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EVALUATION OF NEW REVERSE OSMOSIS MEMBRANES FOR THE SEPARATION OF TOXIC COMPOUNDS FROM WASTEWATER

FINAL REPORT

By

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In the first year of this study, efforts were made to select the most effective reverse osmosis membrane materials for treating the MUST hospital wastewaters. This was accomplished with the advent of the NS-100 and the aromatic polyamide membranes.

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During the second year of the study, an extensive study on the characteristics of the NS-100 membrane was conducted. These studies included formulation of mathematical models for optimizing the casting conditions for flat sheet NS-100, predicting its performance under various operating conditions, and relating its surface structure to its degree of separation of organic compounds using a simple test with sodium chloride solution. In addition, exploratory work was conducted on the potential application of both NS-100 and aromatic polyamide membranes (B-9 and B-10 permeators) to other wastewaters.

The objectives of the third and last year of this study were to evaluate the engineering parameters involved in applying NS-100 membranes to the treatment of wastewater. The tasks included optimizing the casting of tubular NS-100 membrane, evaluating the chemical stability of NS-100 towards oxidants, studying the effects of additives on the ability of the membrane to maintain its performance, and developing a computer program for the design of a large treatment plant using results of tests on single tubes or tubular modules.

The major tasks completed during the past three years of the study are well documented in the nineteen papers published mostly in scholarly and refereed journals, along with encouraging comments from Dr. S. Sourirajan, the leading authority in the field of reverse osmosis, as shown in Appendix I and II of the final report.

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TABLE OF CONTENTS

		Page
1.	INTRODUCTION	1
2.	FABRICATION OF EQUIPMENT	2
	2.1 Test Cells	2
	2.2 Flat Sheet Membrane Casting Apparatus	2
	2.3 High Capacity Pumping System	3
	2.4 Tubular Membrane Test Section	3
3.	PERFORMANCE OF NEW MEMBRANES	8
	3.1 Membrane Contributors	8
	3.2 Selection of Model Organic Compounds	8
	3.3 Analytical Procedures	8
	3.4 Testing of Flat Sheet Membranes	13
	3.5 Testing of Hollow Fiber Membranes	13
	3.6 Testing of Tubular Membranes	17
	3.7 Results and Discussion	17
4.	CASTING OF NEW MEMBRANES	32
	4.1 CA Membrane	32
	4.2 CAB and CA(blend) Membranes	32
	4.3 Crosslinked-PEI Membrane (NS-100)	34
5.	CRITERION OF ION SEPARATION	39
	5.1 Results and Discussion	40
6.	REMOVAL OF ORGANIC COMPOUNDS WITH NEW MEMBRANES	49
	6.1 Removal of Thirteen Model Compounds	49
	6.1.1 Results and Discussion	52
	6.2 Removal of Pesticides	66
	6.2.1 Results and Discussion	72
	6.3 Removal of Alcohols, Aliphatic Acids, and Amines by NS-100 Membranes	81
	6.3.1 Results and Discussion	83
7.	OPTIMIZATION OF MEMBRANE PERFORMANCE	96
	7.1 Two-Level Factorial Design	96
	7.2 Fractional Factorial Design	98
	7.3 Constrained Optimization	102
	7.4 The First Series of Designed Experiments	102
	7.5 The Second Series of Designed Experiments	116
	7.6 The Third Series of Designed Experiments	126
	7.7 The Fourth Series of Designed Experiments	134
	7.8 Results and Discussion	141

