accumulation of the rejected species takes place at the membrane surface. This phenomena is called concentration polarization. RO membranes achieve the rejection of the solutes or ions because the flux of solvent through the membrane is much higher than the flux of the rejected solute. At steady state, solute is assumed not to accumulate on the membrane, so that solute transport by diffusion away from the membrane surface must take place simultaneously with convective transport towards the membrane. For this reverse diffusion to occur, a negative concentration gradient must exist, with a higher solute or ion concentration at the membrane surface than in the bulk solution. Therefore in order to analyze the problem of concentration polarization, one must understand the transport phenomena at the membrane-solute interface.

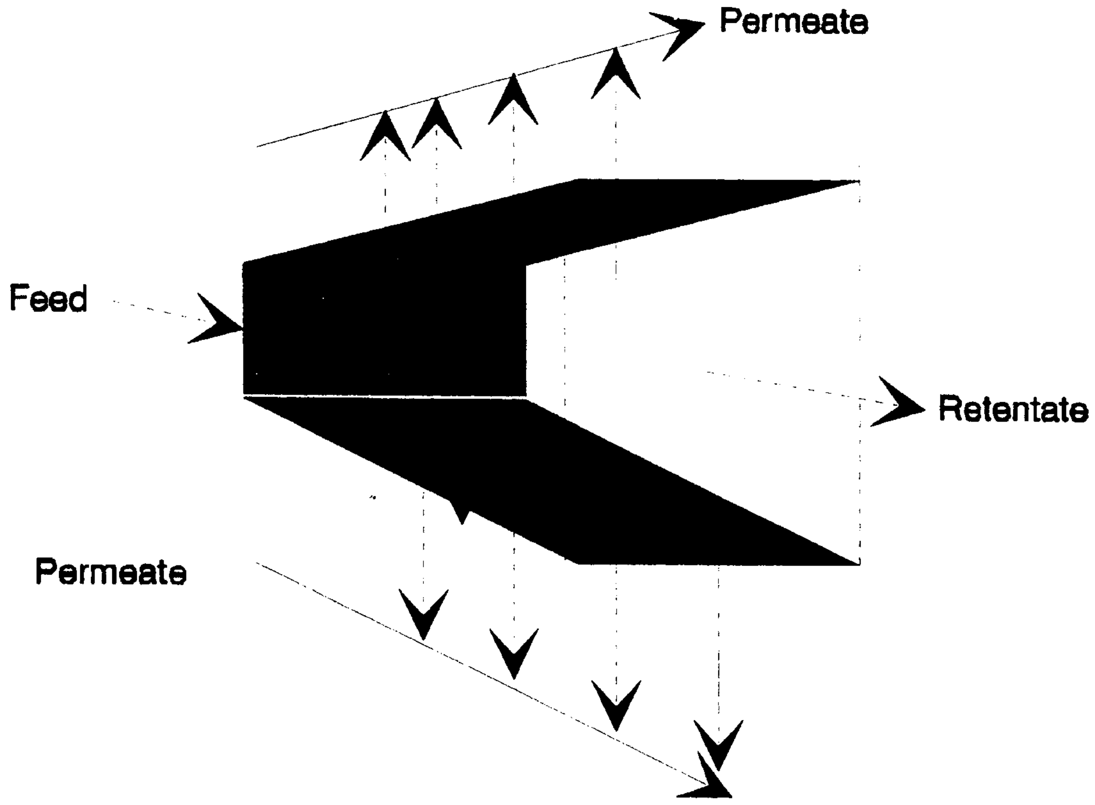

Figure 4: Crossflow Filtration.

The factors influencing this phenomena are as follows:

1. Fraction of solute rejected by the membrane,
2. Distribution of feed flow over the membrane surface,

3. Geometry of the RO module, and
4. Concentration and nature of the solute deposited on the membrane surface.

It is frequently a serious problem in membrane operations. The consequences are (Matthiasson and Sivik, 1980):

1. An increase in chemical potential at the surface reduces the driving force for the filtration,
2. If the wall concentration of solute reaches the saturation concentration, precipitation on the membrane surface increases the hydrostatic resistance, and
3. High concentration of solute at the membrane interface increases the risks for changes in composition of the membrane material due to chemical attack.
4. The deposition of the solute on the surface can change the separation characteristic of the membrane.

Therefore, in economic appraisal of RO, it is important to have accurate equations predicting solute build-up at the membrane surface. Also in fundamental modeling the effect of concentration polarization must be predicted to evaluate the solute rejection mechanisms.

The concentration polarization of ions tend to become progressively worse as the membrane operation continues. As the effective filtration area decreases due to carbonate, sulfate, or other scaling, the water flux decreases and there is a decrease as well in ion rejection by the membrane. This decrease in permeate rejection gives an indication of concentration polarization. Minimization of concentration polarization necessitates the use of crossflow or tangential cycling mode. The velocity of crossflow must be in the turbulent flow regime (above Reynolds number of 3000). Different types of mixing promoters have been used in the feed flow channel to induce turbulence such as spiral-wound module.

Dresner (1964), Fisher et al. (1964), Sherwood et al. (1965), Brian (1965) and Gill et al. (1965) are the first few investigators who attempted to analyze the concentration polarization in RO using the equations of change (Bird et al., 1960). Dresner (1964) analyzed the thin-channel problem under laminar flow conditions for a case of complete solute rejection and constant wall permeation flux. With these assumptions, the transport equations were decoupled and, using the velocity field given by Berman (1953), Dresner obtained an approximate solution for concentration polarization. Fisher et al. (1964) modified Dresner's solution and applied it to tubular membranes. Sherwood et al. (1965) solved the same problem as Dresner (1964) using a Graetz-type analogy. Brian (1965) studied the same problem but with variable wall flux conditions. Assuming that the osmotic pressure is proportional to salt concentration and that the transmembrane pressure drop is insignificant, Brian obtained a concentration-dependent wall-permeation velocity. To solve the diffusion equation by a finite-difference method as a part of an iterative scheme, Brian used the fluid flow field given by Berman (1953), but excluded the terms containing the wall Reynolds number. Gill et al. (1965) also solved the same problem using a perturbation series solution. Since then a large number of analyses of concentration polarization have appeared (Raridon et al., 1966 ; Kimura and Sourirajan, 1968; Strathman and Keilin, 1969; Sheppard and Thomas, 1970 ; Srinivasan and Tien, 1970; Gill et al., 1971; Johnson and McCutchan, 1972; Hieber, 1974; Doshi and Gill, 1975; Hung and Tien, 1976; Chang and Guin, 1978; Drioli and Belluci, 1978; Mahlab et al., 1978; Leung and Probstein, 1979; Mathiasson and Sivik, 1980; Kleinstreuer and Paller, 1983; Ma et al., 1985; Gill et al., 1988; Illias and Govind, 1993). An excellent review of concentration polarization and fouling can be found in Matthiasson and Sivik (1980).

The effect of concentration polarization can be modeled by two fundamentally different approaches. The first approach is by the numerical integration of the transport equations (i.e. mass and momentum balances with the corresponding laws of diffusive transport). The analysis by this method is complex and can be found in Rautenbach and Albrecht (1989). The other approach is by the film model (Bird et al., 1960), originally proposed by Sourirajan (1970), based on the concept of mass transfer coefficients (MTC). The second approach is considered here.

The film model assumes that even in turbulent flow a laminar boundary layer is present next to the membrane surface. During the transport process, a steady state is achieved where the convective transport of solutes to the membrane surface is counterbalanced by a diffusive flow of the rejected solutes from the membrane surface. Let C_{S1} and C_{S2} are the concentration of the bulk solute and the concentration of the solute at the membrane surface and 'δ' is the boundary layer thickness. The back diffusion from the membrane can be assumed to follow Fick's law:

$$D_{SW}\frac{dC_S}{dy}$$

Where D_{SW} is the diffusivity of the solute and $\frac{dC_S}{dy}$ is the rate of change of solute concentration. The flux of the solute to the membrane is:

$$\frac{C_S}{C}(N_S + N_W)$$

All symbols are defined in the notation section. At steady state, mathematically:

$$N_S = \frac{C_S}{C}(N_S + N_W) - D_{SW}\frac{dC_S}{dy} \tag{II-9}$$

Rearranging the above equation and integrating with the appropriate boundary conditions (Kimura and Sourirajan, 1967; Sourirajan, 1970) :

$$C_{S2} = C_{S3} + (C_{S1} - C_{S3})\exp(\frac{N_S + N_W}{C}\frac{\delta}{D_{SW}}) \tag{II-10}$$

Defining the mass transfer coefficient in the conventional manner of the film theory (Bird et al., 1960),

$$k = \frac{D_{SW}}{\delta} \tag{II-11}$$

Substituting this in equation (II-10), we have:

$$C_{S2} = C_{S3} + (C_{S1} - C_{S3})\exp(\frac{N_S + N_W}{kC}) \tag{II-12}$$

The ratio of $\frac{C_{S2}}{C_{S1}}$ is often known as concentration polarization modulus. This quantification of concentration polarization is specific to flat geometry. Because the geometry in a spiral-wound module and hollow-fiber module are complex, the ratio is extremely difficult to quantify analytically. However the above expression can be effectively used, since the membrane thickness is extremely thin.

The magnitude of the MTC, k, is a function of the nature of the solute, its concentration, membrane-parallel feed flow rate (degree of turbulence) on the high pressure side of the membrane and the cell geometry. This model predicts that the degree of concentration polarization is determined by the diffusion coefficient of the solute, the feed flow rate and thickness of the boundary layer. The diffusion coefficient is usually determined by the solute and the solvent used, and the feed flow rate is properly maintained as high as possible, so that the effect of concentration polarization is normally controlled by reducing the thickness of the boundary layer. This is normally achieved by using a high recirculation rate to create turbulence near the membrane surface, on the high pressure side. As mixing on the high pressure side increases, the MTC increases and concentration of the solute near the wall, C_{S2}, decreases and approaches C_{S1}.

The MTC is not affected by the flux itself. It is suggested that a Sherwood type relationship for forced convective flow:

$$\mathrm{Sh} = f\,(\mathrm{Re}, \mathrm{Sc}, \mathrm{Geometry}) \tag{II-13}$$

can be used to determine the MTC, since the total density and diffusivity vary only little across the boundary layer.

For turbulent flow conditions , the most popular correlations used are those based on the Chilton-Coulbourn (Bennet & Myers, 1982) and Deissler (1961) analogies:

$$\mathrm{Sh} = 0.023\,\mathrm{Re}^{0.8}\,\mathrm{Sc}^{0.33} \tag{II-14}$$

$$\mathrm{Sh} = 0.023\,\mathrm{Re}^{0.875}\,\mathrm{Sc}^{0.25} \tag{II-15}$$

The above mass transfer correlations are borrowed from non-porous smooth duct flow and their application in the case of membrane operations have been criticized by many authors, since neither the porosity and roughness of membrane nor the change of physical properties like viscosity or diffusivity due to concentration polarization are taken into consideration. Belfort and Nagata (1985) have shown that friction coefficients are higher for flows in a duct with wall suction. Chatterjee and Belfort (1986) have developed velocity profiles and pressure distribution for cases with wall suction. Belfort (1989) has given a review of various fluid flow models incorporating permeation. Gekas and Hallstrom (1987) have proposed modified correlation for cases with porous walls. Gekas and Olunde (1988) have tried to experimentally verify various correlations. Recently Ramani (1992) has derived a correlation based on a new concept of MTC. All these studies have given a new direction to the study of mass transport mechanism in RO.

As to be discussed latter, spiral-wound modules cover 90% of all the RO units used. In these modules turbulent promoters or channel spacers are usually used to increase the streamwise velocity parallel to the membrane surface and increase the MTCs. One approach is to consider that within the spacing nets or fibers the concentration increases, and when the feed passes over the nets, the solution is mixed to a new uniform concentration. The mesh step model, derived by Winograd et al.(1973) has been used to describe the concentration polarization and mixing phenomena.

This model characterizes the net by two parameters; the pitch (or mesh length) and the mixing efficiency of one mesh. The hypothesis is that the fluid, when coming into contact with the net of one mesh, undergoes a more or less complete mixing depending on the efficiency, which tends to make it homogeneous, thus restoring concentration equality. According to the mesh step model, the spacing net effect on the MTC, k, can be described as:

$$k = D_{SW}^{2/3} \eta^{-1/6} A_{ch}^{-1/2} (0.753) [\frac{K_e}{(2-K_e)M}] Q_l^{1/2} \qquad \text{(II-16)}$$

For a given module with a given spacing net, both K_e and M should be constant, and hence can be replaced by another constant.

Chiolle et al. (1978) have also proposed a one-dimensional model of RO in parallel-wall channels with turbulent promoting nets. Their model however is based on that of Winograd et al. (1973). Promoter investigation have also been carried out by Shock and Miquel (1987), Chang et al. (1986, 1987), and recently by Polyakov and Karelin (1992).

For a fixed flow rate and cell geometry Matsuura et al. (1974) has shown that 'k' varies as a function of the diffusivity of the solute to the 2/3 power:

$$k = k_{ref} (\frac{D_{SW}}{D_{SW}, ref})^{2/3} \qquad \text{(II-17)}$$

If 'k' is known for a reference solute, then 'k' for any other solute can be estimated using the above equation provided the diffusivity of the solute and the reference solute are known. Essentially in this model it is assumed that 'k' does not varies throughout the membrane system. This assumption is reasonable when the feed flow rate is reasonably constant.

Fouling

Fouling is the deposition and accumulation of suspended and colloidal particles on the membrane surface and within the pores. Fouling is usually an irreversible and time-dependent phenomena, which distinguishes it from concentration polarization phenomena (Merson and Lee, 1976; Suki et al. , 1984; Reihanian et al. , 1983). Excellent review on membrane fouling can be found in Matthiasson and Sivik (1980) and Kleinstreuer and Belfort (1984). Fouling has the greatest influence on RO design. It is the fouling potential of the solution that usually determines the economic feasibility and the success or failure of the membrane application. The fouling potential determines the permeate rate the membrane will produce, which in turn defines the total amount of membrane area needed. This specifies the overall size of the system and the capital and operating costs.

Fouling can be minimized several ways (Phelps, 1991):

1. Selection of the membrane polymer which is least likely to interact with the foulant. This is an area of active research.
2. Increasing the crossflow velocities to 10-20% above the normal velocities. This will often diminish fouling by reducing the degree of concentration polarization.
3. The use of pulsed feed flow, reversing the direction of feed flow (Potts et al. , 1981), and periodic air sparging. These are active areas of research.
4. Pretreatment of the solution by either pH or temperature adjustments (Cheryan, 1986).

5. Optimizing prefiltration, recovery levels, and cleaning frequency. And,
6. Modifying the membrane element design.

The concentration of foulants at the membrane surface increases with increasing permeateflux and product recovery rate. A system designed to operate at a high flux is likely to experience high fouling rates and will require frequent chemical cleaning. The factor used to measure membrane fouling is Silt Density Index (SDI). Empirical correlation between the SDI and fouling have shown that the SDI must be less than 4 or even 3 to minimize the rate of colloidal fouling of membranes or to obtain successful longterm performance. Definition and determination procedure of SDI is discussed in detail in PEM (Permasep Engineering Manual, Bulletin 504, 1982; Quinn, 1985; Ko and Guy, 1988). Epstein (1979) classified fouling as,

1. Precipitating
2. Particulate
3. Chemical reaction
4. Corrosion
5. Biological
6. Freezing

This classification is applied to solid heat transfer but is also partly applicable to membrane surfaces. Detailed discussion on membrane fouling, feed pretreatment, used to minimize membrane fouling, and membrane cleaning can be found in Rautenbach and Albrecht (1989), Mudler (1991), and Guy (1980), Lepore and Ahlert (1988), Kaakinen and Moody (1985), Rudie et al. (1985), and Ridgeway et al. (1984, 1985).

Modules

Practical application of RO requires a compact structure, one offering a high productivity of treated water per unit volume occupied by the device. The main requirement of a membrane module is to arrange the membrane in such a way that the feed stream is separated from the permeate stream. Other requirements are as follows (Belfort, 1988):

1. Mechanical stability, such as supporting a fragile membrane under the operating differential pressures for RO.
2. Hydrodynamic consideration, such as minimizing concentration polarization, including build-up of solute and fouling layers on or in the membrane surface, to impede membrane performance. And,
3. Economic considerations, such as obtaining high membrane-packing density to reduce capital costs of the pressure vessels and designing the unit for ease of membrane replacement.

In practice four different arrangements of membranes are used namely plate-and-frame, tubular, hollow fibers, and spiral-wound. A detailed review of RO membrane modules using fluid mechanics can be found in Belfort (1988). Comparison of various RO modules is presented below in Table IV. (Phelps, 1991; Pohland, 1981). As can be seen from the above table, Spiral-wound and hollow fiber modules are more effective than tubular and plate-and-frame modules. Therefore the trend is towards spiral-wound and hollow fiber modules. Presently, with few exceptions, all commercial units use spiral-wound modules. A brief description of the spiral-wound modules is presented below.

Spiral-wound modules:

Detailed description of spiral-wound modules can be found in Ko and Guy (1988), Turby and sleigh (1974), Pohland (1981), Jackson (1990), Allegrezza (1988), Kremen and Riedinger (1971), Kremen (1977), Larson et al. (1968, 1967), and Riedinger et al. (1968). In these modules, flat sheet membranes are made in long rolls, 40 or 60 inches wide and fabric spacers are placed within these membranes. The three sides of

Table IV.: Comparison of Membrane Configurations

Characteristic	Spiral-Wound	Hollow fiber	Tubular	Plate & frame
Membrane area (m^2 / m^3)	1000	16500	335	165
Device Volume (ft^2 / ft^3)	300	5000	100	50
Cost	Low	Low	High	High
Packing Density	High	Very High	Low	Moderate
Pressure Capability	High	High	Medium	high
Membrane Polymer choices	Many	Few	Few	Many
Fouling Resistance	Fair	Poor	Very good	Fair
Cleanability	Fair	Poor	Good	Fair

these membranes are closed. The fourth, open side is sealed around the openings of a central core. The water that permeates from the outside is directed by the sandwiched spacer to flow into the openings of the central tube. One side of each membrane faces feedwater. The other side interfaces the treated permeate. The spacers are of a mesh construction designed to create turbulence in the flowing feed water stream. The entire assemblage is spirally wound around a central core or pipe. Each such packet is called a leaf. From three to five leafs are normally spirally wound around a core. The feed water enters from one end of the tube surrounding the core with its spirally wound leaves, and concentrate exits the other. The permeating water emerges from the central pipe. The optimization of the membrane surface derives from using two membrane areas per single permeate spacer, and from the disposition of the whole in cylindrical form.

Spiral-wound units come in modular form and can be additively assembled to form units of whatever capacity is required.Spiral-wound modules have the advantage of velocities, thus reducing concentration polarization possibilities. The nature of the spacer materials is an important aspect of RO technology. The first spiral modules to be produced contained cellulose acetate membranes. But the range of membranes currently available are much wider and includes proprietary products from Dupont, UOP, FilmTec, Toray, DDS and Hydranautics. The basic design of spiral-wound module is same except that of Japanese Toray module, in which the feed stream is introduced axially but flows spirally inwards in a similar fashion to the permeate. A typical spiral-wound module arrangement is shown in Figure 5.

Transport Models

The flow of solvent through the membrane is described in terms of a flux. The expression for the volumetric flux of the, J_W, is

$$J_W = \frac{Q_3}{S} \tag{II-18}$$

where Q_3 is the volumetric flow rate of the permeate and S is the membrane surface area. The molar flux, N_W, is

$$N_W = (\frac{Q_3}{S})C_d = (\frac{Q_3}{S})C \tag{II-19}$$

where C_d is the solvent permeate concentration or density. For dilute systems (constant density systems) the solvent permeate concentration can be assumed to be that of the solution. ‘C ‘is the molar density of the solution. The fluxes of solute and solvent

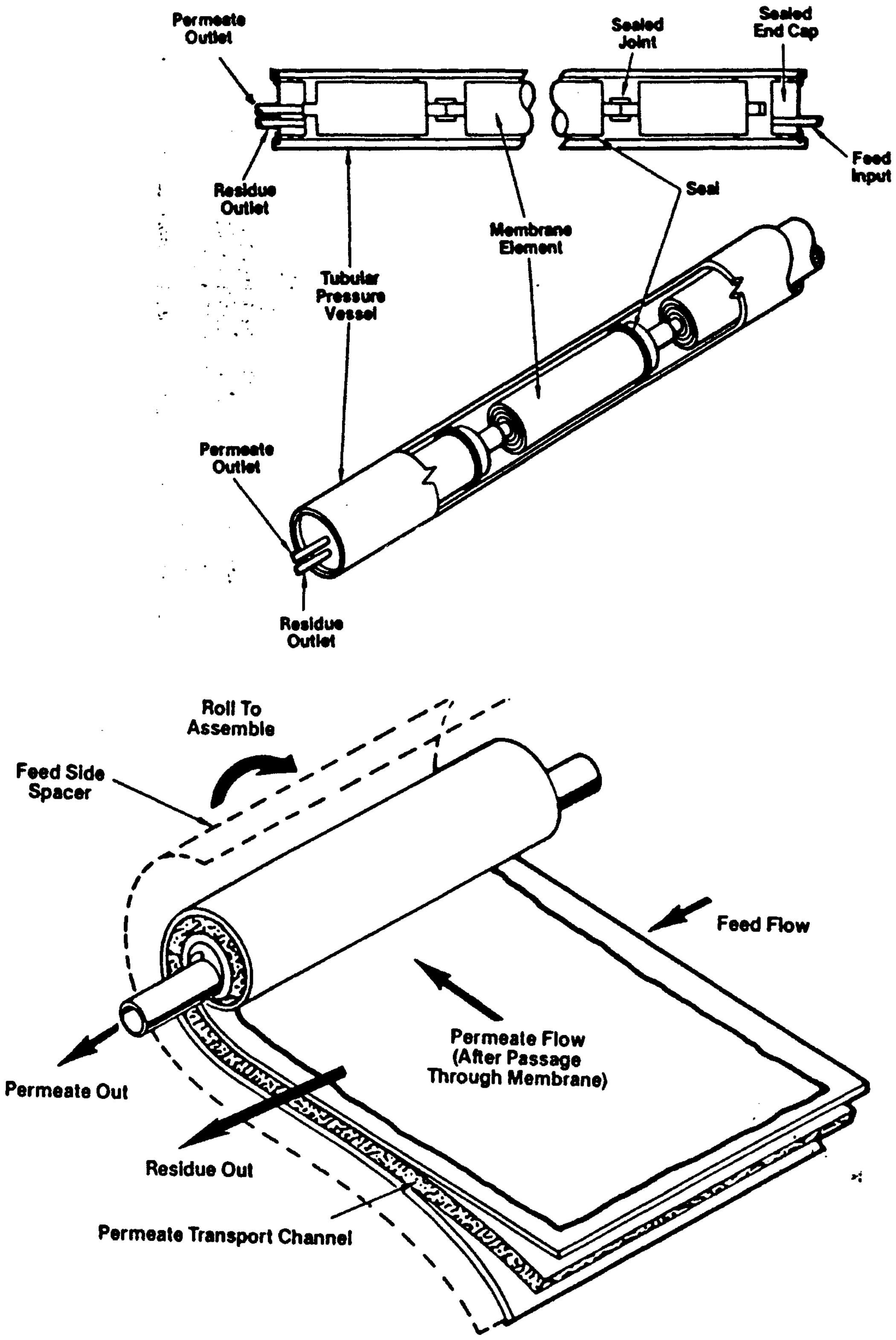

Figure 5: Spiral-wound module

through the membrane are related to the permeate concentration by material balance as :

$$C_{S3} = \frac{CN_S}{N_S + N_W} \tag{II-20}$$

Where N_S is the solute flux.

Many membrane mass transport models exist that describe the transport of solute and solvent through the membrane at constant operating conditions. In these models some of the coefficients have to be determined by experiments. The success of a model can be measured in terms of its ability to describe mathematically the experimental or operational data with the coefficients that are reasonably constant over the range of the operating conditions. In these models the experimental data on flux and separation is converted into some transport coefficients. These transport coefficients are then used along with the model to predict the performance of the RO membranes over a wide range of operating conditions. Several models for the mass transport in RO membranes have been developed. A review of these membrane mass transport models can be found in Jonsson (1980), Soltanieh and Gill (1981), and Dickson (1988).

All the membrane mass transport models are derived from two independent general approaches. The first models developed, are based on nonequilibrium or irreversible thermodynamics, where the membrane is treated as a black box in which relatively slow processes are taking place near equilibrium. These models don't require information on mechanism of transport. Theories of irreversible thermodynamics can be found in deGroot and Masur (1962), and Katchalsky and Curran (1975) among others. In the second approach, some mechanism of membrane transport is assumed and fluxes are related to the driving forces that exist in the system. Thus, in this method the physiochemical properties of the membrane and solution are involved in the model. If all of the information on the membrane and solution is available then one can predict the membrane performance without having experimental data under actual operating conditions. Therefore the second approach is advantageous to the first approach. The models derived by the first approach are called phenomenological models. The models derived by the second approach are also divided into two types. First, the nonporous transport models specifically assume that the membrane is nonporous. Second, porous transport models specifically assume that the membrane is porous. The membrane mass transport models can be classified as follows:

A. Phenomenological models:

1. Kedem-Ketchalsky Model (1958)
2. Spiegler-Kedem Model (1966)

B. Nonporous Transport Models:

1. Solution Diffusion Model (Lonsdale, Merten and Riley, 1965)
2. Solution Diffusion-Imperfection Model (Sherwood et al., 1967)
3. Extended Solution Diffusion Model (Burghoff, 1980; Jonsson, 1980)

C. Porous Transport Models:

1. Finely Porous Model (Merten, 1966)
2. Preferential Sorption-Capillary Flow Model (Kimura and Sourirajan, 1967)
3. Surface Force-Pore Flow Model (Sourirajan and Matsuura, 1981a, 1981b)

All these models have been shown to be special cases of Statistical-mechanical model which has been described by Mason and Lonsdale (1990). Another important feature of membrane mass transport models is the understanding of two points. The first is which type of transport, diffusive or convective is more important to membrane semipermeability. The second is what parameters best characterize a real membrane. Muldowney and Punzi (1988) have investigated this problem both theoretically and experimentally for cellulose acetate RO membranes. Recently Mehdizadeh and Dickson (1989, 1991) have presented a modified Finely Porous Model and a modified Surface Force-Pore Flow Model.

The theoretical details and mathematical derivation of these models are not presented here since they are extensively covered in the literature (Jonsson, 1980; soltanieh and Gill, 1981; Dickson, 1988). The criteria for choosing a transport model is really arbitrary. However most of the published work on RO either use Solution Diffusion model or Preferential Sorption Capillary Flow model, better known as Kimura-Sourirajan Analysis (KSA). According to Dickson (1988), if a solute is highly rejected by the membrane and no unusual behavior is expected, then the KSA model is quite sufficient. If the solute is not highly rejected, then the finely-porous model should be preferred. If unusual behavior is expected, then modified surface force-pore flow model should be preferred. According to Soltanieh and Gill (1981), for highly rejecting membranes, the solution-diffusion model is quite satisfactory. The solution diffusion model and KSA model is discussed here.

Solution-Diffusion Model

This model incorporates three steps: sorption, diffusion and desorption. In this model it is assumed that both solvent and solute dissolve in the homogeneous nonporous surface layer of the membrane. Transport of both solute and solvent are assumed to take place independent of one another. Transport of both solvent and solute occurs by molecular diffusion under the chemical potential gradient through the membrane. The permeability of a species is equal to the product of the solubility and the diffusivity

for that species. The water flux is proportional to the solvent chemical potential difference (usually expressed as the effective pressure difference across the membrane), and the solute flux is proportional to the solute chemical potential difference (usually expressed as the solute concentration difference across the membrane). The solubilities and diffusivities of solvent and solute are important parameters of the model.

The solvent and solute fluxes, respectively are:

$$J_W = \frac{D_{WM} C_{WM} \bar{V}_W}{RT\Delta x}(\Delta P - \Delta\pi) = A(\Delta P - \Delta\pi) \qquad \text{(II-21)}$$

$$N_S = \frac{D_{SM} K}{\Delta x}(C_{S2} - C_{S3}) = B(C_{S2} - C_{S3}) \qquad \text{(II-22)}$$

The group of coefficients in the above equation is called solvent permeability coefficient, A and the solute permeability coefficient, B, respectively.

$$A = \frac{D_{WM} C_{WM} \bar{V}_W}{RT\Delta x} \qquad \text{(II-23)}$$

$$B = \frac{D_{SM} K}{\Delta x} \qquad \text{(II-24)}$$

Where D_{SM} and D_{WM} are the diffusivities of the solute and the solvent in the membrane, respectively ; $\bar{V}_W$ is the partial molar volume of water ; T is the temperature ; Δx is the actual thickness of the membrane skin; and K is the partition coefficient or solubility defined as follows:

K= (kg solute / m^3 membrane) / (kg solute / m^3 solution)

Where K is a measure of the relative solute affinity to (K>1.0) or repulsion from (K<1.0) the membrane material. One restriction of the Solution-diffusion model is that separation obtained at infinite flux is always equal to 1.0. However, this limit is not reached by many solutes. For this reason, the solution-diffusion model is appropriate for solute-solvent-membrane systems where the separation is close to 1.0. The primary advantage of this model is that it is simple and has only two adjustable parameters.

The above two transport equations are used for the design of RO plants. Parameters A and B are determined by experiment. They are independent of the concentration on both sides of the membrane. The membrane constant A decreases slightly with increasing operating pressure, whereas the constant B is almost independent of pressure. Membrane compaction of the active layer is the main reason for the pressure dependence of A, but the larger part of this compaction is reversible and A will readjust to its original value when the pressure is removed (Rautenbach and Albrecht, 1989). The reversible compaction of the solvent permeability coefficient, A, can be described by

$$A = A_0 \exp(\alpha_P \frac{\Delta P}{P_0}) \tag{II-25}$$

where A_0 is the reference solvent peremability coefficient; P_0 is the reference pressure; and ΔP is the pressure difference. The empirical pressure coefficient for cellulose acetate membranes produced by inversion is for example,

α_P= -0.003 to -0.005

The lower figure is valid for seawater desalination membranes with a high salt rejection and with low permeate flux, which are operated at high transmembrane pressure differences. The higher figure is valid for membranes for brackish water desalination with a low salt rejection and with a high permeate flux.

Membranes are also subject to an irreversible long-term compaction. As a result permeate flux decreases as operating time progresses. The selectivity however remains constant. Irreversible membrane compaction increases with increasing operating pressure. Both membrane constants are however dependent on temperature. Their temperature dependence can be described by an Arrhenius type equation:

$$A = A_0 \exp(\alpha_T \frac{T - T_0}{T_0}) \tag{II-26}$$

$$B = B_0 \exp(\beta_T \frac{T - T_0}{T_0}) \qquad \text{(II-27)}$$

with coefficients $\alpha_T = 7.1$ and $\beta_T = 3.0$ for cellulose acetate membranes. This temperature dependence of A and B must be taken into consideration, at least in principle, since changes in the membrane constants result in proportional changes in the corresponding fluxes. For practical purposes, however, the temperature dependence of B is often neglected. Since A and B are 'real' membrane constants, a plot of A against B provides a very useful basis of discussion of membrane properties and for efficient comparisons. Permeabilities are linked to membrane constants A and B and the active layer or skin layer thickness Δx by Lonsdale (1975):

$$P_w = CA\Delta x \qquad \text{(II-28)}$$

$$P_s = B\Delta y \qquad \text{(II-29)}$$

where P_w and P_s are the water and solute permeabilities respectively. The actual rejection coefficient can be related to the membrane constants as:

$$R' = [1 + \frac{B}{A(\Delta P - \Delta\pi)}]^{-1} \qquad \text{(II-30)}$$

This model is simple and very valuable in practice.

The preferential sorption-capillary flow model or KSA model

This model has been described in detail by Kimura and Sourirajan (1967), Sourirajan (1970, 1977), Agarwal and Sourirajan (1969a, 1969b), Sourirajan and Matsuura (1985a, 1985c), and Matsuura et al. (1975) for use in cellulose acetate membranes, and by Dickson et al. (1975,1976) for use in AP membranes. Most of the work in this area has been carried out by Sourirajan. This model is based on the preferential sorption-capillary flow mechanism proposed by Sourirajan(1963). The membrane is modeled by assuming that the membrane surface is microporous and transport occurs only through the pores in the membrane skin layer. The membrane has a preferential attraction for water, and the resulting sorbed layer of the permeate is forced through the membrane pores by pressure. Therefore solute separation and flux are determined both by physiochemical interaction between the solute-solvent-membrane system and by the number, size, and size distribution of pores. The fact, that 100% selectivity is never achieved is easily explained by the size distribution of the pores.

The basic equations are similar to that of the solution-diffusion model except that the concentration at the membrane surface has been related to the bulk concentration by using the film theory. The solvent flux is viscous in nature, and therefore the driving force for solvent transport is given by the effective pressure as in solution-diffusion model. The solute flux is diffusive in nature and is driven by the concentration gradient. The solute flux, and the solvent flux, are given by:

$$N_S = (\frac{D_{SM}K}{\delta})(C_{S2} - C_{S3}) \tag{II-31}$$

$$N_W = A(\Delta P - \Delta\pi) \tag{II-32}$$

Where A is the pure water permeability constant; ΔP is the applied pressure difference; $\Delta(= \pi(X_{S2}) - \pi(X_{S3})$; $\pi(X_{S2})$ is the osmotic pressure corresponding to a mole fraction of solute X_s; X_{S2} and X_{S3} are the mole fractions of solute in the high pressure side and low pressure side, respectively; D_{SM} is the diffusion coefficient of the salt in the membrane; K is the distribution coefficient; and (is the effective membrane thickness. The term

$D_{SM}K / \delta$ is treated as a single parameter and called the solute transport parameter. The two parameters of the model are A, and $D_{SM}K / \delta$. The effect of pressure and temperature on the pure water permeability coefficient A can be represented by equation (II-25) and (II-26) discussed above. The solute transport parameter and the pure water permeability coefficient are assumed to be independent of the operating feed flow rate and concentration.

For very high concentrations the solution-diffusion model and the preferential sorption-capillary flow model may differ. The solute transport parameter and the pure water permeability coefficient are determined experimentally. This model allows the calculation of rejection for any electrolyte without the need for experiments if the figures for two different salts are known. This model has been applied to a wide variety of solutes and membranes by Sourirajan and co-workers (1977, 1985).

Design Methods

The design of a RO unit depends on the required quantity of product water and the quality of feed and product water. These variables would determine the design method and the kind of module configuration and membrane used. The parameters affecting the performance of membrane modules can be classified into four categories, as shown in Table V.. One of the important feed properties is the concentration of various solutes. Increase in solute concentration increases the osmotic pressure and reduces the net driving force for the permeate flux. The feed temperature affects the viscosity and hence the flow resistance through the feed and permeate channels and through the membrane pores. Feed temperature and pH can also have a significant effect on solute solubility, membrane characteristics, and solute diffusion in solution and through the membrane.

Important operating parameters are the flow rate and pressure of the feed entering the module. Increase in flow rate reduces the concentration polarization and fouling. The driving force for the permeate flow through the membrane increases with the pressure. Pure water permeability of the membrane and solute rejection parameter are used in the selection of the membranes. Membrane life and ease of replacement need to be considered for the overall economic evaluation of a module. Finally, module geometry and membrane area per unit module volume are important in the design of a membrane module. Cartwright (1989) has presented an excellent paper on pilot plant and plant design.

Table V.:-Important Parameters in the design of RO (Doshi, 1988)

Feed Properties
    Solution composition
    Temperature
    pH
Operating parameters
    Feed flow rate
    Feed pressure
Membrane properties
    Pure water permeability
    Solute rejection coefficient
    Membrane life and ease of replacement
Module parameters
    Feed channel geometry and dimensions
    Permeate channel geometry and dimensions
    Characteristic of support or packing material for feed and permeate channel if necessary

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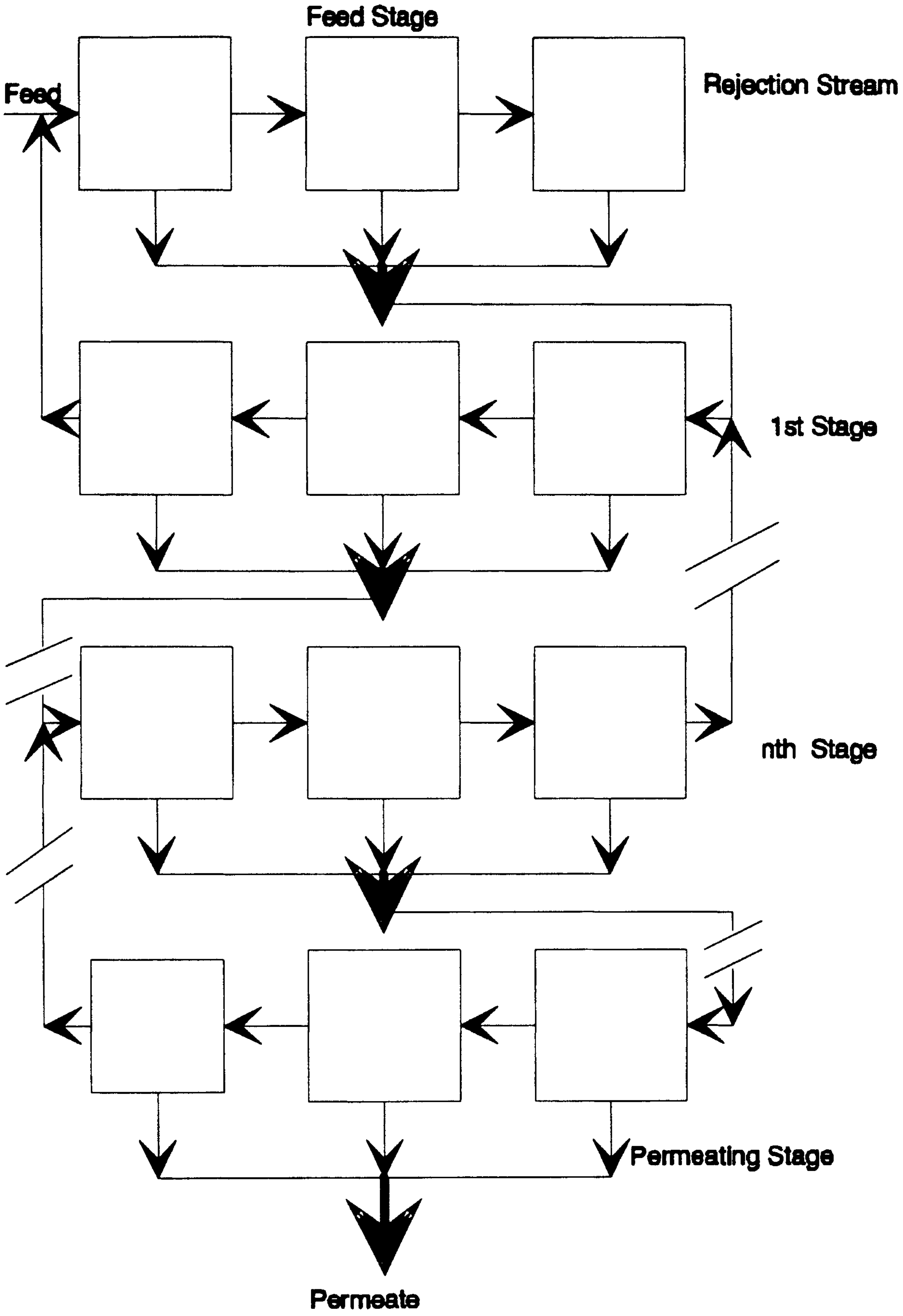
Many design methods of industrial and domestic units have been developed for RO. Due to the low intrinsic permeability of the polymeric materials, large membrane area must be used in industrial plants in order to achieve practical solvent recovery or solute separation, so the membrane has been fitted to modules of different configurations. As discussed above two types of modules are frequently used: spiral-wound and hollow-fiber, though tubular modules are still used in some older plants. These modules can be connected in 'straight-through flow' or 'tapered flow' arrangements which make up the whole plant. The first arrangement presents a constant flow section for the feed stream and the latter presents a periodic reduction of the flow cross section in order to restore the feed velocity to the initial value and minimize the concentration polarization. Also these arrangements can be of concentration mode or separation mode as shown below in Fig 6.

All the design methods depend on membrane mass transport models to predict RO performance for many modules. Kimura and Sourirajan (1967) analyzed theoretically the practical results of RO of cellulose membranes for certain inorganic salts. Their work depended on the equations of solution-diffusion model and concluded several equations for solute transport. Kimura et al. (1969) found an equation for the design of several stages RO process in terms of dimensionless variables, which was related to the analysis of Kimura and Sourirajan (1967). Ohya and Sourirajan (1969) concluded an approximate design method in terms of dimensionless variables, similar to that given by Kimura et al.(1969). It was confirmed latter on by Agarwal and Sourirajan (1969a). Ohya and Taniguchi (1975) and Taniguchi (1978) analyzed the experimental results obtained on spiral wound membranes in studying the effect of membrane properties and specifications on the transport and differential equations derived by Ohya and Sourirajan (1969).

Most membrane processes, despite their simplicity and economy, are limited by the technical difficulties of controlling mass transfer at the high pressure side of the membrane which causes fouling (Huang and Tien, 1976) and concentration polarization. This is one of the problems that confronts the designer because the actual performance



Separation Mode

Fig 6: Module arrangements.

depends on the wall concentration which is in turn a function of solvent and solute fluxes (Sherwood et al., 1965; Sourirajan, 1970) through an implicit transcendental relationship. The application of such relationships to rigorous design is too complex to be practical. For that reason, all system design approaches available introduce one or more simplifying assumptions (constant or total separation, dilute solution, negligible concentration polarization, constant mass transport coefficient, unobstructed high pressure channel flow, etc.).

Most approaches assume a mass transport model and then integrate these equations over the length of the membrane module. For simple models an analytical solution is possible after some assumptions have been introduced (Sirkar and Rao, 1981, 1983), but for more complicated models, a numerical solution is required (Tweddle et el.,1980). Mathematical models, which divide the whole plant into discrete portions of small area connected in series, have also been worked out (Chiolle et al., 1978; McCutchan and Goel, 1974). These models calculate the solvent and solute fluxes inside one elementary volume using the outlined procedure: then the overall performance is calculated by recursive equations accounting for the solute and solvent material balances, pressure drop, MTC change, and any variation in the intrinsic characteristic of the membrane in each portion. After the elementary volume has been chosen properly, the above design methods apply to all module configurations and flow arrangements. Tweddle et al. (1980) determined a method to study the specification and properties of membrane configurations by numerical equations, in the same manner as that found in Ohya and Taniguchi (1975) and Taniguchi (1978).

In cases where the solvent flux is much greater than the solute flux, Dandavati et al. (1975) found an implicit equation for the recovery fraction and an explicit equation for the product concentration of a hollow fiber module. Sirkar and Rao (1981, 1983) also derived approximate explicit equations for calculating the length of tubular modules equipped with almost perfect rejecting membranes under the turbulent and laminar flow conditions. Latter Sirkar and Dany (1982) and Sirkar et al. (1982) published an approximate design equation for spiral-wound modules based on the same assumptions as those used in the derivation of equations for tubular modules. Sirkar and Dany (1982) improved the design equations further and concluded a third equation with less percentage error. Saltonstall and Lawrence (1982) also derived a simple but less accurate design equations based on average feed stream concentration between feed and concentrate.