		Page
8.	RESISTANCE OF NS-100 MEMBRANE TO OXIDANTS	144
	8.1 Resistance to Chlorine	144
	8.2 Resistance to Ozone	144
	8.3 Resistance to Chromate	147
9.	METHODS FOR MINIMIZING MEMBRANE FOULING	149
	9.1 Pretreatment of Wastewaters	149
	9.2 Membrane Cleaning Techniques	151
	9.3 Additives	154
10.	DESIGN AND OPTIMIZATION OF A LARGE SCALE RO PLANT	156
	10.1 Objectives and Scope	156
	10.2 Mathematical Modeling	156
	10.2.1 An Analytical Model from a Mechanistic Approach	159
	10.3 Casting of NS-100 Tubular Membranes	167
	10.3.1 Experimental Procedure and Apparatus	167
	10.4 Data Acquisition	172
	10.5 Empirical Correlation of Experimental Data	174
	10.5.1 Effect of Operating Pressure Upon Pure Water Permeability Coefficient	174
	10.5.2 Effect of Interfacial Concentration Upon Salt Permeability Coefficient	174
	10.5.3 Discussion of the Empirical Correlations	174
	10.5.4 Computer Prediction	180
	10.6 A General Regression Technique for Modeling	184
	10.6.1 An Analytical Model from Black-Box Experimentation	200
	10.6.2 Nonlinear Coefficient Estimation by Least Squares	202
	10.6.3 Comparison of Mechanistic and Regression Models	204
	10.7 Optimization Techniques	209
	10.7.1 Numerical Optimization of Nonlinear Multivariable Functions	210
	10.7.2 Estimation of Coefficients by Marquardt's Method	212
	10.7.3 Optimization by Steepest Descent	214
	10.8 Plant Optimization Technique	222
	10.9 Plant Layout	223
	10.10 Economic Analysis	225
	10.11 Comparison of Plant Optimization to Non-optimum Results	226

		Page
11.	RECOMMENDATIONS	233
12.	NOMENCLATURE	234
13.	REFERENCES	238
14.	APPENDIX I - CORRESPONDENCE	245
	APPENDIX II - PUBLICATIONS	248
	APPENDIX III - EQUIPMENT	251
	APPENDIX IV - COMPUTER CODES	254
	APPENDIX V - TOXICITY DEFINITIONS	308

LIST OF TABLES

Table		Page
1	Candidate Membranes and Their Contributors	9
2	Organic Compounds Commonly Occurring in Hospital Wastewater	10
3	Chemical Structures of Model Compounds and Their Use in a Hospital	12
4	Performance of Candidate Membranes at 600 psi, 24°C and 0.30 gpm Feed Flow Rate	14
5	Performance of Candidate Membranes at 1,500 psi, 24°C and 0.30 gpm Feed Flow Rate	15
6	Summary of the Performance of B-9 Permeator at 400 psi, 24°C and 75% Conversion	16
7	Summary of the Performance of Two Tubular Modules of Universal Oil Products	18
8	Test of the Reproducibility of the Cast CA Membranes	33
9	Preliminary Comparison of the Performance of the Cast and the Contributed Membranes at 600 psi, 24°C and 0.30 gpm	35
10	Preliminary Comparison of the Performance of the Crosslinked-PEI Membranes at 600 psi, 24°C and 0.30 gpm	38
11	Prediction of Separation of Individual Cations in Aqueous Solution Containing a Mixture of Metallic Chloride	48
12	Reverse Osmosis Membranes, Their Abbreviations, Configurations and Suppliers	50
13	Organic Compounds for Membrane Testing	51
14	Average Permeate Fluxes and Overall Solute Separations of Reverse Osmosis Membranes	60
15	Separation of Soluble Organics in Sewage and Secondary Effluents by Reverse Osmosis	65
16	Classification and Properties of Pesticides Tested	68