Evnagelista (1985) found a graphical-analytical method for straight-through and tapered flow arrangements, irrespective of the geometrical configuration of the modules. The derived equations were dependent on Sirkar's findings (1981) using the same assumptions for all the module types. In the same year Gupta (1985) presented dimensionless design equations, analyzed in a different way, for the tubular and spiral wound modules. He utilized the same theoretical bases and assumptions for transport of solute and solvent which were used by Sirkar et al. (1981, 1982) and concluded more accurate equations than those of Sirkar et al. (1981, 1982). Prasad and Sirkar (1984) developed analytical equations for a multisolute feed to a tubular module. Latter Prasad and Sirkar (1985) derived analytical design equations for multicomponent feed to a spiral-wound module based on their earlier work for tubular module. Palanki and Gupta (1987) extended the equations derived by Gupta (1985) for multisolute systems with the assumption of noninteracting solutes. Recently Hameed (1989) has presented a design method suitable for execution on a computer.

Considering the hydrodynamic aspect of accurate RO design, the works of Berman (1953), Belfort (1988), and Pneuli (1969), among others represent important contributions. Of special interest are those works accounting for the effect of the turbulence promoting net on both the hydrodynamics (Pneuli, 1969; Miyoshi et al., 1980; Focke and Nuijens, 1984) and the MTC (Kuroda et al., 1983; Light and Tran, 1981; Winograd et al., 1973) in the high pressure channel. Ohya et al. (1987) presented a method to specify RO system considering degree of freedom of the system. To include the effect of change in operating conditions, Zhou et al. (1991) presented several engineering equations or, rather, correction factors.

Extensive work (Gill and Bansal, 1973; Bansal and Gill, 1974; Doshi et al., 1977; Soltanieh and Gill, 1983) has been done on optimal design and performance of hollow-fiber modules through both rigorous and approximate approaches. Based on two parameter model, Rautenbach and Dahm (1984, 1987) presented a numerical algorithm for spiral wound modules with constant permeate cross section, similar to that of Kabadi et al. (1979) for hollow-fiber modules. It takes account for the pressure drops in the permeate and concentrate compartments, polarization on the high pressure side and concentration changes along the module axis. Evangelista and Jonsson (1988a, 1988b) have also derived analytical and numerical design equations the same way, but based on a three parameter model (Pusch, 1977).

A recent addition to this list is the design method of Costa and Dickson (1991). Their method is based on a system design model, where any membrane mass transport model can be used. The model describes the material balances, the MTC, and the pressure drop independently of the membrane mass transfer model. This approach was extended for spiral-wound modules by Dickson et al. (1992). An object oriented software development approach has been followed by Papafotiou et al. (1991). They have presented the prototype of a knowledge based expert system for the ROdesign. The method is based on a class of objects which encapsulate the behavioral knowledge of RO as well as the mechanism for its exploitation. They have adopted a two-level hierarchical design procedure. On the first level the general characteristics of the plant are defined.

On the second level, the plant structure is determined by first designing the high pressure stage. The design process continues adding more stages to the plant structure until the product quality confirms to the input specifications. Niemi and Palosaari (1994) presented a flowsheet simulation program, suitable for precise design of tubular RO modules. They have used the UNICORN (Rose, 1984) simulation program in their work.

Multicomponent System Modeling

In the high purity water industry, product water quality is usually specified in terms of allowable, or required, concentration of each ion. This is because the concentration of some ions can be tolerated more than others. However the concentration limit and range of individual ion depends on the user. Therefore the conventional practice of using total dissolved solids (TDS) for product water quality is inadequate. This necessitates the need for analytical techniques for predicting RO separation for individual ions present in the feedwater. A lot of work has been done in developing models for single solute separation. However, most natural water sources, and individual aqueous solutions contain several ions. The application of RO for the separation and fractionation of such mixed solute systems containing a number of ions is of practical interest. In spite of the great research effort studying RO, relative little attention has been given to the question of whether the equations developed to describe the behavior of single solute systems may be applied to multisolute systems. Therefore the development of suitable methods of predicting RO membrane performance for such mixed solute systems, is an area of great importance in high purity water industries.

The prediction of performance for such mixed solute systems is considerably more complex than the prediction for single solute systems. The major complications to the prediction process are as follows-

1. There may be strong solute solute interactions. The characterization of such multicomponent systems would require a determination of (n/2).(n-1) coupling coefficients in addition to n permeabilities of the n components composing the solution. This will require time consuming experiments to determine the coupling coefficients.
2. It is difficult to estimate the osmotic pressure of such multicomponent systems and would need detailed experimentation to obtain such data.
3. The model parameters need to be calculated for each individual species. This will require a large body of experimental data.

There are other complications such as partially dissociated multicomponent systems, strong solute-membrane interaction and charged membranes (Dickson, 1988). These problems are usually overcome by assuming no ion-ion interactions and each ion act independent of each other, since it is quite realistic for most membrane-solution systems (Pusch, 1990) except in the case where two electrolytes, present in the feed solution, possess a common ion.

Very few studies have been reported on this area. Some of the earliest investigation with multicomponent systems were made by Sourirajan (1963, 1964). Hodgson (1970) first reported the development of a suitable method for predicting membrane performance for multicomponent systems involving several ions in aqueous solution. Hodgson (1970) treated the membrane as a solution-diffusion barrier and did not impose the requirement that the membrane surface be nonporous and homogeneous. He used Debye-Huckel theory to calculate distribution coefficients for both ions and salts. But he did not include the effect of concentration polarization in his analysis. The approach of Lonsdale et al. (1975) is based on a an extension of Donnan equilibrium and solution-diffusion model for RO transport. They too ignored the effect of concentration polarization in their analysis. Therefore the analyses of Hodgson (1970) and Lonsdale et al. (1975) does not contain any terms for MTC on the high pressure side of the membrane. This limits the significance of their analyses since mass transfer plays a major role in RO. Sourirajan (1970) has also analyzed multicomponent systems. His approach is based on a simple additivity principle and he considered concentration polarization in his analysis. In all these reports, the theoretical analysis and its experimental verification were limited to multicomponent systems involving a common ion. Other workers (Erickson et al., 1966; Eliash and Bennion, 1977; Pusch and Walch, 1978) have also studied the treatment of solutions containing more than one electrolytes.

Ranagarajan et al. (1978a, 1978b, 1979, 1985) have reported a detailed analysis of multicomponent systems applicable to cellulose acetate membranes and have experimentally verified their prediction technique. Their analysis is based on Kimura-Sourirajan transport equations. They have taken into account the concentration polarization effect and have assumed that there is no cationic-anionic interaction in the feedwater. They have also derived analytical expressions for the solvent or water flux, interfacial distribution coefficients for the ions, transport parameters for the ions and ion-flux through the membranes with respect to each ion. They used the data on free energy parameter for different ions obtained earlier (Matsuura et al., 1975) to calculate the solute transport parameter for the different single salts containing the ions involved in the multicomponent system. Their prediction technique needs only a single set of experimental data on membrane specifications given in terms of membrane constant 'A' and solute transport parameter for sodium chloride. They also extended their analysis to multisolute systems with a common cation. In the earlier articles (Rangarajan et al., 1978a, 1978b, 1979, 1985), they investigated their prediction technique for mixed solute systems. They extended their prediction technique for individual ions present in the feedwater in a later work (Rangarajan et al., 1985b).

Though the prediction technique of Rangarajan et al. (1985b) is the only widely investigated and experimentally verified report in this field, it has a number of limitations. Some of the limitations of their work are as follows:

1. It is extremely complex. The complexity of the prediction technique increases with the number of ions present in the feedwater and their electrostatic charges. This is because of the need to retain electroneutrality at the membrane, in the feed, permeate and the concentrate.
2. The analysis is only valid for cellulose acetate membranes. The membrane constant 'A' and the solute transport parameter for sodium chloride are experimentally determined.
3. A single average value of MTC on the high pressure side of the membrane is used. This assumption is reasonable only when the feed flow rate is reasonably constant. But for large systems a significant portion of the feed is removed as permeate and the feed rate decreases throughout the membrane module. Also to understand the separation characteristic of each ion, individual MTC should be used.
4. The geometry of the membrane is not considered. The geometry plays an important role in the separation characteristic of ions. Also the presence of channel spacers or turbulent promoter nets affect the rejection of ions. And,

5. Their analysis is applicable to a small membrane area. Though a latter article by Matsuura and Sourirajan (1985) have derived a system analysis technique for both batch and continuous operations, they have not provided the results of prediction calculations or the experimental results for continuous systems.

Therefore a more detailed analytical technique is required to investigate the predictability of membrane performance for multicomponent feed systems. As mentioned earlier, Spiral-wound modules are mostly used in all high purity water production systems. Therefore it is of prime interest to study the rejection characteristics of these modules for multicomponent feed systems. The geometry of spiral-wound modules plays an important role in its rejection characteristic. Also to determine the total membrane area or number of modules required to treat a particular feed water, it is necessary to study the effect of number of modules on degree of separation of individual ions.

Therefore, the objective of this thesis is to set up theoretical framework for predicting the rejection of individual ions in a multicomponent system by RO membranes. This work is based on the work of Rangarajan et al. (1978a, 1978b, 1979, 1985). Theeffect of geometry of the spiral-wound module is considered and is contained in the mass transfer term. The MTC on the high pressure side is described by the mesh step model of Winograd et al. (1973). Dickson et al. (1992) had proposed an algorithm for multicomponent system but never published their results. They had also derived system analysis equations. They have suggested that the manufacturer opropsed pressure drop equation should be used. Therefore the equation proposed by FilmTec Corporation (1984) is used to calculate the pressure drop in each modules. Detailed mathematical expressions are presented in the model derivation section and in Appendix B of this thesis.

High Purity Water Applications

Though the applications of RO is numerous, in this section we will confine ourselves to industrial applications involving high-purity water. The high-purity water applications for RO of prime interest can be classified broadly into two main categories,

1. Electronics Water
2. Boiler Feed and Power Generator Water

Electronics Water

Semiconductor fabrication requires ultrapure water of high resistivity (18 MΩ.cm) and very low levels of particulate in great quantities. There are several reference standards, the most important being those of the American Society for Testing and Materials (ASTM) and Semiconductor Equipment and Materials Institute, Inc.(SEMI).

The semiconductor industry in Japan has related the water quality requirements to the scale of device integration. Membrane processes are playing an ever increasing role in improving the water treatment processes and Japanese membrane companies are claiming better purification techniques (McPherson and Bedford, 1986). In the United Kingdom, Plessey Research Caswell, Ltd., has developed guidelines for water quality (Stewart et al., 1987) for UK The requirements for ultrapure water in the electronic industry have defined and redefined the term 'ultrapure water' (Frith, 1983). The advancements in the semiconductor technology in the last decade have justified better purification technologies and analysis techniques (Gach et al., 1986).

The water specialist in the semiconductor industry is trained to understand the complex manufacturing process. The rapid growth in the semiconductor industry worldwide has created a strong interest in developing new methods of water purification. Water is the most common fluid used in the electronic industry. Pure water used in these industries is very aggressive and will dissolve many materials used for water treatment, distribution and processing. This property of pure water is its main advantage as the universal cleaning solvent. Ionic impurities present in the water can alter the current-carrying properties of a critical semiconductor surface in a variety of ways. Ionic impurities may diffuse into the surface of an integrated circuit, rendering nonconductive channels conductive. Therefore semiconductor manufacturing requires water of very high resistivity. Historically, distillation was first used to remove inorganic salts dissolved in water; but even triple distilled water (in quartz) can produce only 3MΩ.cm resistivity water. Today the combination of RO with IEX is capable of producing 18MΩ .cm resistivity. A typical component layout in a semiconductor facility is shown below (Cartwright, 1989) in Figure 7.

Colloids, total organic carbon (TOC), and particles less than 0.1 μm are most difficult to remove in any feed water supplies. Membrane processes, especially RO, are claiming such removal capabilities. A classical relationship has been developed between particles, microparticles, colloids, macromolecules, molecules, and ions (Frith, 1988).

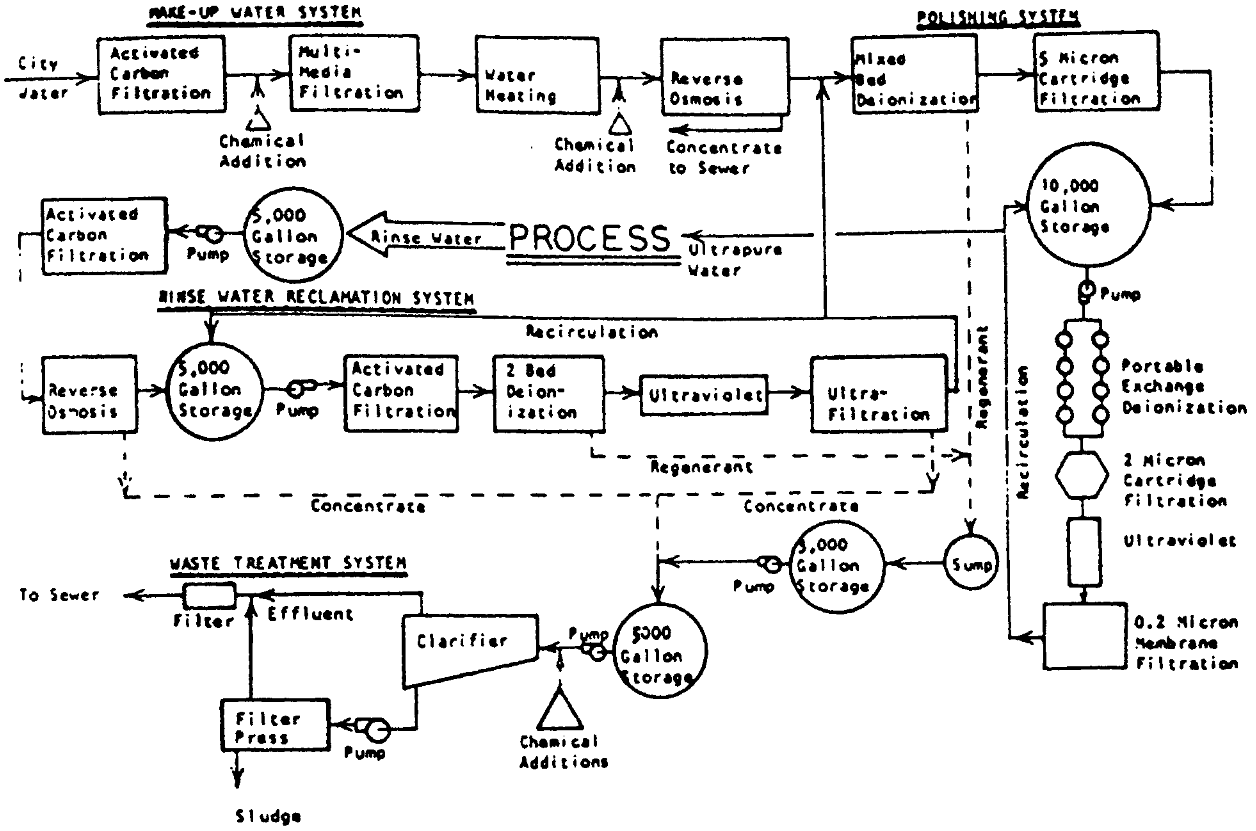


Figure 7.: Water treatment component layout in a semiconductor facility (Source: Cartwright, 1989)

Table VI illustrates the approximate range of such materials and the corresponding units for removal or concentration.

Table VI.: Relative Size Versus Removal Efficiency (Frith, 1988)

Contaminant	Micrometer (= 1000 Angstorm units)	Nominal Molecular Weight	Removal Process
Particles	100	-	Sand filtration
Particles	10	-	Depth filtration
Particles	1	1,000,000	Microporous membrane filtration
Colloids	0.1	200,000	Submicron membrane filtration
Macromolecules	0.01	20,000	Ultrafiltration
Ions	0.001	200	RO

Removal of macromolecules can be effected by using both RO and ultrafiltration membranes. But low molecular weight organics pass through ultrafiltration membranes with 1000 to 10000 nominal molecular weight ratings. RO is however , very effective in removing many of the organics found in the natural water supplies. Water-soluble organic compounds with molecular weights greater than 300 are almost totally removed and compounds between 100 and 300 molecular weight are generally 90% removed. The use of RO to achieve the removal of the higher-molecular-weight organics is the most effective way of removing TOC. In conjunction with IEX, it would yield water with a resistivity of 18 MΩ.cm and less than 50 ppm of organics (McGarvey and Tamaki, 1989). It is extremely beneficial to remove these organic compounds before they enter the IEX columns, since the resins are easily fouled by high-molecular-weight compounds like humic acid. Organics are, in fact, the number one contaminant to monitor and control in many high purity water applications.

IEX systems can treat moderate (550 ppm) to low TDS (total dissolved solids, expressed as ppm $CaCO_3$) water economically. For larger volumes, a succession of cation- and anion-exchange columns are easiest to regenerate and most economical. However, since IEX reactions are reversible , the removal of dissolved ions is less than total. Successful production of 18 MΩ.cm water usually requires a mixed bed IEX where breakthrough can be eliminated. Unfortunately, these mixed bed exchanges are not easily regenerated and are very expensive. However RO systems can effectively treat high TDS (3000 ppm) to moderate TDS (500 ppm) water. Thus, if RO precedes IEX , the incoming TDS can be reduced by 90 to 95% before being treated by IEX. This reduces the work load on the IEX columns drastically, but by itself RO cannot produce 18MΩ.cm resistivity economically.

The first applications of RO reported in the literature for semiconductor use claimed a 80 to 85 percent of ions that were originally removed by two bed IEX resins (Nusbaum et al., 1971). The time of regeneration for the mixed bed units downstream increased from days to nearly a month. Also, sulfuric acid can be used safely as a cation regenerant due to the elimination of the divalent salts in the RO permeate. The value of RO in the past 10 years can be noted by the complete elimination of the two bed IEX and the use of less chemicals for regeneration of the mixed beds. Colloidal particles and organic compounds were a serious problem in the deionization process before the use of semipermeable membranes upstream. The cost of operating deionization units and frequent resin replacements have greatly reduced with the RO pretreatment.

New RO membranes have demonstrated a high degree of silica removal (Scofield et al., 1986; Walker and Larson, 1985). Silica can be present in the soluble and insoluble (Colloidal) form. Both reactive and nonreactive silica are cause for concern in electronics applications. Silica one of the many materials that severally foul the resin. Both higher quality product water after deionization and reduced cost of regeneration prove the value of RO in application with high silica levels in the feed water supply.

To remove trace levels of microscopic contamination, point-of-use membrane filters are mostly employed. These filters are used in the industry as protective barrier to control particulates in the polishing stage of the water system. With the future needs for finer filtration at the points of use, RO membranes may be the only solution (Frith, 1988). The use of more efficient RO membranes in the primary stages of treatment provides many advantages to the point of use as well as protecting the IEX throughout the entire system. Particles, colloids, organics, and ionic concentrations are greatly reduced with efficient operation of the RO units.

It is clear from the above that the combination of RO and IEX is more effective than either one alone. Quinn et al. (1971) have evaluated and compared IEX and RO systems on both technical and economic basis to determine the optimum combination of the two. Porter (1988) has graphically compared the economics of the two individual processes with hybrid (RO + IEX) systems. In his data Porter assumed a 7-year operating period with the plant amortization over 3 years at 7.5% interest. He has concluded that for a 1 million gal/day plant, the RO operating costs are insensitive to changes in the influent TDS (this assumption is reasonable since for TDS below 1500 ppm osmotic pressure is not significant). On the other hand, IEX costs increase proportionately with increase in the TDS. Thus, at low influent TDS levels, IEX operating costs are lower than those for RO. The crossover point is about 560 ppm TDS for a 7-year operating period and will shift to higher TDS values for shorter operating periods (710 ppm for a 3-year period). This is because of higher capital costs associated with RO plants compared with those for IEX plants.

New technologies have been developed using RO membranes (McPherson and Bedford, 1986; Katz and Clay, 1986; Pittner et al., 1985). The application of semipermeable RO membranes are no longer limited to their original application of sea or brackish water desalination. They are now widely used for efficient removal of specific ions, soluble organics, colloids, and particles (Sourirajan and Agarwal, 1970; Gupta, 1986). Frith (1988) has classified the application of RO in high purity industries into the following categories:

1. Pretreatment
2. Primary treatment
3. Polishing
4. Point of use
5. Reclaim
6. Waste treatment

Achieving this high quality electronics grade water requires the use of virtually all the technology available to the water treatment specialist. Chlorination, filtration, softening, carbon filtration, reveres osmosis, deionization, ultrafiltration, microfiltration, ozonation and ultraviolet sterilization are all commonly used in the production of ultrapure water. In no other application is system expertise so strongly required. In addition to the treatment technologies, the design and operation of the storage and distribution is also extremely critical. Depending upon the purposes intended, water used in semiconductors are prepared using different combinations of the above mentioned units. Since such a large number of alternative choices are possible, the design of semiconductor pure water manufacturing system is often difficult. Two system choices are possible: either single-pass RO followed by primary and secondary mixed-bed polishing, or double-pass RO with service-exchanged mixed-bed polishing. Sinha (1990) has given a useful summary of the processes and variations that are possible in the design of pretreatment stages.

Boiler Feed and Power Generator Water

RO is also extensively used to remove organics, salts, and silica ahead of deionizers in boiler feed systems. The requirements for water quality vary greatly with the type of boiler system. The primary concerns in the boiler are related to scale prevention, corrosion protection, and blowdown control. Table VII summarizes the problem, cause and remedy related to this application. Although this description is simplistic, many common problems related to boiler feed can be solved by controlling water hardness, alkalinity, silica and total dissolved solids. Perhaps the simplest method to control these problems is RO. The technology is straightforward and can reduce blowdown frequency by a factor up to 10.