Table		Page
17	Removal of Chlorinated Pesticides by Reverse Osmosis	73
18	Removal of Organophosphorous Pesticides by Reverse Osmosis	74
19	Removal of Miscellaneous Pesticides by Reverse Osmosis	74
20	Performance of NS-100 Membranes when Tested with 500 ppm Sodium Chloride Solution at 600 psig and 25°C	82
21	Removal of Isomers of Butylamine by NS-100 Membranes	90
22	Alternative Notations for the 2^3 Factorial Design	97
23	The Construction of the 2^{4-1} Fractional Factorial Design	100
24	Lower and Upper Levels of Variables Studied in First Series of Design Experiments	104
25	Experimental Conditions and Average Performance of NS-100 Membranes in First Series of Design Experiments	106
26	Coefficients of the Regression Equations of Salt Rejection and Permeate Flux for First Series of Design Experiments	108
27	Observed and Calculated Salt Rejection for First Series	110
28	Observed and Calculated Permeate Flux for First Series	112
29	Main Effects and Two-Factor Interaction Effects of Variables in the First Series to Salt Rejection and Permeate Flux	114
30	Lower and Upper Levels of Variables Studied in Second Series of Design Experiments	118
31	Experimental Conditions and Average Performance of NS-100 Membranes in Second Series of Design Experiments	119
32	Coefficients of the Regression Equations of Salt Rejection and Permeate Flux for Second Series	120
33	Observed and Calculated Salt Rejection for Second Series	121
34	Observed and Calculated Permeate Flux for Second Series	122
35	Main Effects and Two-Factor Interaction Effects of Variables in the Second Series to Salt Rejection and Permeate Flux	123

Table		Page
36	Lower and Upper Levels of Variables Studied in the Third Series of Design Experiments	128
37	Experimental Conditions and Average Performance of NS-100 Membranes in Third Series of Design Experiments	129
38	Coefficients of the Regression Equations for Salt Rejection and Permeate Flux for the Third Series	130
39	Observed and Calculated Salt Rejection and Permeate Flux in the Third Series	131
40	Main Effects and Two-Factor Interaction Effects of Variables to Salt Rejection and Permeate Flux in the Third Series	132
41	Levels of the Variables and Responses Observed for Verification of Third Series Predicted Optimum Performance	135
42	Experimental Conditions and Observed Responses for the Fourth Series of Design Experiments	137
43	Levels of the Variables Studied in the Fourth Series of Design Experiments	138
44	Coefficients of the Regression Equations for Salt Rejection and Permeate Flux and Observed Versus Calculated Values	139
45	Main Effects and Two-Factor Interaction Effects for Salt Rejection and Permeate Flux in the Fourth Series	140
46	Performance of NS-100 Membrane After Soaking in Aqueous Solutions Containing Chlorine Residuals	145
47	Performance of NS-100 Membranes After Soaking in Aqueous Solutions Containing Ozone Residual	146
48	Performance of NS-100 Membranes when Tested with a 5000 ppm Sodium Chloride Solution Containing Sodium Chromate	148
49	Membrane Cleaning Techniques for Reverse Osmosis	152
50	NS-100 Membrane Casting Variables for Flat Sheet Membrane	168

Table		Page
51	Optimized NS-100 Membrane Casting Variables for Flat Sheet Membrane	169
52	Membrane Casting Variables for Tubular Membranes	171
53	Comparison of Computer Predicted Values to Experimental Data	199
54	Tabulation of Non-optimum Operating Conditions and Results	227
55	Tabulation of Optimum Operating Conditions and Results	228
56	Tabulation of Optimum Operating Conditions and Results - Quadratic Model	232

LIST OF FIGURES

Figure		Page
1	Schematic and Operational Diagram of the Membrane Casting Equipment	3
2	Schematic Diagram of the High Pumping Capacity System	5
3	Drawing of the Tubular Test Section	7
4	RO Separation of Organic Compounds in Aqueous Solutions Using Cellulose Acetate Base Membranes	20
5	Effect of pH of Feed Solution and Degree of Dissociation on Separation of Phenol	22
6	Rejections of Organic Solutes Consisting of Hydroxyl Group by Cellulose Acetate Membrane and Its Derivatives	23
7	Flux of Cellulose Acetate Base RO Membranes with Organic Compounds in Aqueous Solutions	24
8	RO Separation of Organic Compounds in Aqueous Solution Using Polyamide Membranes	26
9	RO Separation of Organic Compounds in Aqueous Solutions Using NS-1 Membranes	27
10	Comparison of RO Separation of Organic Compounds Using Different Types of Membranes	28
11	Comparison of Separation of Organic Compounds by the Tubular NS-1 and MINI-MODULE (CA) from UOP Fluid System	29
12	Flux of New RO Membranes with Organic Compound in Aqueous Solutions	30
13	Partial Reaction Product of Polyethylenimine with m-Tolylene 2,4-Diisocyanate	37
14	Relative Permeabilities of Cations	41
15	Relative Permeabilities of Anions	42
16	Reduced Permeabilities of Cations	44
17	Reduced Permeabilities of Anions	46
18	Separation of Sodium Chloride	53
19	Separation of Methanol, Ethanol and i-Propanol	54

Figure		Page
20	Separation of Acetic Acid and Formaldehyde	55
21	Separation of Acetone and Ethyl Ether	56
22	Separation of Urea and Glycerol	57
23	Separation of Phenol and Hydroquinone	58
24	Separation of Aniline and Methyl Acetate	59
25	Schematic of Abcor's Test Cell	71
26	Removal of n-Alkyl Alcohols	84
27	Steric Effect on the Removal of Isomers of Propanol, Butanol and Pentanol	86
28	Removal of Methylamine at Various Degrees of Ionization	88
29	Comparison of the Removal of Primary and Secondary Amines	89
30	Removal of Acetic Acid at Various Degrees of Dissociation	91
31	Removal of Formic Acid at Various Degrees of Dissociation	92
32	Removal of n-Alkyl Acids	93
33	Steric Effect on the Removal of Isomers of Butyric and Valeric Acids	94
34	Removal of Model Compounds by NS-100 Membranes at 600 psi and 24°C	95
35	Pretreatment for Reverse Osmosis Process	150
36	Flowchart of Major Research Efforts and Relationship to Each Other	157
37	Basic Modeling Techniques	158
38	Velocity and Concentration Profiles During Reverse Osmosis Desalination of a Salt Solution in Turbulent Flow	161
39	Effect of Operating Pressure Upon Pure Water Permeability Coefficient	175

Figure		Page
40	Effect of Operating Pressure Upon Pure Water Permeability Coefficient	176
41	Effect of Operating Pressure Upon Pure Water Permeability Coefficient at Elevated Pressures	177
42	Effect of Interfacial Concentration Upon Salt Permeability Coefficient	178
43	Effect of Interfacial Concentration Upon Salt Permeability Coefficient	179
44	Comparison of Predicted and Experimental Product Rate as a Function of Operating Pressure	181
45	Listing of Computer Code Used to Predict Water Quantity and Quality	185
46	Comparison of Predicted and Experimental Product Rate as a Function of Feed Concentration	188
47	Comparison of Predicted and Experimental Product Rate as a Function of Feed Concentration	189
48	Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Concentration	190
49	Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Concentration	191
50	Comparison of Predicted and Experimental Product Rate as a Function of Feed Rate	192
51	Comparison of Predicted and Experimental Product Rate as a Function of Feed Rate	193
52	Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Rate	194
53	Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Rate	195
54	Comparison of Predicted and Experimental Product Rate as a Function of Operating Pressure	196
55	Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Operation Pressure	197

Figure		Page
56	Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Operating Pressure	198
57	Two-dimensional Selection of Least Squares Coefficients	205
58	Comparison of Mechanistic and Quadratic Polynomial Models	206
59	Comparison of Mechanistic and Quadratic Polynomial Models	207
60	Comparison of Mechanistic and Quadratic Polynomial Models	208
61	Two-dimensional Geometric Interpretation of the Gradient	215
62	A Sequence of Steepest Descent Moves	216
63	Calculation of a Two-dimensional Gradient	218
64	Two-dimensional Steepest Descent with Optimum at a Boundary	220
65	Two-dimensional Steepest Descent with Variable Held on Boundary and Released	221
66	Generalized Reverse Osmosis Desalination Plant Layout	224
67	Non-optimum Plant Geometry	229
68	Optimum Plant Geometry	229
69	Optimum Plant Geometry - Quadratic Model	231