Table VII: (Osmonics, 1991)

Problem	Cause	Remedy
scale build-up Silica, TOC	water hardness, evaporation	water softener, RO, IEX
frequent blowdown	TDS	RO, IEX
corrosion TOC, silica	TDS, oxygen	RO, IEX, vacuum degasifier

The first application of RO for boiler feedwater was reported by H. Rowland (1971) of the Burbank, California, Public Services Department. Though the Burbank plant was small (10000 gal / day) they reported a savings of 33% as a result of a five- to tenfold increase in DI water between regenerations, decreased chemical cost (by 90 to 95%), extended life of the IEX resins, improved water quality, and lower manpower and maintenance requirements.

Also RO is widely used on recirculating cooling-tower blowdown. During recirculation, the concentration of some dissolved solids such as $CaSO_4$ reaches supersaturation levels and precipitates as scale deposits. To minimize scale buildup, some fraction of the cooling water is continuously discharged as blowdown and fresh water is added to make up the loss. The waste discharged as blowdown is high in TDS and contains 5 to 20 ppm of chromate, phosphate, and chlorinated hydrocarbons used as corrosion inhibitors and algaecides. RO membranes are capable of demineralizing the cooling-tower blowdown for reuse but are inadequate for removing chromates.

D'Auria et al. (1987) have described TOC (Total organic carbon) management in power generation (Millstone Unit two) by RO. Millstone unit two is an 800-megawatt pressurized water reactor nuclear power station drawing water from Long Island for both makeup and cooling purposes. High chloride values were traced to halogenated organic compounds added to the feedwater from the makeup water. The average TOC of the makeup water was found to vary seasonally from 600 to 1200 ppb. Pretreatment with polyamide thin-film composite RO membrane reduced the TOC levels of the subject water more effectively than any other treatment methods. The RO unit operated at 66% to 85% recovery yielded 96% rejection. A test of 30 days duration revealed that 100 gpm RO system could produce water typically containing less than 50 ppb of TOC. Associated benefits were improved condensate and makeup demineralizer performance, a possible diminution of ion throw by the DI beds, and a decrease in the chloride ion levels in the stream generators (D'Auria et al., 1987).

New Design Concepts

The advancements in membrane technology internationally have radically changed the concepts to produce ultrapure water. Semipermeable RO membranes are considered to be the long-term solution to improve water quality for critical applications. Two new design concepts have been employed in semiconductor pure water systems over the last 10 years. The triple membrane system and the double-pass RO have been installed as major water purification systems. The triple membrane system is a compact trailer mounted design (Katz and Clay, 1986). It uses ultrafiltration, electrodialysis reversal, and RO. This water is then polished to the desired final quality with the mixed bed IEX resins.

Double-pass RO systems were previously used in potable water from seawater and pharmaceutical grade water applications. The quality of water produced in such systems is acceptable to meet the specifications, but maintenance costs are high. Therefore this concept has not received wide acceptance. Though there use in semiconductor facilities is limited, the initial results prove the economic value of this method versus the traditional two bed / mixed bed design (Pittner, 1986). A general treatment of double-pass operations was presented by Comb and Schneekloth (1989). Meltzer (1991) has described double-pass RO systems in detail. Ammerer and Dahmen (1990) have reported on a double-pass RO system utilizing two spiral-wound PA/PA membranes addressed primarily to the removal of high silica content. Their results clearly showed the advantages of two-passed RO over single pass.

The use of double-pass RO systems may limit the use of two-bed IEX systems. The mixed beds will always be needed where single-pass RO is used. The mixed bed IEX act as a polisher and therefore is needed to be coupled with single-pass RO systems. However a double-pass RO system can eliminate some of the mixed bed application. Mixed beds cost more, and are more difficult to operate. However they confer a high quality to the water. According to Yabe et al. (1989), a single-stage RO, useful in reducing the ionic content of water to 5% to 10% of its original value, can be product-staged to yield water with resistivities of 1 to 3 MΩ.cm on a continuos basis. However for 18 MΩ.cm resistivity, IEX treatment is necessary.

Gagnon and Cheney (1991) stated that RO with polishing mixed-bed deionization is most cost-effective when the feed water TDS levels are 300 ppm or greater; between 150 and 300 ppm, either RO or two-bed IEX may be employed; below 150 ppm of TDS, two-bed ion-exchange followed by a polishing mixed bed is most appropriate. For semiconductor applications. The water will be most likely be treated by RO because of the concern with particles and TOC.

Reverse Osmosis/Ion Exchange Arrangements

Various arrangements of IEX and RO units are used on different water systems depending on the intended purification. Some utilize IEX before RO, others reverse the order. However mostly IEX is used after RO. IEX is sometimes used in advance of the RO in order to reduce or prevent fouling of the membranes. An example is where the feedwater is high in silica content. Typically, where silica content in the waste stream exceeds 120 ppm, there is a great potential for RO membrane fouling. If the feed water contains 80 ppm of silica, and if feed water recovery is only 50% or so, the reject water may contain about 160 ppm of silica. In such situations, particularly where high water recovery is desired, the prior treatment by IEX will reduce the silica content (Meltzer, 1991). Some believe that IEX resins are more easily fouled by silica than RO. The form of the silica probably governs.

The installation of RO after IEX unit was utilized by Lewis et al. (1989) to reduce both particle counts and TOC levels in the rinse water for semiconductors. Quinn (1989) believed that a computer-designed RO / IEX program could led to the rapid optimization of the RO / IEX system, including the selection of the RO membranes from among the types available. If the feed water contains high levels of foulants, a spiral-wound configuration would be selected. Where high pressure and rejection membranes are used, IEX capital and operating Costs are minimized by the use of a simple mixed-bed deionizer.

In the power industry, the more usual arrangement is for the RO unit to precede IEX. There the focus is on colloid removal. RO membranes successfully accomplishes this. If the IEX resins were first in line, it is feared that the colloids, usually constituted of organics, silica, and inorganics would not be captured by the IEX. They would penetrate the IEX beds. If, on the other hand, RO treatment came first, even if it resulted in colloidal destabilization and ionic release, harm would be prevented by subsequent IEX action. Moreover, RO is more tolerant to organics than IEX. In all applications, the primary motivation in preceding the IEX with RO is to minimize the frequency of the resin regeneration, with reduction in regeneration chemical consumption. McAfee and McCormack (1988) stated that the placement of an RO unit before IEX beds increased the service life of the latter twentyfold, and paid back the investment in the RO within 4 years.

Reverse Osmosis or Ion Exchange

The choice between the two methods is always an important issue in the design of water treatment systems. Some excellent references on this issue are Benedek and Johnson (1988) and Whipple et al. (1987). The economics involved are usually the overriding considerations, however, reflecting the quality of the raw water; the application intended; and the quality of the treated water that is desired, in what quantities, over what period of time, and at what flowrates. Clearly no one method is the better for all situations. Some of the important features of both the methods are described below:

1. RO is more cost intensive. The biggest capital cost for RO is that of the membrane, usually amortized over a three year period. The next largest cost for RO is the electric power needed for its pumps. RO tends to use much more energy than IEX. However RO operational costs are lower unless the TDS is very low.
2. The cost incurred in IEX reflects the straight costs of the resins and their regenerant chemicals. The choice is often made on the basis of TDS reduction as a function of the cost. RO costs are relatively independent of feed TDS, while IEX capital and operating costs increase significantly with increased TDS.

economics of operations are the ultimate concern. The costs of electrical energy may also be a deciding factor. Where the cost of pumping water and heating is low, RO is favored. Where electricity, water, and sewage are expensive, RO is less attractive. Above all whatever is selected, it must meet the need of the desired water quality.

CHAPTER III

MODEL DEVELOPMENT

Introduction

As discussed in Chapter II, multicomponent system modeling of reverse osmosis is complicated by the need for a large body of experimental data. Therefore any modeling approach has to be accompanied by experiments. These experiments are needed to determine different transport properties, such as diffusivity, mass transfer coefficient, osmotic pressure, etc., and the transport parameters used in the flux expressions. Very little data on the osmotic pressure and diffusivity of the ions is available in the literature. These data are necessary to describe the transport of the ions and water through the membranes. For multicomponent systems involving several ions, it is extremely difficult to determine the osmotic pressure even by experimentation. Therefore, an attempt is made in this work to model a reverse osmosis system which requires minimum experimentation, or uses the data available in the literature.

The starting point in the model development is the selection of a membrane mass transport model. As discussed earlier, these models can be classified as either two parameter or three parameter models. Model parameters are determined experimentally. Because less experimentation is needed, a two parameter model is selected for this work. Deciding which membrane transport model best represents a certain feed-membrane system or the amount of modeling detail required for a desired accuracy, is difficult to determine. The decisions must be made by considering the relative errors and mathematical complexities imposed by the assumptions made in various transport models. Therefore any previous experience or work on the application of these transport models are beneficial. Most of these transport models were proposed for single salts and extension of these models for multicomponent systems involving several ionic species is often complex.

For these reasons, and other complications as described in Chapter II, multicomponent modeling of reverse osmosis is truly complex and may not be practical for everyday calculations. However it has a lot of applications. This will help the user to select a suitable reverse osmosis unit, capable of treating the required feed water for their high purity water system, and the manufacturer of the reverse osmosis units, in effectively rating and designing their systems. Other critical applications include failure detection and performance evaluation of reverse osmosis in comparison to other units used for high purity water production, and optimization of the unit with respect to several variables including cost of manufacturing and operation. On a broad scale, an opportunity exists to develop flowsheet simulation software for reverse osmosis which can either be used alone or in conjunction with other pretreatment units such as microfiltration etc. and post treatment units such as ion-exchange or ultrafiltration used in ultrapure water production systems.

The initial model development is based on the desire to study the effect of operating parameters such as temperature, pressure, feed flow rate, feed concentration and other conditions not considered in any previous modeling efforts. These requirements include the consideration of the following effects on the performance of the reverse osmosis system:

1. cations to anions ratio.
2. valence of the ions and the monovalent to divalent ratio.
3. area of the membrane.
4. number of modules in a system.
5. module geometry and configuration of the module assembly.
6. turbulence promoter nets.

Another important criteria during the model development was computational effort and time requirement for different cases. Because of the mathematical model complexity, it is necessary to understand the effect of different terms on reverse osmosis performance prediction. This helps in the development of suitable algorithms for computation. Other considerations of theoretical interests are as follows:

1. Comparison of the various membrane mass transfer models on describing a particular feed-membrane system.
2. Difference in prediction results with and without concentration polarization term in the model.
3. Effect of the mass transfer coefficient of the ions on the rejection characteristics of the reverse osmosis membrane system.
4. Effect of the pressure drop in the module arrangements on the prediction results.
5. Difference in prediction results with and without osmotic pressure term in the model.
6. Since most of the previous investigations were carried out with cellulose acetate membranes, experimental data on other membrane materials can yield valuable information for comparison of performances of different membranes.

For multicomponent systems, time consuming and tedious experiments are needed to furnish data to determine model parameters. Therefore, it is extremely beneficial to correlate the results for different ions with a simple solute such as sodium chloride, which can be determined experimentally. This will save a lot of experimental effort and time. Such approach was followed by Rangarajan et al. (1976, 1978a, 1978b, 1979, 1985). Their investigation is the primary reference of this work.

Assumptions

The model is based on the following assumptions:

1. There is no ion-ion or ion-membrane interactions in the multicomponent feed water-membrane system, and each ion acts independent of others. This assumption is valid for most membrane-feed water systems and is essential to avoid the complication of considering the coupling coefficients of different ions.

2. The osmotic pressure of the electrolyte solution is the result of combination of the contribution from each ion to the total osmotic pressure. The osmotic pressure contribution of each ion is proportional to its mole fraction. For the purpose of calculations, the osmotic pressure of an electrolyte solution involving several ions can be approximated by the following equation proposed by (Rangarajan et al., 1984),

$$\pi(\Sigma X_i^* + \Sigma X_j^*) = \Sigma B_i^*(X_i^*)X_i^* + \Sigma B_j^*(X_j^*)X_j^* .$$

The symbols are explained in the nomenclature. This assumption is essential since it is usually difficult to determine the osmotic pressure of the solution containing several ions. In view of the infinite number of solution composition possible for concentrated boundary solution and permeate solution for a given feed composition, it is not possible to obtain the osmotic pressure data for all possible compositions experimentally. Also there is no theoretical approach to calculate osmotic pressure of solutions containing several ions. With this assumption, sets of $B_i^*(X_i^*)$ and $B_j^*(X_j^*)$ could be evaluated at different mole fractions from the literature data on osmotic pressure of several salts by regressional analysis by the method described by Rangarajan et al. (1984). From $B_i^*(X_i^*)$ and $B_j^*(X_j^*)$ values, for any known composition of a solution, the osmotic pressure of the solution can be calculated.

3. The feed water is relatively dilute and particulate free. The density of the water is the same throughout the system. In any high purity water treatment system, the reverse osmosis unit is never used alone, and, in most cases, is used in conjunction with other separation units. The reverse osmosis unit is usually placed in the downstream side of the treatment system. The feed water to the reverse osmosis unit is effectively pretreated to protect the membranes from particulate and other forms of fouling.

4. The membrane is microscopically uniform with negligible charge density. Reverse osmosis membranes, unlike the ion exchange membranes, carry no charges. Also this assumption is essential to establish electroneutrality condition at each phase of the membrane.

5. Fluid properties are essentially constant. Though some of the properties such as diffusivity and osmotic pressure are temperature dependent, the effect is usually negligible. Also the membranes are usually operated at constant temperature since fluctuation hampers the performance.

6. Modules are spiral-wound type. They are connected in series either in a pressure vessel or otherwise such that there is no back-mixing between the units.

7. The flow of the locally produced permeate in the porous substructure of the membrane is unhindered.

8. The Kimura-Sourirajan model is valid for the mass transport in the membrane. The KSA model is adopted in this work. This membrane mass transport model is the most widely investigated and experimentally verified model in reverse osmosis. The flux expression are based on the KSA model in conjunction with the concentration polarization model.

9. Immediate and complete mixing of the locally produced permeate with the bulk flow in the permeate channel.

10. Turbulence flow conditions exist in the feed channels. Spacers or nets are used between the membranes to increase turbulence and mass transfer across the membrane.

11. The concentrate or flow rate of the permeate in each module is not affected by the permeate in the neighboring modules.

12. Negligible contribution of the ionic fluxes to the volumetric flux through the membrane. The solvent flux or the water flux is much greater than the ionic fluxes; $N_W >> N_i^{\bullet}$.

13. Negligible diffusive mass transport in comparison with the convective transport in the main flow direction of each channel ($\dot{m}_{diff} / \dot{m}_{conv}$ ratio can be estimated to about 10^{-8} at most).

14. Neglect the curvature of the channels. This assumption is justified since the ratio of the channel height to the module diameter is very small. The spiral wound modules are made up of flat membranes with constant geometrical shape (curvature, deformation and compaction are neglected).

15. No cross-mixing in channels, i.e., the diffusive transport orthogonal to the main flow direction is neglected. This simplifying assumption seems justified since $\dot{m}_{diff} / \dot{m}_{conv}$ is about 10^{-7} at the most.

16. No convective flow due to the pressure gradients orthogonal to the main flow direction in each channel.

17. The mass transfer coefficient on the high pressure side is estimated by the mesh-step model of Winograd et al. (1973). In cases dealing with univalent ions only mass transfer coefficient can be averaged for the whole system. In cases where the flow rate of the feed is constant, the mass transfer coefficient can be assumed to be proportional to the 2/3 power of diffusivity.

18. Concentration polarization is absent on the low-pressure side of the membrane and that on the high pressure side of the membrane is evaluated by the film concept assuming the membrane to be a flat sheet.

19. Empirical correlations of the manufacturers, for the pressure drop across the membrane modules, are valid. In this case the pressure drop across the membrane modules is calculated using the correlation of the Film Tec Corporation.

20. For any salt or ion, the ratio of diffusion through the membrane to that in water is a constant (Hoffer and Kedem, 1972), i.e.,

$$\frac{D_{SM}}{D_{SW}} = \frac{D_{iM}}{D_{iW}} = \text{constant}$$

Explanation of Symbols

A brief description of the symbols used in this model is presented here. In a reverse osmosis unit, three phases are generally involved, namely the solute phase, the solvent or water phase and the membrane phase. The particular phase of the quantities can be identified from its subscripts. The subscripts S, W and M refer to salt, water and membrane phase, respectively. Ions are identified by the asterisk on the quantities. In any quantity, the first subscript i, 1, 2, 3 etc. refers to the indicated ions, and the second subscript M, 1, 2 or 3 refers to the indicated location in the membrane (M= membrane phase, 1= bulk solution on the high pressure side of the membrane, 2 = concentrated boundary solution on the high pressure side of the membrane, and 3 = permeate or the product solution on the low pressure or atmospheric pressure side of the membrane).

The ions of importance in high purity water treatment can be classified into two categories: (i) simple ions such as sodium, magnesium, calcium, potassium, chloride, sulfate, nitrate, bicarbonate, and (ii) heavy metals such as cadmium, copper, zinc, mercury, silver, cyanide, phosphate, chromate, silicate, etc. In this work eight simple ions are considered. They are represented as follows: cations are numbered in odd numbers (sodium =1, potassium = 3, magnesium = 5, and calcium = 7), and anions are numbered in even numbers (chloride = 2, sulfate = 4, nitrate = 6, and bicarbonate = 8). The system selected contains 4 univalents and 4 divalents. The model can be expanded for systems containing more ions and the ions can be represented by the above mentioned manner. The solute transport parameter according to KSA model is denoted by $(\frac{D_{SM}K}{\delta})$. Symbol 'X' is used to denote the mole fraction of the ions or the solutes. Other symbols are self-explanatory and are defined at the beginning of this thesis.

Theory of membrane transport in reverse osmosis

The basic equations of RO transport for single solute systems have been derived by various membrane transport models as described in chapter II. These equations are generally valid for aqueous solutions. Depending on the mechanism of transport, two flux expressions, namely the solute or ion flux expression and the solvent or water flux expression, completely describe the RO separation process. The membrane, during the transport, acts as a barrier. According to the KSA model, the solute flux through the membrane is proportional to the concentration gradient across the membrane and can be expressed as:

$$N_S \alpha (\frac{c_{M2} X_{SM2} - c_{M3} X_{SM3}}{\delta}) \qquad \text{(III-1)}$$

The solute flux, N_S , is diffusive in nature and therefore the proportionality constant in the above relationship is the diffusivity of the solute through the membrane. So the solute flux expression can be written as,

$$N_S = D_{SM} (\frac{c_{M2} X_{SM2} - c_{M3} X_{SM3}}{\delta}) \qquad \text{(III-2)}$$

Where X_{SM2} and X_{SM3} are mole fractions of solute in the membrane in equilibrium with X_{S2} and X_{S3} respectively. c_{M2} and c_{M3} are the molar densities corresponding to X_{SM2} and X_{SM3} in the membrane. For simplifying the analysis, a linear equilibrium relationship is assumed between X_S and X_{SM}, which can be expressed as,

$$KcX_S = c_M X_{SM} \qquad \text{(III-3)}$$

where K is the partition coefficient. Using the above relationship, the solute flux relationship can be expressed as,

$$N_S = (\frac{D_{SM}K}{\delta})(c_2X_{S2} - c_3X_{S3}) \tag{III-4}$$

The quantity $(\frac{D_{SM}K}{\delta})$ is called the solute transport parameter.

The solvent flux is assumed to be viscous in nature. According to the KSA model, the membrane has a preferential attraction for water, and the transport takes place through the pores of the membrane. Therefore the solvent flux, N_W, through the membrane is proportional to the effective pressure gradient for the fluid flow through the membrane.

$$N_W \alpha \Delta P \tag{III-5}$$

Effective driving pressure through the membrane can be expressed as:

$$\Delta P = (P_1 - P_3) - \Delta\pi \tag{III-6}$$

where, Δ(is the effective driving pressure and P_1 and P_3 are the pressure at the feed and the pressure at the permeate respectively. Δ(is the osmotic pressure gradient across the membrane and can be expressed as:

$$\Delta\pi = \pi(X_{S2}) - \pi(X_{S3}) \tag{III-7}$$

where $\pi(X_{S2})$ and $\pi(X_{S3})$ are the osmotic pressure of the fluid at the membrane boundary and at the permeate respectively. Since the permeate is normally at atmospheric pressure, P_a , $(P_1 - P_3)$ can be approximated by the operating gauge pressure, P.

$$P_1 - P_3 \approx P_1 - P_a = P \tag{III-8}$$

Substituting in the above equation, we have

$$\Delta P = \cancel{A}[P - \{\pi(X_{S2}) - \pi(X_{S3})\}] \tag{III-9}$$

Substituting equation in Equation   we have

$$N_W = A[P - \{\pi(X_{S2}) - \pi(X_{S3})\}] \tag{III-10}$$

where A is the proportionality constant called the pure water permeability constant.

As can be seen from the solute flux expression, the quantity X_{S2} , the concentration of the solute at the membrane, is needed for computing the solute flux. As explained in chapter II, this is determined from the concentration polarization phenomena. The concentration polarization phenomena, as derived from the film theory, can be expressed as,

$$\frac{N_S + N_W}{kc_1} = \ln[\frac{X_{S2} - X_{S3}}{X_{S1} - X_{S3}}] \tag{III-11}$$

Since it is assumed, $N_W >> N_S$, $N_S + N_W$ in the above expression can be effectively replaced by N_W. Therefore Equation (III-11) can be written as,

$$\frac{N_W}{kc_1} = \ln[\frac{X_{S2} - X_{S3}}{X_{S1} - X_{S3}}] \qquad \text{(III-12)}$$

$$\text{or, } X_{S2} = X_{S3} + (X_{S1} - X_{S3})e^{(\frac{N_W}{kc_1})} \qquad \text{(III-13)}$$

The solute mole fraction of the permeate can be expressed as,

$$X_{S3} = \frac{N_S}{N_S + N_W} \qquad \text{(III-14)}$$

Equations (III-4), (III-10), (III-13), (III-14) completely describe the RO transport of a single solute through any membrane.