I. INTRODUCTION

This final report presents the results of a project entitled "Evaluation of New Reverse-Osmosis Membranes for the Separation of Toxic Compounds from Wastewater" conducted for the U. S. Army Medical Research and Development Command under contract No. DADA 17-73-C-3025. In the first year of the study, efforts focussed on selecting the most effective reverse osmosis membrane materials for treating MUST hospital wastewaters. The new NS-100 and aromatic polyamide membranes were found to be the most promising.

During the second year of the study, an extensive study of the characteristics of the NS-100 membrane was conducted. These studies included formulation of mathematical models for optimizing the casting conditions for flat-sheet NS-100, predicting its performance under various operating conditions, and relating its structure to its separation capability for organic compounds by means of a simple test using a sodium chloride solution. In addition, exploratory work was conducted on the potential application of both NS-100 and aromatic polyamide membranes (B-9 and B-10 permeators) to other wastewaters. As a result of the first year's effort, the latter membranes were also found to be excellent in separating the low-molecular-weight polar organics from aqueous solutions.

The objectives of the third and last year of this study were to evaluate the engineering parameters involved in applying the NS-100 membrane to the treatment of wastewater. The tasks included optimizing the casting of tubular NS-100 membranes, evaluating the chemical stability of NS-100 toward oxidants, studying the effects of additives on the ability of the membrane to maintain its performance, and developing a computer program for the design of a large treatment plant using the results of tests on single tubes and tubular modules.

The major tasks completed during the past three years of the study are well documented in the nineteen papers, most of which were published in scholarly and refereed journals, as indicated in the publications list in Appendix II. The contribution of these publications to the science and engineering of reverse osmosis are reflected in the letters written by Dr. Sourirajan, the leading authority on reverse osmosis, upon reviewing most of the results of this project (see Appendix I). Recommendations for future work on optimizing the design of plants with modular configurations other than tubular and membrane materials other than NS-100 are given at the end of this report.

2. FABRICATION OF EQUIPMENT

2.1 Test Cells

Three stainless steel high pressure test cells were fabricated by the machine shop in the University. The drawings shown in Appendix III are essentially based on the design of Manjikian (1967). In order to study the mass transfer characteristics for membrane separation, the flow pattern of the feed should be well-defined. Most of the commercially available test cells fail to satisfy this criteria since the feed solution in these cells is normally stirred by a magnetic stirring bar. The feed in our cells flows radially from the center to the edge of the circular cell. As a result, study of the mass transfer mechanism with our test cells is made possible.

2.2 Flat Sheet Membrane Casting Apparatus

A membrane casting machine was constructed based on the design of Boddie (1969). The operational diagram is shown in Figure 1. A 3/8" thick glass plate is firmly secured to the upper part of the stainless steel carriage. It is upon this glass plate that the polymer solution is placed immediately before the membrane film is cast. The carriage is mounted upon two parallel 1 1/2" diameter stainless steel rods allowing the carriage to travel back and forth in a single direction. The carriage is drawn down along the inclined parallel rods at a constant speed with a 1/6 HP, 106 rpm electric motor. Actual casting of the polymer film occurs as the carriage moves smoothly from position 1, where the polymer solution resides on the glass plate, to position 2 where the polymer solution has been spread into a thin film by the doctor blade. During its travel from the doctor blade to the chilled water surface, a portion of the good solvent is evaporated along with the formation of the active layer on the membrane surface. The evaporation time, which is an important factor in governing the membrane performance, can be controlled by detaining the carriage at position 2 for the desired time interval before submerging the carriage into the chilled water (1.5 - 2.5°C). Membrane thickness is controlled by carefully adjusting the clearance between the doctor blade and the glass plate. In position 3, the cast film is gelled in the ice-cold water which is chilled by a refrigeration unit.