Basic transport equations applicable to multicomponent systems

For a RO system containing several ions, under steady state isothermal operating condition, the flux expressions for the ions and the water can be written in the following form using the KSA model. The derivations of Rangarajan et al. (1978, 1979, 1984) is used for the ionic flux expressions. The equations are similar to that for the single salt systems and were derived using the same approach.

Solvent or Water flux expression

In this case the osmotic pressure gradient is given by:

$$\Delta\pi = \pi(\sum X^{\bullet}_{i2} + \sum X^{\bullet}_{j2}) - \pi(\sum X^{\bullet}_{i3} + \sum X^{\bullet}_{j3}) \qquad \text{(III-15)}$$

Using Equation (III-15), the solvent or water flux equation can be written as:

$$N_W = A[P - \{\pi(\sum X^{\bullet}_{i2} + \sum X^{\bullet}_{j2}) - \pi(\sum X^{\bullet}_{i3} + \sum X^{\bullet}_{j3})\}] \qquad \text{(III-16)}$$

As explained in assumption 2, the osmotic pressure of the solution is approximated by assumption 2. Using Equation (III-16) the solvent flux expression can be written as,

$$N_W = A[P - \{(\sum B_{i2}^{\bullet} X_{i2}^{\bullet} + \sum B_{j2}^{\bullet} X_{j2}^{\bullet}) - \pi(\sum B_{i3}^{\bullet} X_{i3}^{\bullet} + \sum B_{j3}^{\bullet} X_{j3}^{\bullet})\}] \qquad \text{(III-17)}$$

Where $B_i^{\bullet}$ and $B_j^{\bullet}$ refers to the value of $X_i^{\bullet}$ and $X_j^{\bullet}$ respectively.

Ionic Flux Expression

The cationic flux equation can be written as,

$$N_i^{\bullet} = (\frac{D_{iM}^{\bullet} K_{i2}^{\bullet}}{\delta}) c_2 X_{i2}^{\bullet} - (\frac{D_{iM}^{\bullet} K_{i3}^{\bullet}}{\delta}) c_3 X_{i3}^{\bullet} \qquad \text{(III-18)}$$

where, i = 1, 3, 5, ...

The anionic flux expression can be written as,

$$N_j^{\bullet} = (\frac{D_{jM}^{\bullet} K_{j2}^{\bullet}}{\delta}) c_2 X_{j2}^{\bullet} - (\frac{D_{jM}^{\bullet} K_{j3}^{\bullet}}{\delta}) c_3 X_{j3}^{\bullet} \qquad \text{(III-19)}$$

where, j = 2, 4, 6, ...

Using assumption 3, we have:

$$c = c_1 = c_2 = c_3$$

and incorporating assumption 3 into Equation (III-19), we have:

$$N_i^* = (\frac{D_{iM}^* K_{i2}^*}{\delta})cX_{i2}^* - (\frac{D_{iM}^* K_{i3}^*}{\delta})cX_{i3}^* \qquad \text{(III-20)}$$

and

$$N_j^* = (\frac{D_{jM}^* K_{j2}^*}{\delta})cX_{j2}^* - (\frac{D_{jM}^* K_{j3}^*}{\delta})cX_{j3}^* \qquad \text{(III-21)}$$

To represent the concentration of the ions at the boundary layer, the concept of concentration polarization is used. Using the film theory, we have:

For cations,

$$X_{i2}^* = X_{i3}^* + (X_{i1}^* - X_{i3}^*)\exp[\frac{N_W + \sum N_i^* + \sum N_j^*}{k_i c}] \qquad \text{(III-22)}$$

For anions,

$$X_{j2}^* = X_{j3}^* + (X_{j1}^* - X_{j3}^*)\exp[\frac{N_W + \sum N_i^* + \sum N_j^*}{k_j c}] \qquad \text{(III-23)}$$

Where k_i and k_j are the mass transfer coefficient of the cation I and anion j respectively on the high pressure side of the membrane.

Since it is assumed that $N_W >> \sum N_i^* + \sum N_j^*$, the above two equations reduces to

$$X_{i2}^* = X_{i3}^* + (X_{i1}^* - X_{i3}^*)\exp[\frac{N_W}{k_i c}] \qquad \text{(III-24)}$$

and

$$X_{j2}^* = X_{j3}^* + (X_{j1}^* - X_{j3}^*)\exp[\frac{N_W}{k_j c}] \qquad \text{(III-25)}$$

Defining,

$$\Omega_i = \exp[\frac{N_w}{k_i c}] \qquad \text{(III-26)}$$

and

$$\Omega_j = \exp[\frac{N_w}{k_j c}] \qquad \text{(III-27)}$$

and incorporating Equation (III-26) and (III-27) into Equation (III-24) and (III-25) we have,

$$X_{i2}^{\bullet} = X_{i3}^{\bullet} + (X_{i1}^{\bullet} - X_{i3}^{\bullet})\Omega_i \qquad \text{(III-28)}$$

and

$$X_{j2}^{\bullet} = X_{j3}^{\bullet} + (X_{j1}^{\bullet} - X_{j3}^{\bullet})\Omega_j \qquad \text{(III-29)}$$

The permeate mole fractions of the cations and the anions respectively are given by,

$$X_{i3}^{\bullet} = \frac{N_i^{\bullet}}{N_w + \sum N_i^{\bullet} + \sum N_j^{\bullet}} \qquad \text{(III-30)}$$

and

$$X_{j3}^{\bullet} = \frac{N_j^{\bullet}}{N_w + \sum N_i^{\bullet} + \sum N_j^{\bullet}} \qquad \text{(III-31)}$$

Using assumption 12, Equations (III-30) and (III-31) reduces to,

$$X_{i3}^{\bullet} = \frac{N_i^{\bullet}}{N_w} \qquad \text{(III-32)}$$

Where z_i and z_j are the valence of the cations and the anions respectively.

The Equations (III-17), (III-20), (III-21), (III-28), (III-29), (III-32) and (III-33) completely describe the transport of ions in the RO system.

Expression for the Ionic Intrafacial Equilibrium Constants (K_i^* and K_j^*)

For single salt systems, the quantity K is a true equilibrium constant and is independent of salt concentration. But for multicomponent systems containing several ions, the corresponding quantity K_i^* and K_j^*, unlike K, are dependent on the concentration of the ions. This dependence on the composition is because of the competition between the ions for distribution between the aqueous feed and the membrane.

For single salt system, K is defined as:

$$K_{ij} = \frac{c_M (X_{ij})_M}{cX_{ij}} \qquad \text{(III-39)}$$

This definition is slightly different from that of Rangarajan et al. (1978, 1979, 1984) in the sense that the position of numerator and denominator has been changed. This has been done to make the derivation consistent with other membrane mass transport model such as Solution-diffusion model. When the concentration of the solute is expressed in terms of the ionic concentration, the interfacial equilibrium constant for the salt is given by,

$$K_{ij}^{\pm} = \frac{(c_M X_{iM}^*)^{z_j} (c_M X_{jM}^*)^{z_i}}{(cX_i^*)^{z_j} (cX_j^*)^{z_i}} \qquad \text{(III-40)}$$

and

$$K_{ij}^{\pm} = K_{ij}^{(z_i+z_j)} = (K_i^*)^{z_j} (K_j^*)^{z_i} \qquad \text{(III-41)}$$

For the detailed derivation of the above relationship, refer to Rangarajan et al. (1984).

Expression for the Ionic Solute Transport Parameters, $(\frac{D^{*}_{iM}K^{*}_{i}}{\delta})$ and $(\frac{D^{*}_{jM}K^{*}_{j}}{\delta})$

Since the ions are in equilibrium between the aqueous feed and the membrane, the ionic equilibrium constants can be determined from Equation if $(c_M X^{*}_{iM})$ can be obtained in terms of the composition (cX^{*}_{i}) with which the membranes are in contact. Using Assumption 20 and the electroneutrality condition in the membrane phase, Rangarajan et al. (1984) have derived expression for ionic equilibrium constants. These expressions were further used by Rangarajan et al. (1984) for derivation of the ionic solute transport parameters. Defining two quantities Ψ_{12} and Ψ_{13} as follows:

$$\Psi_{12} = (\frac{D^{*}_{1M}K^{*}_{12}}{\delta})(\frac{cX^{*}_{12}}{D^{*}_{12}}) \tag{III-42}$$

and

$$\Psi_{13} = (\frac{D^{*}_{1M}K^{*}_{13}}{\delta})(\frac{cX^{*}_{13}}{D^{*}_{13}}) \tag{III-43}$$

and using the derived expression of Rangarajan et al. (1984) for ionic solute transport parameters, the ionic flux expressions can be written as:

For cations,

$$N^{*}_{i} = D^{*}_{i}[\{\frac{(D_{SM}K/\delta)_{i2}}{D_{i2}}\}^{(1+\frac{z_i}{z_2})}\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^{(\frac{z_i}{z_1}+\frac{z_i}{z_2})} \times \{(\frac{\Psi_{12}}{cX^{*}_{12}})^{(\frac{z_i}{z_1})}(cX^{*}_{i2}) - (\frac{\Psi_{13}}{cX^{*}_{13}})^{(\frac{z_i}{z_1})}(cX^{*}_{i3})\}] \tag{III-44}$$

and for anions,

$$N_j^\bullet = D_j^\bullet[\{\frac{(D_{SM}K/\delta)_{1j}}{D_{1j}}\}^{(1+\frac{z_j}{z_1})} \times \{(\frac{cX_{12}^\bullet}{\Psi_{12}})^{(\frac{z_j}{z_1})}(cX_{j2}^\bullet) - (\frac{cX_{13}^\bullet}{\Psi_{13}})^{(\frac{z_j}{z_1})}(cX_{j3}^\bullet)\}] \qquad \text{(III-45)}$$

For the ions selected in this study, the flux expressions can be written as:

For Sodium (i=1),

$$N_1^\bullet = D_1^\bullet[\Psi_{12} - \Psi_{13}] \qquad \text{(III-46)}$$

For Chloride (j = 2),

$$N_2^\bullet = D_2^\bullet[\{\frac{(D_{SM}K/\delta)_{12}}{D_{12}}\}^2 \times \{(\frac{cX_{12}^\bullet}{\Psi_{12}})(cX_{22}^\bullet) - (\frac{cX_{13}^\bullet}{\Psi_{13}})(cX_{23}^\bullet)\}] \qquad \text{(III-47)}$$

For Potassium (i=3),

$$N_3^\bullet = D_3^\bullet[\{\frac{(D_{SM}K/\delta)_{32}}{D_{32}}\}^2\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^2 \times \{(\frac{\Psi_{12}}{cX_{12}^\bullet})(cX_{32}^\bullet) - (\frac{\Psi_{13}}{cX_{13}^\bullet})(cX_{33}^\bullet)\}] \qquad \text{(III-48)}$$

For Sulfate (j = 2),

$$N_4^\bullet = D_4^\bullet[\{\frac{(D_{SM}K/\delta)_{14}}{D_{14}}\}^3 \times \{(\frac{cX_{12}^\bullet}{\Psi_{12}})^2(cX_{42}^\bullet) - (\frac{cX_{13}^\bullet}{\Psi_{13}})^2(cX_{43}^\bullet)\}] \qquad \text{(III-49)}$$

For Magnesium (i=3),

$$N_5^\bullet = D_5^\bullet[\{\frac{(D_{SM}K/\delta)_{52}}{D_{52}}\}^3\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^4 \times \{(\frac{\Psi_{12}}{cX_{12}^\bullet})^2(cX_{52}^\bullet) - (\frac{\Psi_{13}}{cX_{13}^\bullet})^2(cX_{53}^\bullet)\}] \qquad \text{(III-50)}$$

For Nitrate (j = 3),

$$N_6^{\bullet} = D_6^{\bullet}[\{\frac{(D_{SM}K/\delta)_{16}}{D_{16}}\}^2 \times \{(\frac{cX_{12}^{\bullet}}{\Psi_{12}})(cX_{62}^{\bullet}) - (\frac{cX_{13}^{\bullet}}{\Psi_{13}})(cX_{63}^{\bullet})\}] \qquad \text{(III-51)}$$

For Calcium (i=7),

$$N_7^{\bullet} = D_7^{\bullet}[\{\frac{(D_{SM}K/\delta)_{72}}{D_{72}}\}^3\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^4 \times \{(\frac{\Psi_{12}}{cX_{12}^{\bullet}})^2(cX_{72}^{\bullet}) - (\frac{\Psi_{13}}{cX_{13}^{\bullet}})^2(cX_{73}^{\bullet})\}] \qquad \text{(III-52)}$$

For Bicarbonate (j = 8),

$$N_8^{\bullet} = D_8^{\bullet}[\{\frac{(D_{SM}K/\delta)_{18}}{D_{18}}\}^3 \times \{(\frac{cX_{12}^{\bullet}}{\Psi_{12}})^2(cX_{82}^{\bullet}) - (\frac{cX_{13}^{\bullet}}{\Psi_{13}})^2(cX_{83}^{\bullet})\}] \qquad \text{(III-53)}$$

Using Equation (III-32) we have:

$$X_{13}^{\bullet}N_W - N_1^{\bullet} = 0 \qquad \text{(III-54)}$$

Substituting the values of $N_1^{\bullet}$ from Equation (III-46) into the Equation (III-54), we have:

$$X_{13}^{\bullet}[AP - A\{(\sum B_{i2}^{\bullet}X_{i2}^{\bullet} + \sum B_{j2}^{\bullet}X_{j2}^{\bullet}) - (\sum B_{i3}^{\bullet}X_{i3}^{\bullet} + \sum B_{j3}^{\bullet}X_{j3}^{\bullet})\}] - D_1^{\bullet}[\Psi_{12} - \Psi_{13}] = 0 \qquad \text{(III-55)}$$

Similarly,

$$X_{23}^{\bullet}N_W - N_2^{\bullet} = 0 \qquad \text{(III-56)}$$

Substituting the values of $N_2^{\bullet}$ from Equation (III-47) into the Equation (III-56), we have:

$$X_{23}^{\bullet}[AP - A\{(\sum B_{i2}^{\bullet}X_{i2}^{\bullet} + \sum B_{j2}^{\bullet}X_{j2}^{\bullet}) - (\sum B_{i3}^{\bullet}X_{i3}^{\bullet} + \sum B_{j3}^{\bullet}X_{j3}^{\bullet})\}] - D_2^{\bullet}[\{\frac{(D_{SM}K/\delta)_{12}}{D_{12}}\}^2 \times \{(\frac{cX_{12}^{\bullet}}{\Psi_{12}})(cX_{22}^{\bullet}) - (\frac{cX_{13}^{\bullet}}{\Psi_{13}})(cX_{23}^{\bullet})\}] = 0 \qquad \text{(III-57)}$$

Similarly,

$$X_{33}^{\bullet}N_W - N_3^{\bullet} = 0 \qquad \text{(III-58)}$$

Substituting the value of $N_3^{\bullet}$ from Equation (III-48) into Equation (III-58), we have:

$$X_{33}^{\bullet}[AP - A\{(\sum B_{i2}^{\bullet}X_{i2}^{\bullet} + \sum B_{j2}^{\bullet}X_{j2}^{\bullet}) - (\sum B_{i3}^{\bullet}X_{i3}^{\bullet} + \sum B_{j3}^{\bullet}X_{j3}^{\bullet})\}] - D_3^{\bullet}[\{\frac{(D_{SM}K/\delta)_{32}}{D_{32}}\}^2\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^2 \times \{(\frac{\Psi_{12}}{cX_{12}^{\bullet}})(cX_{32}^{\bullet}) - (\frac{\Psi_{13}}{cX_{13}^{\bullet}})(cX_{33}^{\bullet})\}] = 0 \qquad \text{(III-59)}$$

Similarly,

$$X_{43}^{\bullet}N_W - N_2^{\bullet} = 0 \qquad \text{(III-60)}$$

Substituting the values of $N_4^{\bullet}$ from Equation (III-49) into Equation (III-60), we have:

$$X_{43}^{\bullet}[AP - A\{(\sum B_{i2}^{\bullet}X_{i2}^{\bullet} + \sum B_{j2}^{\bullet}X_{j2}^{\bullet}) - (\sum B_{i3}^{\bullet}X_{i3}^{\bullet} + \sum B_{j3}^{\bullet}X_{j3}^{\bullet})\}] - D_4^{\bullet}[\{\frac{(D_{SM}K/\delta)_{14}}{D_{14}}\}^3 \times \{(\frac{cX_{12}^{\bullet}}{\Psi_{12}})^2(cX_{42}^{\bullet}) - (\frac{cX_{13}^{\bullet}}{\Psi_{13}})^2(cX_{43}^{\bullet})\}] = 0 \qquad \text{(III-61)}$$

Similarly,

$$X_{53}^{\bullet}N_W - N_2^{\bullet} = 0 \qquad \text{(III-62)}$$

Substituting the value of $N_5^{\bullet}$ from Equation (III-50) into Equation (III-62), we have:

$$X_{53}^{\bullet}[AP - A\{(\sum B_{i2}^{\bullet}X_{i2}^{\bullet} + \sum B_{j2}^{\bullet}X_{j2}^{\bullet}) - (\sum B_{i3}^{\bullet}X_{i3}^{\bullet} + \sum B_{j3}^{\bullet}X_{j3}^{\bullet})\}] - \\ D_5^{\bullet}[\{\frac{(D_{SM}K/\delta)_{52}}{D_{52}}\}^3\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^4 \times \{(\frac{\Psi_{12}}{cX_{12}^{\bullet}})^2(cX_{52}^{\bullet}) - (\frac{\Psi_{13}}{cX_{13}^{\bullet}})^2(cX_{53}^{\bullet})\}] = 0 \tag{III-63}$$

Again,

$$X_{63}^{\bullet}N_W - N_2^{\bullet} = 0 \tag{III-64}$$

Substituting the value of $N_6^{\bullet}$ from Equation (III-51) into Equation (III-64), we have:

$$X_{63}^{\bullet}[AP - A\{(\sum B_{i2}^{\bullet}X_{i2}^{\bullet} + \sum B_{j2}^{\bullet}X_{j2}^{\bullet}) - (\sum B_{i3}^{\bullet}X_{i3}^{\bullet} + \sum B_{j3}^{\bullet}X_{j3}^{\bullet})\}] - \\ D_6^{\bullet}[\{\frac{(D_{SM}K/\delta)_{16}}{D_{16}}\}^2 \times \{(\frac{cX_{12}^{\bullet}}{\Psi_{12}})(cX_{62}^{\bullet}) - (\frac{cX_{13}^{\bullet}}{\Psi_{13}})(cX_{63}^{\bullet})\}] = 0 \tag{III-65}$$

Again,

$$X_{73}^{\bullet}N_W - N_2^{\bullet} = 0 \tag{III-66}$$

Substituting the value of $N_7^{\bullet}$ from Equation (III-52) into Equation (III-66), we have:

$$X_{63}^{\bullet}[AP - A\{(\sum B_{i2}^{\bullet}X_{i2}^{\bullet} + \sum B_{j2}^{\bullet}X_{j2}^{\bullet}) - (\sum B_{i3}^{\bullet}X_{i3}^{\bullet} + \sum B_{j3}^{\bullet}X_{j3}^{\bullet})\}] - \\ D_7^{\bullet}[\{\frac{(D_{SM}K/\delta)_{72}}{D_{72}}\}^3\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^4 \times \{(\frac{\Psi_{12}}{cX_{12}^{\bullet}})^2(cX_{72}^{\bullet}) - (\frac{\Psi_{13}}{cX_{13}^{\bullet}})^2(cX_{73}^{\bullet})\}] = 0 \tag{III-67}$$

and lastly,

$$X^{\bullet}_{83}N_W - N^{\bullet}_2 = 0 \tag{III-68}$$

Substituting the value of $N^{\bullet}_8$ from Equation (III-53) into Equation (III-68), we have:

$$\begin{aligned} &X^{\bullet}_{83}[AP - A\{(\sum B^{\bullet}_{i2}X^{\bullet}_{i2} + \sum B^{\bullet}_{j2}X^{\bullet}_{j2}) - (\sum B^{\bullet}_{i3}X^{\bullet}_{i3} + \sum B^{\bullet}_{j3}X^{\bullet}_{j3})\}] - \\ &\qquad D^{\bullet}_8[\{\frac{(D_{SM}K/\delta)_{18}}{D_{18}}\}^3 \times \{(\frac{cX^{\bullet}_{12}}{\Psi_{12}})^2(cX^{\bullet}_{82}) - (\frac{cX^{\bullet}_{13}}{\Psi_{13}})^2(cX^{\bullet}_{83})\}] = 0 \end{aligned} \tag{III-69}$$

Equations (III-55), (III-57), (III-59), (III-61), (III-63), (III-65), (III-67), and (III-69) are to be solved simultaneously for determining the mole fraction of the ions in the permeate $(X^{\bullet}_{i3})$ and $(X^{\bullet}_{j3})$.

Since density is assumed to be constant throughout the system, the solvent molar flux can be converted into the volumetric flow rate by the following equation:

$$\frac{Q_3}{A_m} = \frac{N_W}{c} \tag{III-70}$$

or,

$$Q_3 = N_W(\frac{A_m}{c}) \tag{III-71}$$

Where A_m is the area of the membrane.

Expression for Mass Transfer Coefficient on the High Pressure Side of the Membrane

The most important aspect of determining the concentration of the ions at the boundary layer is the knowledge of the mass transfer coefficient of the ions on the high pressure side of the membrane. The mass transfer coefficient of the ions vary from ions to ions. As discussed in chapter II, the mass transfer coefficient is dependent on the ion, solution viscosity, and flow pattern and flow rate in the feed channel. It is always beneficial to have turbulence flow in the flow channel. This is dependent on the flow pattern over and around the feed channel. In order to increase the mixing, turbulence promoter nets or channel spacer are used, especially in spiral-wound RO modules.

Also any modeling effort of this nature should take into account the computing effort required for detailed simulation. In order to reduce the computation, Rangarajan et al. (1978) have used the following correlation originally proposed by Matsuura and Sourirajan (1973),

$$k_i^* = k_{NaCl}[D_i^*/D_{NaCl}]^{2/3} \qquad \text{(III-72)}$$

Where k_i^* and k_{NaCl} are the mass transfer coefficient of ion i and NaCl respectively. D_i^* and D_{NaCl} are the diffusivity of ion i and NaCl respectively. The advantage of using such a correlation is that, the mass transfer coefficient of any ion can be related to that of NaCl provided the diffusivity of the ion and the diffusivity of NaCl, in water is known. The data on diffusivity of different ions in water are available in Parsons (1959). The value of k_{NaCl} can be obtained from the KSA analysis of the experimental data with NaCl feed. The disadvantage of this approach are that (i) it needs additional experimentation. (ii) diffusivity data of all ions are not available and available only standard temperature. To simplify further, Rangarajan et al. (1978) have used the average value of the mass transfer coefficient of all ions, that is:

$$k_{av} = \frac{\sum k_i^* + \sum k_j^*}{i+j} \qquad \text{(III-73)}$$

This approach though saves a lot of computation is erroneous since it uses the same value of mass transfer coefficient for all ions. This will result in erroneous prediction of rejection of ions. To add to it this approach does not take into account the effect of turbulence promoter nets. This approach is reasonable when the feed flow rate is constant and permeate recovery is low. But for large systems, the feed flow rate decreases throughout the modules. For these reasons, in order to increase the predictability, an accurate expression for the mass transfer coefficient of the ions should be used.

The mass transfer coefficient is very much dependent on the hydrodynamic conditions in the channel. The hydrodynamic condition varies from module to module. Also the geometry of the channel differs for different module types. Therefore the effect of the geometry of the module can be incorporated into the mass transfer expression. In this model we are concerned with spiral-wound modules. In spiral-wound modules the hydrodynamic conditions are dependent on feed florw rates, channel geometry and the performance of the turbulence promoter nets or spacers. Many models have been developed to describe the mass transfer coefficient in channels (Bird et al., 1960; Kuroda et al., 1983; Hicks and Mandersloot, 1968; Flemmer et al., 1982; Winograd et al., 1973). Most of these approaches are semi-empirical.

The mesh step model of Winograd et al. (1973), originally proposed for electrodialysis system, describes the above mentioned effects well. In this model the spacing net effect is described by two quantities, namely the mesh step, M and the mixing efficiency, K_e. For a given module with a given spacing net, both the mesh step and the mixing efficiency are expected to be constant (Dickson et al., 1992) and hence K_eM is constant. The quantity K_eM can be replaced by a constant , σ. Using this model the mass transfer coefficient of the ions can be calculated as follows:

$$k_i^* = \sigma D_i^{*2/3} \eta^{-1/6} A_{ch}^{-1/2} Q_1^{1/2} \qquad \text{(III-74)}$$

The symbols are defined in the nomenclature. The above equation explicitly relates the feed flow rate and physical parameters of the ion and the solution to the mass transfer coefficient of the ion. Handling the mass transfer equation and its use in the overall model is described in chapter IV.

RO System Model

In general RO systems consist of a number of modules connected to one another either in series or parallel or both. The number of modules in a system vary from a few to even hundred depending on the requirement. In addition to this there may also be either concentrate recycling or permeate recycling or both present in the RO systems. In the separation mode the permeate is usually recycled whereas in the concentration mode the retentate or concentrate stream is recycled. However in many applications, especially high-purity water production, systems recycling is avoided to protect the membranes and the water quality. As a rule of thumb, 25% of the feed is generally thrown away as reject from any RO system. Operation of any RO system can be either batchwise or continuous. In high purity water production invariably the continuous mode of operation is used. In this model development a continuous mode of operation is assumed. Further assumption made for simplification of the analysis are as follows:

1. No recycling stream present in the system.
2. Modules have uniform cross section (not tapered) and are of the same size and type.
3. The RO system is used for preparation of high purity water (high degree of ion removal).

Module Material Balance

In any RO system the feed conditions at the inlet are known. Using a forward approaching method, the feed condition at the inlet to each module can be determined throughout the system. For end to end connected modules, the feed to i'th module is in fact the retentate or concentrate from the (i+1)'th module.

Assuming the total number of module in the system to be ‘n’ and using forward marching technique, the total mass balance and individual ionic mass balance for the n’th module can be written as follows:

overall mass balance,

$$[Q_1]^n = [Q_1]^{n+1} + [Q_3]^n \tag{III-75}$$

Individual cationic mass balance,

$$[Q_1]^n [cX_{i1}^*]^n = [Q_1]^{n+1} [cX_{i1}^*]^{n+1} + [Q_3]^n [cX_{i3}^*]^n \tag{III-76}$$

Individual anionic mass balance,

$$[Q_1]^n [cX_{i1}^*]^n = [Q_1]^{n+1} [cX_{i1}^*]^{n+1} + [Q_3]^n [cX_{i3}^*]^n \tag{III-77}$$

In the above three equations symbols in bracket, superscripted by ‘n’ refer to n’th module.

The flow rate and the concentration of the outlet stream from each module can be determined by solving the overall mass balance and individual ionic mass balance equations for that module. The inlet feed properties to the (n+1)’th module is assumed to be the same as that of the concentrate from the n’th module. The permeate properties (flow rate and ionic concentrations) are determined by the membrane mass transfer model.

The rejection and recovery for each individual module can be calculated by the following equations:

Recovery,

$$Y = (Q_3/Q_1) \times 100 \qquad \text{(III-78)}$$

and Rejection, for cations,

$$R_i = \left(1 - \frac{X^*_{i3}}{X^*_{i1}}\right) \times 100 \qquad \text{(III-79)}$$

for anions,

$$R_j = \left(1 - \frac{X^*_{j3}}{X^*_{j1}}\right) \times 100 \qquad \text{(III-80)}$$

Where Y is the recovery. R_i and R_j are the rejection of the cations and anions respectively.

System Overall Material Balance

Assuming the total number of module in a system is n_T, the overall performance of the system can be expressed by the overall recovery and overall rejection of ions. Since no recycling is present, the total volumetric flow rate of the permeate can be obtained by summing over the total number of modules,

$$[Q_3]^{out} = \sum_{n=1}^{n_T} [Q_3]^n \qquad \text{(III-81)}$$

The outlet permeating ion concentration can be obtained by averaging over the total number of modules:

for cations,

$$[X_{i3}^{*}]^{out} = \frac{\sum_{n=1}^{n_T}[Q_3]^n[X_{i3}^{*}]^n}{[Q_3]^{out}} \tag{III-82}$$

for anions,

$$[X_{j3}^{*}]^{out} = \frac{\sum_{n=1}^{n_T}[Q_3]^n[X_{j3}^{*}]^n}{[Q_3]^{out}} \tag{III-83}$$

Using the outlet volumetric flow rate of the permeate, the overall recovery can be calculated as,

$$Y^{sys} = (\frac{[Q_3]^{out}}{[Q_1]^0}) \times 100 \tag{III-84}$$

Where $[Q_1]^0$ is the flow rate of the feed at the inlet to the RO system.

The overall rejection of the ions can be calculated using the outlet permeating ion concentrations as:

for cations,

$$R_i^{sys} = (1 - \frac{[X_{i3}^{*}]^{out}}{[X_{i1}^{*}]^0}) \times 100 \tag{III-85}$$

for anions,

$$R_j^{sys} = (1 - \frac{[X_{j3}^{*}]^{out}}{[X_{j1}^{*}]^0}) \times 100 \tag{III-86}$$

Where $[X^*_{i1}]^0$ and $[X^*_{j1}]$ are the concentration of cation 'i' and anion 'j' respectively in the feed at the inlet to the RO system.

Since there is no other exit streams except the permeating streams and the final reject stream, the system must obey the system material balance,

$$[Q_1]^0 = [Q_3]^{sys} + [Q_1]^{out} \tag{III-87}$$

Pressure drop in a module:

The pressure drop in the feed channel across the spiral-wound module can be determined by the usual methods for pressure drop based on turbulent flow conditions because of the presence of the turbulence promoter nets. Therefore the there is no way to theoretically calculate the pressure drop for spiral-wound modules. The best way to calculate the pressure drop is to use the manufacturer suggested equation. Alternatively the friction factor has to be expressed in terms of Reynolds number from the experimental data for different type of channel spacer and usual Darcy-Weisbach form of equation can be used. Harris et al. (1969) have used the second approach. In case the modules are of standard size and shape, the pressure drop equation proposed by FilmTec Corporation can be used. This approach is much easier since the pressure drop is related empirically to the feed flow rate and the module length, both of which are known. The FilmTec equation can be written as:

$$[\Delta P]^n = [P]^n - [P]^{n+1} = 165 \times 10^6 \{[Q_1]^n\}^{1.7} L \tag{III-88}$$

Where superscript 'n' refers to nth module. Q_1 is expressed in m^3/sec unit. 'L' is the length of the module expressed in meter. Minor losses in the pressure tube due to the flow of the feed from one module to the next were assumed to be negligible in this study. The above equation is solved to find the applied pressure in the n+1'th module. That is,

$$[P]^{n+1} = [P]^n - 165 \times 10^6 \{[Q_1]^n\}^{1.7} L \tag{III-89}$$

CHAPTER IV

MODEL SOLUTION

Solution Strategy

Solution of the model equations developed in this thesis is critical to the applicability of the model. The solution of the model is impossible without a computer. The model equations are highly complex and also for simulation a large set of experimental data is necessary. Therefore any set of information can either be fed to the main program in the program body itself as common data or in the form of input data files. Similarly the output or result should be obtained in the form an output file. The result should include the calculation of all stream properties (total flow rate, flow rate of each component, mole fraction of each component, etc.) for each module and for each stage. The simulation program also includes a number of subroutines for units conversion, membrane mass transport model, mass transfer coefficient, pressure drop, system balance equations and numerical solution of the model equations.

The model developed is highly flexible in the sense that the membrane mass transport model can be chosen independent of the system model. All information needed to calculate the permeate concentrations for a given module can be provided in the calling statement to that computer subroutine. The model parameters has to be determined experimentally or from correlation of the existing experimental data. If the model parameters are unknown, then the simulation program should be linked to a nonlinear parameter estimation routine which minimizes the difference between known experimental data and the model calculation.

Since the concentration range of the components are very low, in the range of 100ppm - 1ppb, the density of the system is effectively assumed to be constant. The selection of the units depends on the ease of computation and the nature of the correlations used for various computation. Mole fraction is used for component concentrations in this model. The feed concentration is usually available either in the molar or molal units or in ppm of $CaCO_3$. These units first should be first converted into mole fractions. The permeate is assumed to be at atmospheric pressure. So all the pressure terms should be expressed in the same units. The applied pressure difference is in fact the gage pressure.

Since the system of equations to determine the permeate concentrations are highly nonlinear, very effective numerical method is required for solving them. In total we have eight simultaneous non-linear equations. Newton's method is used for solving these equations. In Newton's method an initial guess is critical to the convergence of the solution. The following techniques are followed to estimate the initial guess values for the system of non-linear equations.

(i) The effect of osmotic pressure is neglected. Therefore Equation (III-16) can be written as,

$$N_W = A[P] \tag{IV-1}$$

(ii) The effect of concentration polarization term is neglected. Therefore Equation (III-24) and (III-25) can be written as,

$$X^*_{i2} = X^*_{i1} \tag{IV-2}$$

and

$$X^*_{j2} = X^*_{j1} \tag{IV-3}$$

Using simplification (i) and (ii), the component permeate concentration equations can be written as,

For cations,

$$X_{i3}^{*}=\frac{D_{i}^{*}}{AP}[\{\frac{(D_{SM}K/\delta)_{i2}}{D_{i2}}\}^{(1+\frac{z_i}{z_2})}\{\frac{D_{12}}{(D_{SM}K/\delta)_{12}}\}^{(\frac{z_i}{z_1}+\frac{z_i}{z_2})}\times\{(\frac{\Psi_{12}}{cX_{12}^{*}})^{(\frac{z_i}{z_1})}(cX_{i1}^{*})-(\frac{\Psi_{13}}{cX_{13}^{*}})^{(\frac{z_i}{z_1})}(cX_{i3}^{*})\}] \qquad \text{(IV-4)}$$

For anions,

$$X_{j3}^{*}=\frac{D_{j}^{*}}{AP}[\{\frac{(D_{SM}K/\delta)_{1j}}{D_{1j}}\}^{(1+\frac{z_j}{z_1})}\times\{(\frac{cX_{12}^{*}}{\Psi_{12}})^{(\frac{z_j}{z_1})}(cX_{j1}^{*})-(\frac{cX_{13}^{*}}{\Psi_{13}})^{(\frac{z_j}{z_1})}(cX_{j3}^{*})\}] \qquad \text{(IV-5)}$$

Equations (IV-4) and (IV-5) are linear equations in terms of X_{i3}^{*} and X_{j3}^{*} and can be determined easily. These values can be used as initial approximation for Newton's method.

An alternative method for determining initial guess has also been suggested (High, & Foutch; 1994). The magnitude of the individual component fluxes and permeate concentrations are of the same order. The solution of the model equations for a single component system yields the permeate concentration value for that component. The value obtained can be used as initial guesses (by Newton's method) for solving the equations for the multicomonent systems, since the values of the components permeate concentration are of the same order.

Generalized Algorithm

A generalized algorithm for the solution of the model is presented here. The flowsheet of the algorithm is presented in Appendix C. It is assumed that the following input data is given.

1. Composition of the feed,
2. Flow rate of the feed,
3. Operating pressure,
4. Membrane specification (parameter A and $(D_{SM}K/\delta)_{NaCl}$),
5. Membrane area of a module and area of the high pressure channel,
6. Physical properties of the ions and the feed water such as diffusivity in water, viscosity, and,
7. Molar density of the solution (else this can be computed from individual densities and mole fractions).

The objective is to find X^*_{i3}'s, X^*_{j3}'s, Q_3, ΔP, R and Y for each stage and module, and for the whole system. The following steps should be followed for calculating the above mentioned quantities.

1. From osmotic pressure vs. mole fraction data a for single salts (from literature), for the range of concentration of interest , determine the osmotic coefficients, B^*_i's and B^*_j's.
2. From membrane specification data on $(D_{SM}K/\delta)_{NaCl}$ and literature data on free energy parameter for Na^+ and Cl^- ions, calculate $\ln C^*_{NaCl}$ for the membrane using Equation (B-18). Using the value of $\ln C^*_{NaCl}$ and literature data on free energy parameter for the ions involved, calculate the solute transport parameters using Equation (B-17).
3. Calculate the mass transfer coefficient of the ions 'k' using Equation (B-14) or (B-15).
4. Solve Equations (III-55), (III-57), (III-59), (III-61), (III-63), (III-65), (III-67), (III-69) simultaneously for determining the mole fraction of the ions in the permeate (X^*_{i3} and X^*_{j3}).

5. Solve Equation (III-71) to obtain permeate flow rate, Equation (III-72) to obtain retentate flow rate and Equation (III-76, 77) to obtain the rejected ionic concentrates.
6. Determine the pressure drop using Equation (III-89) or any other appropriate equation. In the absence of any information on pressure drop, 2-5% drop can be assumed between modules.
7. Repeat the calculation steps 3 to 6 for total number of module or stages.
8. Finally determine the recovery, rejection of individual ions, system permeate flow rate, and permeating system ionic concentrations using Equations (III-84), (III-85, 86), (III-81), and (III-82,83) respectively.

Computer Code Description

A generalized computer code is presented in this thesis. Since the main program is not tested in the absence of experimental results, only the part of the program required to solve the set of non-linear equations is presented here. The code, however, can be modified for modeling of multicomponent RO problems. The main body of the program need not be changed. The units of different quantities and physical properties need to be changed to make them dimensionally consistent. The following points should be noted about the developed program RO:

1. The call to NEWTN is inside DO loop 3. The loop has the primary purpose of stepping the solution of the equations (III- 55, 57, 59, 61, 63, 65, 67, 69) through successive modules, starting with module 1 (M=0, feed to module 1).
2. A common block follows the PARAMETER statement in which some of the arrays are sized by the PARAMETER statement:

The COMMON block has a well-defined format, and contens of the various COMMON areas are briefly described below:

(a). COMMON /M/ contains NSTOP and NORUN.

(b). COMMON /X/ contains the vector of the dependent variables X(1), X(2), X(3) etc.

(c). COMMON /F/ contains the residuals of equations (III-55, 57, 59, 61, 63, 65, 67, 69) that is, the functions X(1) to X(8) which results from taking all the terms of the equations to one side of the equations. The residuals are programmed in the subroutine FUNC called by NEWTN, and the purpose of NEWTN is to find values of X(1), X(2) etc. that makes these residuals zero, which will then be the solutions to equations.

(d). COMMON /C/ has the initial guesses or values of X(1), X(2) etc. at M=0 (i.e at the entry to the first module), X10 to X80, which are to be supplied by the methods discussed. MP is the interval in M (module no) at which solution is to be printed.

(3). The EXTERNAL statement defines two subroutine FUNC and JACOB. FUNC defines the equations residuals as discussed in (c) above. JACOB defines the analytical jacobian matrix of the system of non-linear equations and is also an argument of NEWTN.

(4). Input and output unit numbers are defined as 5 and 6 respectively, and the corresponding files are DATA and OUTPUT as defined in the OPEN statement.

(5). Program RO is written for multiple runs (solutions) of equations (III-55, 57, 59, 61 ,63, 65, 67, 69), and the first run is initiated with NORUN=1 at statement 4.

(6). The set of equations linearized by NEWTN is solved by the standard library subroutine LINPAC.

Numerical Computation Methods

The system of equations developed in this model are highly non-linear. Rice (1983) has listed and evaluated different software for solving systems of non-linear equation. Another excellent review on solving non-linear algebraic equations was published by Sargent (1980). Solving systems of nonlinear equations is the most difficult task in all of numerical computation. The principal method for systems of non-linear equations are based on linear models such as Newton's method or secant method.

The system of simultaneous equations developed in this thesis (III-55, 57, 59, 61, 63, 65, 67, 69), that need to be solved, can be expressed by

$$f_i(X^*_{13}, X^*_{23}, \ldots\ldots\ldots\ldots X^*_{83}) = 0 \qquad (i = 1,2,\ldots\ldots 8) \qquad \text{(IV-6)}$$

Where the f_i's represent real-valued functions. We have eight functions involving the variables $X^*_{13}, X^*_{23}, \ldots\ldots, X^*_{83}$. The objective is to find the values of each variables for which each of the functions become zero. In general, the solution of Equation (IV-1) is a tough problem, since the functions f_i's are highly complex. The direct solution in a finite number of operations is usually impossible. Therefore the best way is to develop an iterative type of solution. The multivariable generalization of the Newton's method (Yakowitz & Szidarovszky, 1989; Carnahan & Wilkes, 1973) is used to solve the developed equations in an iterative manner.

In single-variable Newton's method, if an approximation X_t of the root is given, $f(X)$ is approximated by the linear polynomial tangent plane to the surface $f(X_t)$

$$p(X) = f(X_t) + f'(X_t)(X - X_t) \qquad \text{(IV-7)}$$

The next approximation X_{t+1} is defined to be the root of this linear approximating function. This idea is generalized to our multivariative case.

Let the roots of Equation (IV-1) be approximated by the vector

$$X^{(t)} = [X^{*(t)}_{13}, X^{*(t)}_{23}, \ldots\ldots\ldots\ldots X^{*(t)}_{83}] \qquad \text{(IV-8)}$$

Then the multivariable polynomial can be written as,

$$p_i(X^*_{13}, X^*_{23}, \ldots\ldots\ldots, X^*_{83}) = f_i[X^{*(t)}_{13}, X^{*(t)}_{23}, \ldots\ldots\ldots\ldots X^{*(t)}_{83}] \qquad \text{(IV-9)}$$

$$+\sum_{j=1}^{8}\frac{\partial f_i[X_{13}^{*(t)},\ldots\ldots,X_{83}^{*(t)}]}{\partial X_{j3}^{*}}(X_{j3}^{*}-X_{j3}^{*(t)})$$

(i = 1,2,......,8)

The next approximation X^{t+1} is defined to be the solution of the solution of the corresponding linear equations:

$$p_i(X_{13}^{*},X_{23}^{*},\ldots\ldots\ldots\ldots,X_{83}^{*})=0 \quad (i = 1,2,\ldots,8) \qquad \text{(IV-10)}$$

The higher-dimensional generalization of a derivative $f'(X)$ is called the Jacobian matrix J(X), the (i, j)th element of which can be defined as

$$\frac{\partial}{\partial X_{j3}^{*}}f_i(X_{13}^{*},X_{23}^{*},\ldots\ldots\ldots\ldots X_{83}^{*})$$

Defining $J^{(t)}=J(X^{(t)})$ to be the Jacobian matrix of $[f_1(X),f_2(X),\ldots\ldots\ldots,f_8(X)]$, evaluated at the t'th iteration estimate of $X^{(t)}$ and introducing the column vector $f^{(t)}$ whose (j, 1)th term is $f_j(X^{(t)})$, the multivariable Newton's method can be expressed as

$$X^{(t+1)}=X^{(t)}-(J^{(t)})^{-1}f^{(t)} \qquad \text{(IV-11)}$$

In effect this method reduces the solution of a system of simultaneous nonlinear equations to the repeated solution of a system of simultaneous linear equations. Any standard method can be used to solve the system of linear equations. Convergence is guaranteed if the starting vector is close enough to the solution vector and the Jacobian is never zero.

Techniques for determining the initial guess values is already discussed in this Chapter.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The study reported in this thesis included (a) an extensive literature review on RO fundamentals, designing, modeling, and its application for the production of high-purity water and (b) the development of the theoretical framework for multicomponent system modeling of RO. The major points from the study are summarized below:

Literature on RO

1. The literature on RO is extensive. RO has become an important membrane separation technology and its use is increasing day by day. The vastness of the application of RO and its wide acceptance is reflected by the large number of publications. Inspite of all these published works, the necessary details on RO has never been published in a systematic manner.
2. One of the prime objective of this thesis was to systematize the available literature for future investigation. Nearly 250 references have been cited in this thesis. A critical literature review of RO is presented here. The review covers the articles since the inception of RO to the present applications of RO.
3. Most of the research on RO has been devoted to its applications. Though some work has been done on RO modeling, detailed modeling of membranes, modules particularly spiral-wound modules and a system of modules have not been paid enough attention. Another important area of research that is completely neglected is the modeling of multicomponent feed system containing several ions. It is of both practical and

fundamental importance, particularly in high-purity water using industries, to understand the rejection of individual ions present in a multicomponent feed by RO.

4. The use of RO is no longer limited to desalination. It is presently used for production of electronic grade water, boiler feed water and various other forms of ultrapure water. However these applications are a recent phenomena. Very few works have been published on this area in the open literature. The published articles, on the application of RO for the production of ultrapure water, rarely discuss the theoretical basis of using RO. In this thesis most of the available information on this area is analyzed and is presented in a fundamental manner.

5. The complete understanding of RO requires focus on different aspect of it, such as membrane preparation, unit and system modeling, designing applications, and the problems associated with it. RO is now an important separation tool not only in chemical engineering but also in chemistry, biomedical engineering, pharmaceutical engineering, food engineering and technology, mining technology, environmental engineering and other branches of science and technology. For this reason all possible effort is made in this thesis to cover RO from different points of view.

RO System Model

1. It is possible to extend the basic membrane transport equations developed for single solutes to multicomponent systems containing several ions. This is achieved by assuming no ion-ion interactions or ion-membrane interactions. The membrane is assumed as a selective barrier and preferential sorption capillary flow mechanism is assumed to be valid.

2. This model is based on the Kimura-Sourirajan model for membrane transport and the derivation of Rangarajan et al. (1978, 1979, 1984) for ionic flux expressions. The derivation is applicable to all possible feed systems containing any ions. As long as electroneutrality condition is maintained, the model can handle all possible combinations

of ions. Since complete simulation requires a lot of experimental data for all the ions, the model has to be accompanied by experiments. These data are necessary to obtain model parameters. Effort has been made in this thesis to minimize the dependence of the model on experiments. All the components are related to a single components namely NaCl using previous correlations of Sourirajan and co-workers. As a result, for any multicomponent systems experiments are needed for only component.

3. The inclusion of individual ion flux expressions enables the simulation for all possible ions and of different valence, present in the feed water. Since the system of equations to be solved are highly non-linear, very efficient methods of solving the equations are needed.
4. The membrane transport equations are integrated with system balance equations for development of a system model. The system balance equations depend on module arrangements. All different arrangements of modules can be handled in the model. The pressure drop across the modules can not be neglected and can not be given a fixed value. If available, the manufacturer suggested information on pressure drop should be used to calculate the pressure drop.
5. The effect of module geometry on the performance of RO is included in the mass transfer term and area of the membrane in the module. The effect of concentration polarization is also included in the model and is analyzed using the film concept. In order to solve the model a very robust algorithm is necessary. The system of equations to be solved are highly non-linear. The initial guess value for solvent flux and the solute permeate mole fraction can be obtained by neglecting the effect of osmotic pressure and concentration polarization respectively.

Recommendation

A lot of works need to be done to completely simulate a RO system. The multicomponent system model developed in this thesis can act as the theoretical basis of all future work. The science and engineering of RO has progressed a lot in the last two decades. However with the current trend of computerized designs of various process units, RO has really fallen behind. Very few software are available in this field and some of them were developed long back and do not include many theoretical advancements in the last ten tears. Therefore it is of practical significance to develop an efficient software program or to add it as a program into the process flowsheet simulation software such as ASPEN etc., which can be used to understand and model RO accurately and design various RO systems effectively. The major recommendations are summarized below:

1. The simulation of the performance of the RO unit needs a large set of experimental data. Therefore the model equations developed in this thesis has to be accompanied by experimentation to furnish the model parameters.
2. In order to reduce the number of experiments required, empirical correlations on particular feed and membrane type should be developed to correlate the experimental data for one ion or one solute to other components.
3. The reported works on the dependence of physical parameters such as temperature, pressure, pH, viscosity etc. on the RO membrane performance should be verified and if possible be placed on more accurate theoretical basis.
4. In the absence of the experimental data, the simulations for various cases mentioned in the model development section, chapter III., could not be carried out in this thesis. However an algorithm for solution of the model is provided. These cases and other possible cases should be investigated, since these works have never been done before and are of practical importance.

Development of Flowsheet Simulation Software and Computerized Design Software for RO Unit

In the absence of any efficient software for prediction, evaluation and design of RO systems, there exists a scope to develop a robust software to handle all the above cases. Alternatively the model equation can be programmed and included in different process flowsheeting programs. A detailed proposal for developing the flowsheet simulation software and computerized design software for RO unit is presented here.

The above mentioned softwares can be developed in different stages. Stage 1 should include module 1 and 2 and stage 2 should include module 3 and 4.

Module 1

A) Create a database on different membranes, modules and system arrangement types provided by various manufacturers. It should also include vital data on membranes and modules such as area, maximum operating temperature, pressure, pH, nature and influence of the turbulence promoter nets or spacers and other physical properties of the membranes and modules. Any additional information or empirical correlations suggested by the manufacturers for their products should be carefully included in the database.

B) Create a database of the physical properties of the ions or solutes, such as diffusivity in water and in membranes, viscosity etc., present in the feed water.

Module 2

A) Experiment different feed water types with different membrane and module types to collect data for calculation of model parameters. These data should be used to develop correlations for different feed and membrane types.

B) Based on the experiments with single component all other components should be correlated effectively to reduce the number of experiments required. Based on the experiments devise methods such as regressional analysis to determine the properties of the feed, such as density, osmotic pressure etc., from available experimental data for systems for which the properties are difficult to determine.

Module 3

A) Code the RO multicomponent model equations developed in this thesis for spiral-wound modules and also for all other different modules, into an computer language preferably FORTRAN 77. Since the equations to be solved are highly non-linear, different numerical methods should be investigated and tested in order to evaluate their accuracy and run-time.

B) Investigate the multicomponent model developed in this thesis and if possible modify and develop more accurate models. Investigate different cases discussed in model development section of chapter III and perform sensitivity analysis of the model variables and assumptions used in developing the models.

C) Compare the prediction results and actual RO plant data from various production sites of ultrapure water, namely Semiconductor manufacturing facilities, Power utilities etc.. Verify the applicability of the developed models for a broad range of operating conditions.

Module 4

A) Determine possible system arrangements (series, parallel, series and parallel, without recirculation, with recirculation etc.) and different modes of operation (batch or continuous or semibatch) of RO modules used in the production of high purity water. These systems should be modeled in terms of the feed flow rate and individual ion concentrations present in the feed. The system balance equations is to be selected independent of the membrane transport equations and has to be provided in a separate subroutine.

B) Use the simulation results using the flowsheet simulation software developed in module 3 to develop a computerized design approach for the RO unit. An object-oriented design approach is preferable, in accordance with the current trends in designing of various separation units.

C) Optimize the programs for accuracy and required time for running them. Make the programs error-free and workable on a personal computer for easy access to engineering personnel.

The functional decomposition diagram for the development of the flowsheet simulation software and computerized design software for the RO units is presented in Appendix D.

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APPENDIX A

DERIVATION OF CONCENTRATION POLARIZATION EFFECT IN REVERSE OSMOSIS USING THE FILM-CONCEPT

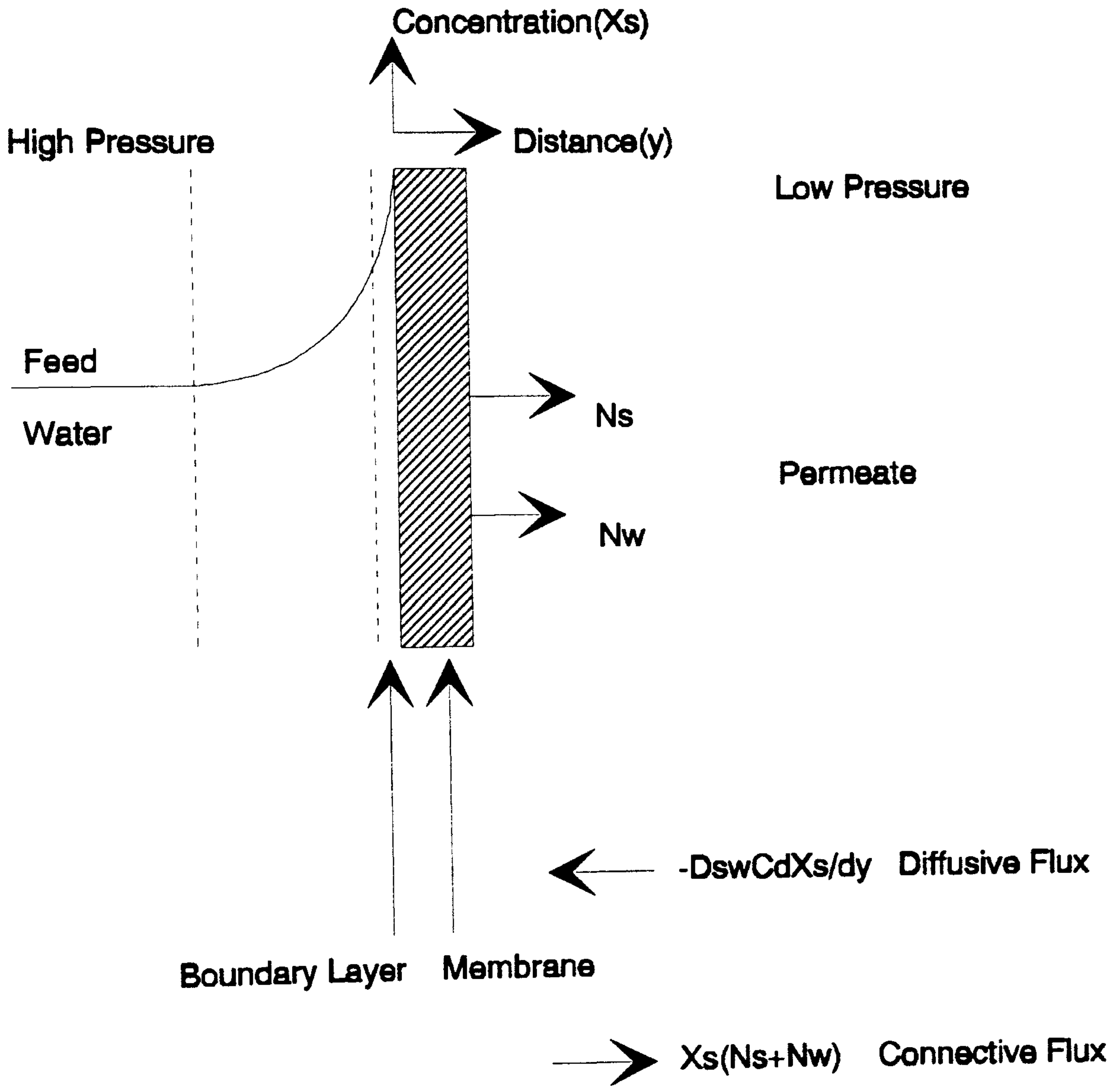


Fig. 8: Concentration Polarization Effect

As explained in Chapter II, concentration polarization effect can be derived in two ways. The derivation is based on the film concept of mass transfer across a boundary layer (Bird, 1960). Sourirajan (1970) first proposed the use of the film concept to derive the concentration polarization effect in reverse osmosis. The following derivation follows from the derivation of Sourirajan (1970) and Rautenbach and Albrecht (1989). Though the previous derivations were applicable for flat membranes, by suitable Assumptions (13, 14, 15, 16 and 18: Model derivation, Chapter III) the same approach is retained for spiral-wound modules.

Since the net solute flux is the sum of the convective flux and the diffusive flux, which are in opposite direction. The solute flux can be written as,

N_S = Convective flux + (- diffusive flux)

or

$$N_S = X_S(N_S + N_W) - D_{SW}c\frac{dX_S}{dy} \tag{A-1}$$

Equation (A-1) can be written in a differential equation form as,

$$\frac{dX_S}{dy} = X_S\frac{(N_S + N_W)}{D_{SW}c} - \frac{N_S}{D_{SW}c} \tag{A-2}$$

But from Equation (III-14), the solute flux can also be written as,

$$N_S = X_{S3}(N_S + N_W) \tag{A-3}$$

Substituting Equation (A-3) into Equation (A-2), we have:

$$\frac{dX_S}{dy} - X_S\frac{(N_S + N_W)}{D_{SW}c} = \frac{(N_S + N_W)}{D_{SW}c}X_{S3} \tag{A-4}$$

Considering the schematic diagram of Figure 8, the boundary conditions for the above differential equations are,

$$\text{At } y = 0,\ X_S = X_{S1} \tag{A-5}$$

$$\text{At } y = L,\ X_S = X_{S2} \tag{A-6}$$

Solving the differential Equation (A-4) with the above boundary conditions, we have:

$$X_{S2} = X_{S3} + (X_{S1} - X_{S3})\exp[\frac{(N_S + N_W)}{c}\frac{L}{D_{SW}}] \tag{A-7}$$

Defining the mass transfer coefficient by the film theory (Bird et al., 1960),

$$k = D_{SW}/L \tag{A-8}$$

Substituting Equation (A-8) into Equation (A-7),

$$X_{S2} = X_{S3} + (X_{S1} - X_{S3})\exp[\frac{(N_S + N_W)}{kc}] \tag{A-9}$$

Using Assumption 12, $N_W >> N_S$, $N_S + N_W$ can be effectively replaced by N_W without significant error,

$$X_{S2} = X_{S3} + (X_{S1} - X_{S3})\exp[\frac{N_W}{kc}] \tag{A-10}$$

Equation (A-10) describes the concentration Polarization effect and the above expression is used in the derivation of the multicomponent model. Though the equation is derived here for single solute, it can be easily extended for multicomponent systems containing several ions by Assumption 1.

APPENDIX B

CORRELATIONS USED IN REVERSE OSMOSIS MODELING

EFFECT OF TEMPERATURE, PRESSURE AND OTHER FACTORS ON THE MODEL PARAMETERS IN REVERSE OSMOSIS

Depending on the nature of the membrane transport model, different correlations have been proposed to explain the effect of temperature and pressure on the model parameters. The solution-diffusion model and the Kimura-Sourirajan model is considered here.

A. **Solution-Diffusion Model**

The following correlations were suggested by Rautenbach and Albrecht (1989). The model parameters in Solution-diffusion model are A, solvent permeability coefficient and B, solute permeability coefficient.

Correlation of A

(1) Pressure:

At a given temperature, $A = A_0 \exp(\alpha_P \frac{\Delta P}{P_0})$ (B-1)

where $\alpha_P = -0.003$ to -0.005 for Cellulose Acetate membranes.

(2) Temperature:

At a given pressure, $A = A_0 \exp(\alpha_T \frac{T - T_0}{T_0})$ (B-2)

where $\alpha_T = 7.1$ for Cellulose acetate membranes.

(3) Viscosity:

At any temperature, $(A.\eta)|_T = (A_0\eta_0)|_{T_0}$ (B-3)

(4) Active layer thickness of the membrane:

$$A = (\frac{\xi}{\Delta y^{0.65}})B^{0.35} \tag{B-4}$$

with

$$\xi = \frac{P_W \overset{)}{V}_W}{P_S^{0.35} \rho_W RT} \tag{B-5}$$

<u>Correlation of B</u>

(1) Pressure:

At a given temperature, $B = \text{constant}$ (B-6)

(2) Temperature:

At a given Pressure, $B = B_0 \exp(\beta_T \frac{T - T_0}{T_0})$ (B-7)

Where $\beta_T = 3.0$ for Cellulose Acetate membranes.

B. Kimura-Sourirajan Analysis

The following correlations were originally proposed by Sourirajan (1970). The model parameters in the KSA model are A, Pure Water Permeability constant and

$(\frac{D_{SM}K}{\delta})$, Solute Transport Parameter. This model is used in this thesis. These correlations are valid for cellulose acetate membranes.

Correlation of A

(1) Pressure:

At a given temperature, $A = A_0 \exp(-\alpha P)$ (B-8)

(2) Temperature:

At a given pressure, $A\mu_W = \text{Constant}$ (B-9)

Correlation of $(\frac{D_{SM}K}{\delta})$

(1) Temperature:

At a given pressure, $(D_{SM}K/\delta)_{NaCl} \propto \exp(0.005T)$ (B-10)

(2) Pressure:

At a given temperature, $(D_{SM}K/\delta)_{NaCl} \propto P^{-\beta}$ (B-11)

(3) Temperature and Pressure:

At a given temperature and pressure, $(\frac{D_{SM}K}{\delta})$ is independent of X_{S2} for completely ionized inorganic solutes.

CORRELATIONS FOR THE MASS TRANSFER COEFFICIENT

Correlation of 'k' for systems with constant feed rate and low permeate recovery

(i) At a given temperature and pressure, $k_{NaCl} \propto Q^n$ (B-12)

(ii) At a given pressure, $k_{NaCl} \propto \exp(0.005T)$ (B-13)

(iii) At any given temperature, pressure and feed flow rate

$$k_{solute} = k_{NaCl}[(D_{SW})_{solute}/(D_{SW})_{NaCl}]^{2/3} \qquad \text{(B-14)}$$

provided the viscosities of the solutions involved are not too different from the viscosity of pure water.

Correlation of 'k' for larger systems and which accounts the effect of the turbulence promoter nets

The mesh step model originally proposed by Winograd et al. (1973) is used in this model. By this model the mass transfer coefficient is related to the diffusivity of the solute, viscosity of the solution, area of the high pressure channel and feed flow rate by the following relationship:

$$k = \sigma D_{SW}^{2/3} \eta^{-1/6} A_{ch}^{-1/2} \{Q_1\}^{1/2} \qquad \text{(B-15)}$$

EMPIRICAL CORRELATIONS FOR PRESSURE DROP

The correlation for pressure drop used in this study was proposed by FilmTec corporation (1984) for spiral-wound modules of 0.5m length and 0.06m diameter.

$$\Delta P = [P_1]^n - [P_1]^{n+1} = 165 \times 10^6 [\{Q_1\}]^{1.7} L \qquad \text{(B-16)}$$

CORRELATION USED IN THE KSA MODEL

The following relationship was originally developed by Matsuura et al. (1975) and Rangarajan et al. (1976) based on the concept of free-energy parameter for ions.

$$\ln(D_{SM}K/\delta)_{salt} = \ln C^{*}_{NaCl} + \sum(-\Delta\Delta G / RT)^{*}_{i} \qquad \text{(B-17)}$$

where, $$\ln C^{*}_{NaCl} = \ln(D_{SM}K/\delta)_{NaCl} - [(-\frac{\Delta\Delta G}{RT})^{*}_{Na^{+}} + (-\frac{\Delta\Delta G}{RT})^{*}_{Cl^{-}}] \qquad \text{(B-18)}$$

APPENDIX C

FLOW DIAGRAM FOR THE SOLUTION OF THE MULTICOMPONENT REVERSE OSMOSIS SYSTEM MODEL DEVELOPED IN THIS THESIS FOR SPIRAL-WOUND MODULES

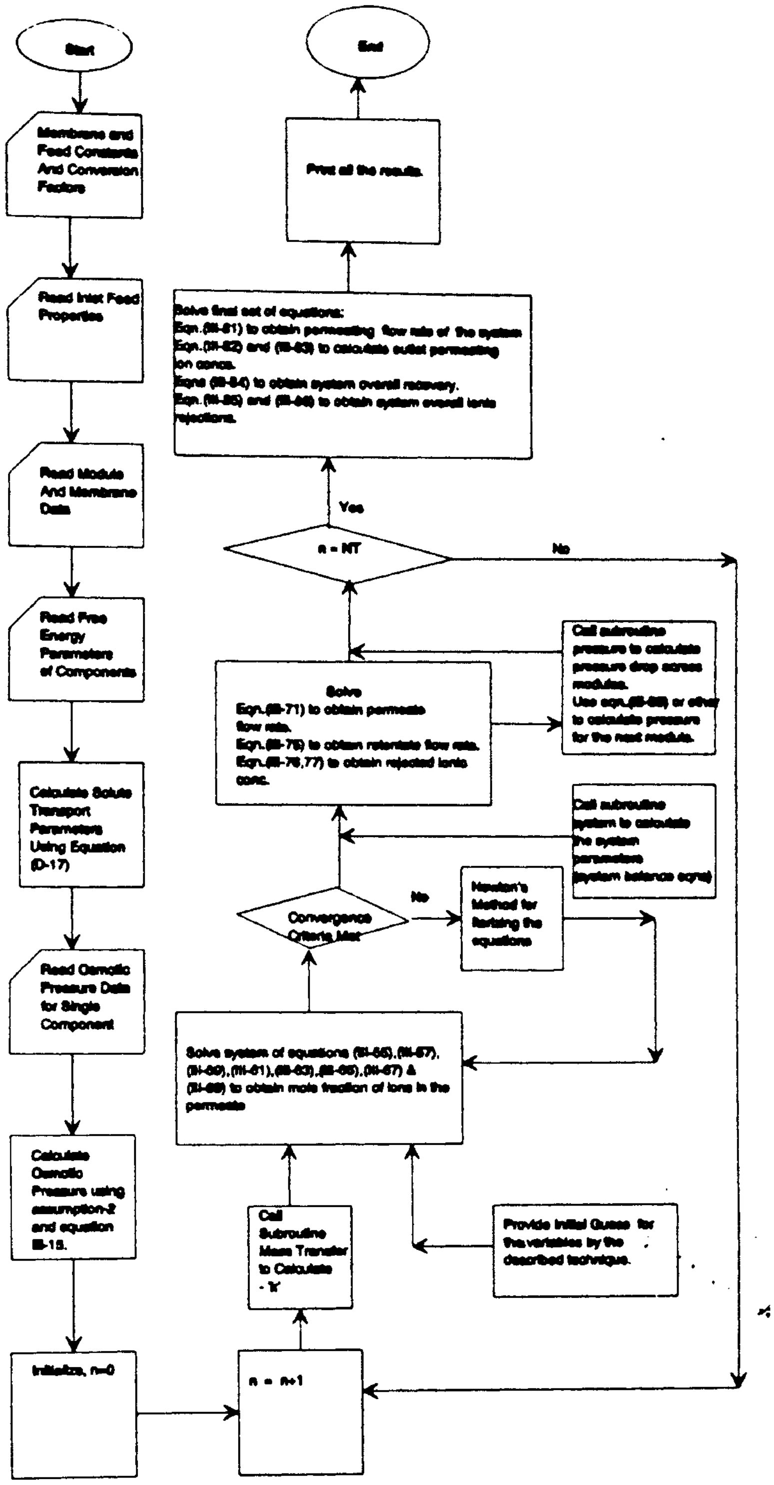


Fig. 9: Flowsheet Diagram.

APPENDIX D

FUNCTIONAL DECOMPOSITION DIAGRAM FOR THE DEVELOPMENT OF A MULTIPURPOSE SOFTWARE FOR THE REVERSE OSMOSIS UNIT USED IN HIGH-PURITY WATER PRODUCTION SYSTEMS

The following abbreviations are used in the functional decomposition diagram.

S1 - STAGE 1; S2 - STAGE 2

M1 - MODULE1; M2 - MODULE2; M3 - MODULE3; M4 - MODULE4

M1A - DATABASE OF MEMBRANES (Manufacturer Supplied)

M1B - DATABASE OF PROPERTIES OF IONS

M1C - DEVELOP THE MATHEMATICAL MODELS

M1AA - MANUFACTURER SUPPLIED INFORMATION

M2A - EXPERIMENT OF DIFFERENT FEED SYSTEMS

M2B - EXPERIMENT WITH DIFFERENT MEMBRANE SYSTEMS

M2AB1 - DEVELOP CORRELATION TO RELATE COMPONENTS

M2AB2 - REGRESSIONAL DATA FOR ANALYSIS TO OBTAIN DATA

M3A -.CODE THE MODEL IN COMPUTER LANGUAGE

M3AA - EFFICIENT NON-LINEAR EQUATION SOLVER

M3B - TEST THE MODEL   M3BB - COMPARE WITH PLANT DATA

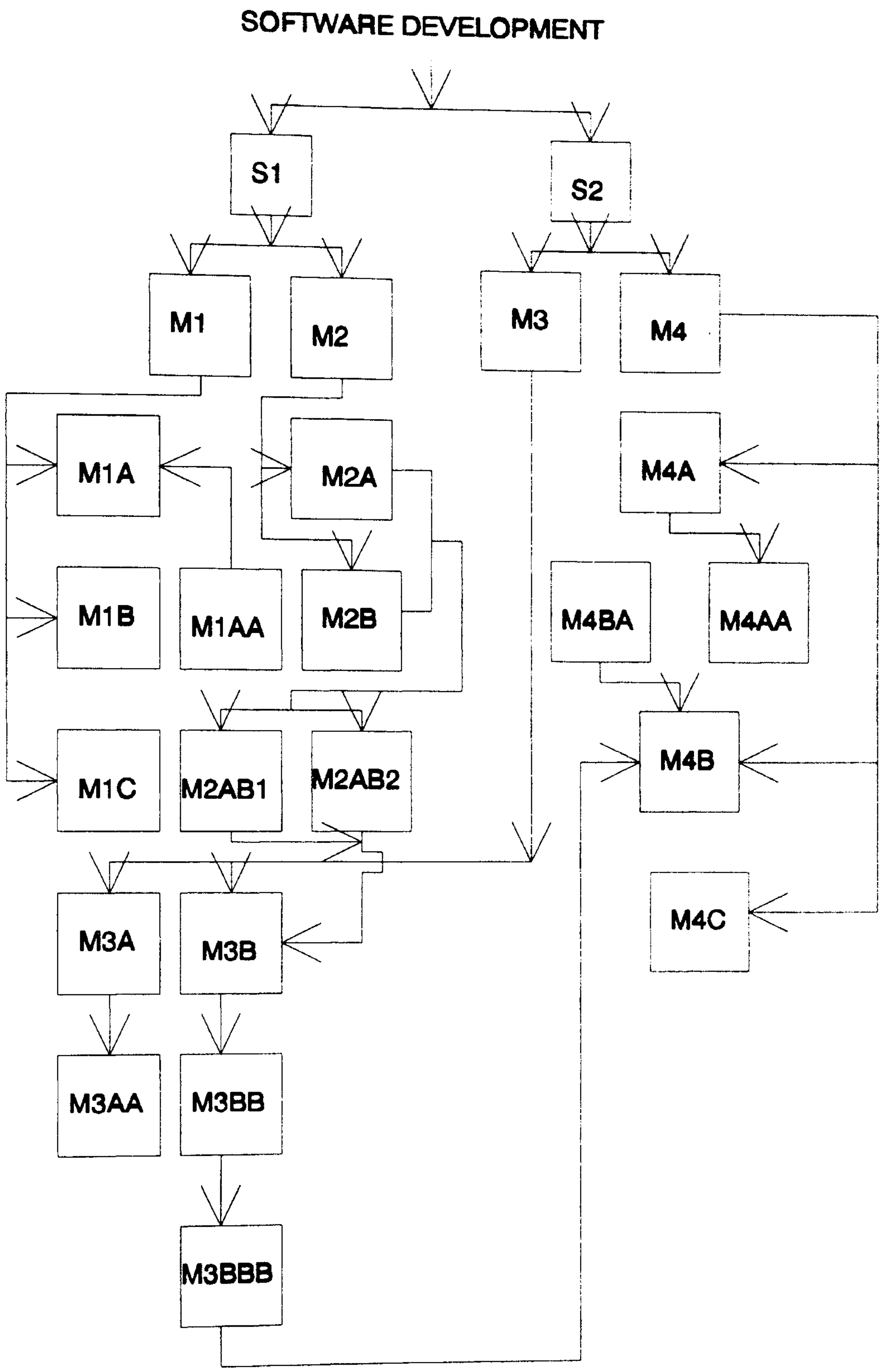
M3BBB - SIMULATION RESULTS

M4A - DETERMINE POSSIBLE SYSTEM ARRANGEMENTS

M4BA - OBJECT ORIENTED APPROACH   M4AA - MODEL THE SYSTEMS

M4B - COMPUTERIZED DESIGN APPROACH

M4C - OPTIMIZE THE PROGRAMS



FUNCTIONAL DECOMPOSITION DIAGRAM

APPENDIX E

COMPUTER CODE FOR SOLUTION OF THE MODEL

```
C ***********************************************************************
C *    PROGRAM RO
C *    PROGRAM TO MODEL THE PERFORMANCE OF MULTICOMPONENT
C *    REVERSE OSMOSIS SYSTEM FOR ULTRAPURE WATER PRODUCTION
C *
C *    THIS PROGRAM IS BASED ON A SPIRAL WOUND RO MODULE.
C *
C *    MEMBRANE MASS TRANPORT MODEL CONSIDERED IS KIMURA-
C *    SOURIRAJAN OR  KSA MODEL.
C *
C *    MASS TRANSFER COEFFICIENT-WINOGRAD ET. AL (1973)(SUGGESTED
C *    METHOD)
C *
C *    PREPARED BY SUNIL KAR
C *    DEPARTMENT OF CHEMICAL ENGINEERING
C *    OKLAHOMA STATE UNIVERSITY
C *    STILLWATER, OKLAHOMA, USA

C*********************** NOMENCLATURE***************************
C
C      ERLIM-  ERROR CRITERIA
C
C      FX(I)-  THE VALUE OF THE NONLINEAR EQUATIONS WHERE I
C      INDICATES  WHICH EQUATION
C
C      N-  THE NUMBER OF NONLINEAR EQUATIONS
C
C      X(I)-  THE INDEPENDENT VARIABLES OF THE PROBLEM
C
C***********************************************************************
C
C      THE ERROR CRITERIA AND THE NUMBER OF NONLINEAR
C      EQUATIONS ARE SPECIFIED IN THE MAIN PROGRAM.
C
```

```
C     THE INITIAL GUESSES ARE SPECIFIED IN SUBROUTINE INITIAL.
C
C     THE FUNCTIONS ARE SPECIFIED IN SUBROUTINE FUNC AND THE
C     PARTIAL DERIVATIVES OF THE FUNCTION WITH RESPECT TO THE
C     INDEPENDENTVARIABLES ARE SPECIFIED IN SUBROUTINE JACOB.
C
C**********************************************************************
      DIMENSION X(10),FX(10),Y(10)
C
C     FILE TO HOLD DOCUMENTATION TITLE
      CHARACTER TITLE(20)*4
      EXTERNAL FUNC, JACOB
C     INITIALIZE THE RUN COUNTER
      DATA NORUN/0/
C     INPUT AND OUTPUT UNIT NUMBERS AND FILES
      NI = 5
      NO = 6
      OPEN (NI, FILE = 'DATA' , STATUS = 'OLD')
      OPEN (NO, FILE ='OUTPUT' , STATUS = 'NEW')
C     STATE THE NEXT RUN
4     NORUN = NORUN + 1
C     READ DATA FILE STARTING WITH DOCUMENTATION TITLE
      READ (NI,900) (TITLE(I), I = 1,20)
C
C     CHECK FOR END OF RUNS (IN THE DATA FILE)
      IF ((TITLE(1) .EQ. 'END') .AND.
     +    TITLE(2) .EQ. 'OF R').AND.
     +    TITLE(3) .EQ. 'UNS')) THEN
C
C     END OF RUNS WAS READ, SO TERMINATE EXECUTION
      STOP
C     CONTINUE RUN WITH CURRENT SET OF DATA
      END IF
C
C     READ INITIAL MODULE NO, FINAL MODULE NO AND PRINT
      INTERVAL  OF MODULES
      READ (NI,901), MO, MF, MP
C
C     READ NUMBER OF EQUATIONS, ERROR TOLERANCE
      PRINT DATA SUMMARY
      WRITE (NO,903), NORUN, (TITLE(I), I=1, 20), MO, MF, MP,
                N, ERLIM
C     INITIAL CONDITIONS
      M = MO
      CALL INITIAL
```

```
C     PRINT THE INITIAL CONDITIONS
      CALL PRINT (NI,NO)
C     NUMBER OF STEPS AND POINTS ALONG THE SOLUTION
      NSTEPS = INT((MF-MO)/MP)
C     STEP THROUGH THE NSTEPS STEPS
      DO 3 NSTEP = 1, NSTEPS
C
C     TAKE A STEP ALONG THE SOLUTION
      CALL NEWTON (N, X,FX,ERLIM)
C     UPDATE MODULE NUMBER AND FIND MODULE QUANTITIES
      M = M + MP
C     UPDATE THE EQUATIONS
       X10 = X(1)
      X20 = X(2)
      X30 = X(3)
      X40 = X(4)
      X50 = X(5)
      X60 = X(6)
      X70 = X(7)
      X80 = X(8)
C     TAKE THE NEXT STEP
3     CONTINUE
C
C     ALL THE STEPS HAVE BEEN TAKEN, SO GO ON
C     TO THE NEXT RUN BY READING THE NEXT SET OF DATA
      GO TO 4
900   FORMAT (20A4)
901   FORMAT (3E10.0)
902   FORMAT (I5, 20X, E10.0)
903   FORMAT (1H1,/,'RUN NO.', I3, '-', 20A4,//,
    +'  INITIAL MODULE NUMBER = ',E10.3,//,
    +'  FINAL MODULE NUMBER = ',E10.3,//,
    +'  PRINT INTERVAL OF MODULE NUMBER = ',E10.3,//,
    +'  SOLUTION BY SUBROUTINE NEWTON',//,
    +'  NUMBER OF EQUATIONS = ',I3,//,
    +'  ERROR TOLERANCE = ',E10.3,//)
      END

      CALL NEWTN(N,X,FX,ERLIM)
C
C     PRINT OUT RESULTS
C
      DO 6 I=1,8
    6 WRITE(NO,*)I,X(I)
      STOP
```

```
      END
C
C***********************************************************************
C
C     SUBROUTINE INITIAL
C
C***********************************************************************
C     DECLARATIVE STATEMENTS
      PARAMETER (N=8)
C
C     COMMON AREAS DEFINED IN MAIN PROGRAM
      COMMON /M/  M, NSTOP, NORUN
     +      /X/  X(N)
     +      /F/  FX(N)
     +      /C/  X10, X20, X30, X40, X50, X60, X70, X80
C
C     INITIAL GUESS
      X10 =
      X20 =
      X30 =
      X40 =
      X50 =
      X60 =
      X70 =
      X80 =
C
C     ESTIMATES OF THE SOLUTION FOR SUBRUTINE NEWTON AT T = 0
      X(1) = X10
      X(2) = X20
      X(3) = X30
      X(4) = X40
      X(5) = X50
      X(6) = X60
      X(7) = X70
      X(8) = X80
C
      RETURN
      END
C
C***********************************************************************
C
C     SUBROUTINE JACOB(N,X,A)
C
C***********************************************************************
C
```

```
C     THIS SUBROUTINE CALCULATES THE PARTIAL DERIVATIVES OF THE
C     THE FUNCTIONS WITH RESPECT TO THE INDEPENDENT VARIABLES.
C     A(I,J) REPRESENTS THE PARTIAL OF THE ITH FUNCTION WITH
C     RESPECT TO THE JTH VARIABLE.
C
C**********************************************************************
C
      DIMENSION A(10,10),X(10),FXB(10),FXD(10)
C
      DELTA=.01
C     CALCULATE FUNCTION VALUE AT X(I)
      CALL FUNC(N,X,FXB)
C     CALCULATE NUMERICAL DERIVATIVES USING FINITE DIFFERENCE
C     EQUATIONS
      DO 1 I=1,N
      X(I)=X(I)*(1.+DELTA)
      CALL FUNC(N,X,FXD)
      X(I)=X(I)/(1.+DELTA)
      DO 2 J=1,N
    2 A(J,I)=(FXD(J)-FXB(J))/X(I)/DELTA
    1 CONTINUE
      RETURN
      END
C
C**********************************************************************
*
C
      SUBROUTINE FUNC(N,X,FX)
C
**********************************************************************
C
C     THIS SUBROUTINE CALCULATES THE VALUES OF EACH NONLINEAR
C     EQUATION GIVEN THE VALUE OF X(I) AND N.  THESE VALUES ARE
C     SUPPLIED TO THIS SUBROUTINE WHEN IT IS CALLED BY NEWTN
C
C**********************************************************************
C
      REAL X(N), FX(N)
C     COMMON AREA FOR THE SOLUTION AT THE PRECEDING TIME STEP
      COMMON /C/ X10, X20, X30, X40, X50, X60, X70, X80
      DIMENSION X(10),FX(10)
      CALL MASS(METHOD, N, X, K)
C     WRITE THE SET OF NONLINEAR EQUATIONS DEVELOPED
      FX(1)=
      FX(2)=
```

```
      FX(3)=
      FX(4)=
      FX(5)=
      FX(6)=
      FX(7)=
      FX(8)=
      RETURN
       END
C
C*********************************************************************
C
      SUBROUTINE MASS (METHOD,N,X,K)
C
C*********************************************************************
C
C     HERE THE MASS TRANSFER COEFFICIENTS OF THE IONS ARE
C     CALCULATED:
C     METHOD:  0 - IMPLIES RANGARAJAN ET AL. METHOD (1978)
C                  1 - IMPLIES WINOGRAD ET AL. METHOD (1973)
C     ACH - AREA OF THE CHANNEL ON HIGH PRESSURE SIDE OF THE
C     MEMBRANE
C     VISC - VISCOSITY OF THE SOLUTION
C     KNACL - MASS TRANSFER COEFFICIENT OF SODIUM CHLORIDE
C     DNACL - DIFFUSIVITY OF SODIUM CHLORIDE
C     SIG - PRODUCT OF MESH STEP AND MIXING EFFICIENCY (CONSTANT)
C     K - MASS TRANSFER COEFFICIENT
C*********************************************************************
      INTEGER N,I
      REAL X(N),Q1,VISC, DNACL, K
      COMMON SG,ACH,Q1,VISC,KNACL
      IF (METHOD .EQ. 0) THEN
C           COMPUTE MTC BY RANGARAJAN ET AL. METHOD (1978)
      DO 111 I = 1,N
      KAV = 0
      K(I) = KNACL*((D(I)/DNACL))**(2/3))
      KAV = KAV + K(I)
 111  CONTINUE
      ELSE
C     COMPUTE MTC BY WINOGRAD ET AL. METHOD (1973)
      K(I) = ((SIG*(D(I)**(2/3)*(VISC)**(-1/6)*(ACH)**(-1/2)*(Q1)
      RETURN
      END

C*********************************************************************
C
```

```
      SUBROUTINE NEWTN(N,X,FX,ERLIM)
C
C************************************************************************
C
C     THIS SUBROUTINE EMPLOYES NEWTON'S METHOD IN ORDER TO
C     SOLVE A SET OF N NONLINEAR EQUATIONS CONTAINING N
C     UNKNOWNS.
C
C     THIS SUBROUTINE IS CALLED BY THE MAIN PROGRAM AND IS
C     SUPPLIED THE VALUES OF THE INITIAL GUESS FOR X(I)'S AS WELL
C     AS THE VALUE OF N.  THIS SUBROUTINE USES THE VALUES OF THE
C     FUNCTION FROM FUNC AND THE VALUES OF THE PARTIAL
C     DERIVATIVES OF THE FUNCTION IN ORDER TO DETERMINE THE
C     SOLUTION. THIS METHOD USES THE LIBRARY ROUTINE LINPAC
C     TO SOLVE THE SYSTEM OF LINEAR EQUATION USED BY NEWTON'S
C     METHOD.
C
C**********************************************************************
C
C
      DIMENSION A(10,10),X(10),FX(10),B(10),RAT(10)
C
C
C     NOTE THAT AA,BB,XX,IPVT 'MUST BE' DIMENSIONED BY N
C
      DOUBLE PRECISION AA(4,4),BB(4),XX(4),IPVT(4)
    1 CONTINUE
      ITEST=0
C
      CALL INITIAL
C     MAKE FUNCTION EVALUATIONS
C
      CALL FUNC(N,X,FX)
      DO 8 I=1,N
    8 B(I)=-FX(I)
C
C     EVALUATE JACOBIAN MATRIX
C
      CALL JACOB(N,X,A)
      DO 32 I=1,N
      DO 32 J=1,N
   32 AA(I,J)=A(I,J)
      DO 35 I=1,N
   35 BB(I)=B(I)
C
```

```
C     CALL LINEAR EQUATION SOLVER
C
      CALL LINPAC(N,AA,BB,XX,IPVT)
C
C     MAKE AN IMPROVED VALUE FOR X(I)
C
      DO 9 I=1,N
      RAT(I)=XX(I)/X(I)
    9 X(I)=X(I)+XX(I)
C
C     CHECK FOR CONVERGENCE
C
      DO 125 I=1,N
  125 IF(ABS(RAT(I)).GT.ERLIM)ITEST=ITEST+1
      WRITE(NO,10)(X(I),FX(I),I=1,N)
   10 FORMAT( 3H X=,E14.7,5X,3H F=,E14.7)
      WRITE(NO,11)
   11 FORMAT( ////)
      IF(ITEST.NE.0)GO TO 1
      RETURN
      END
C
C**********************************************************************
C
      SUBROUTINE LINPAC(N,A,B,X,IPVT)
C
C**********************************************************************
C
C     N - THE NUMBER OF EQUATIONS (INPUT)
C
C     A(I,J) - THE COEFFICIENT OF THE JTH VARIABLE IN THE ITH
C     EQUATION. THE MATRIX MUST BE DOUBLE PRECISIONED AND
C     DIMENSIONED n*n(INPUT)
C     B(I) - THE CONSTANT TERM FOR THE ITH EQUATION. THIS VECTOR
C     MUST BE DOUBLE PRECISIONED AND DIMENSIONED BY n (INPUT).
C     X(I) - THE VALUE OF THE ITH UNKNOWN. THIS VECTRO MUST BE
C     DOUBLE PRECISIONED AND DIMENSIONED BY n (OUTPUT)
C
C     IPVT(I) - A WORK VECTOR WHICH MUST BE DOUBLE PRECISIONED
C     AND DIMENSIONED BY n.
C
C     COMMENT: THIS ALGORITHM IS TAKEN FROM ARGONNE NATIONAL
C     LABORATORY.
C     THE SUBROUTINES HAVE BEEN WRITTEN BY DIFFERENT
C     INDIVIDUALS.
```

```
C
C       IT EMPLOYS PARTIAL PIVOTING AND MATRIX DECOMPOSITION
C       WITH GAUSSIAN ELIMINATION TO EFFICIENTLY SOLVE LARGE SETS
C       OF LINEAR EQUATION
C
C*****************************************************************************
        RETURN
        END
```

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