A constant temperature hot water bath was built for annealing the gelled membrane. The annealing temperature critically determines the pore size, and hence the performance of the membrane. The water temperature is accurately controlled by a thermal regulator accompanied by an electronic relay. According to the manufacturer (Cole-Parmer, Chicago, IL) the temperature can be controlled to an accuracy of 0.01°C.

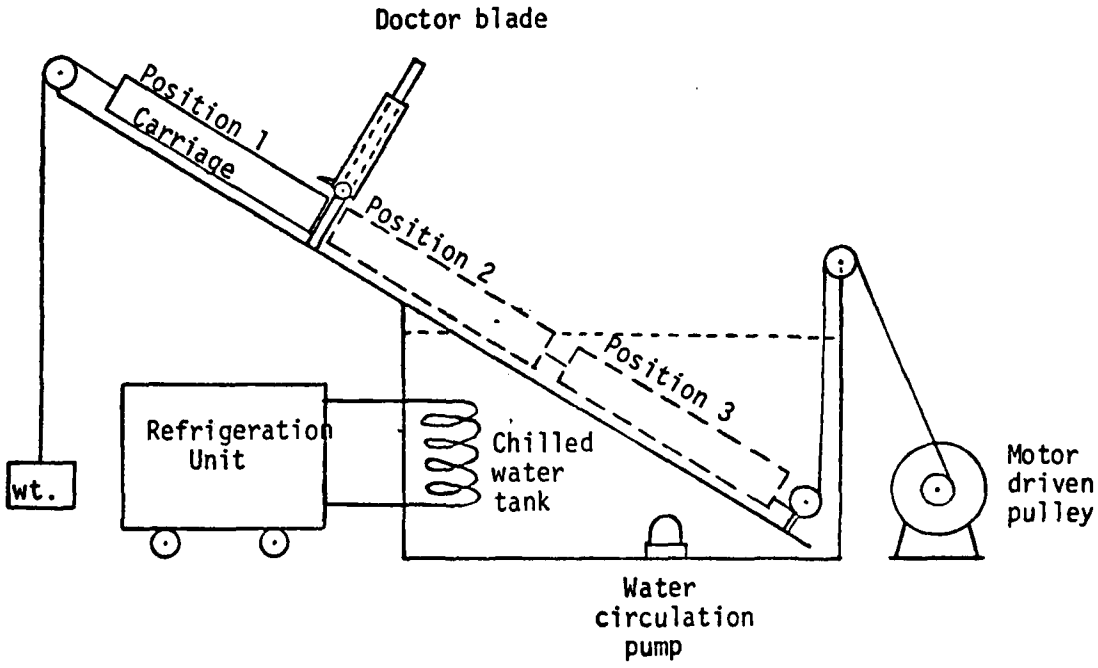


Figure 1. SCHEMATIC AND OPERATIONAL DIAGRAM OF THE MEMBRANE CASTING EQUIPMENT

2.3 High Capacity Pumping System

The basic components of the reverse osmosis test apparatus consist of an experimental test section, a circulation pump loop, and appropriate instrumentation to measure, maintain, and control the operating pressure, feed flow rate, and temperature of the feed solution. The equipment was designed to provide a flexible means for investigation of the hydrodynamic and mass transfer phenomena occurring during reverse osmosis. Tubular test sections can be tested at pressures ranging from atmospheric to 68 atmospheres at feed rates up to twenty two liters per minute (Re = 42,000 for 1.27 cm ID tube), and temperatures ranging from approximately 15° to 90°C. Materials of construction were selected to be exceptionally resistant to the corrosive action of aqueous salt solutions. Feed solutions can come in contact only with Type 316 stainless steel, nylon, polypropylene plastic and glass. The names of equipment manufacturers and their addresses are listed in Appendix III.

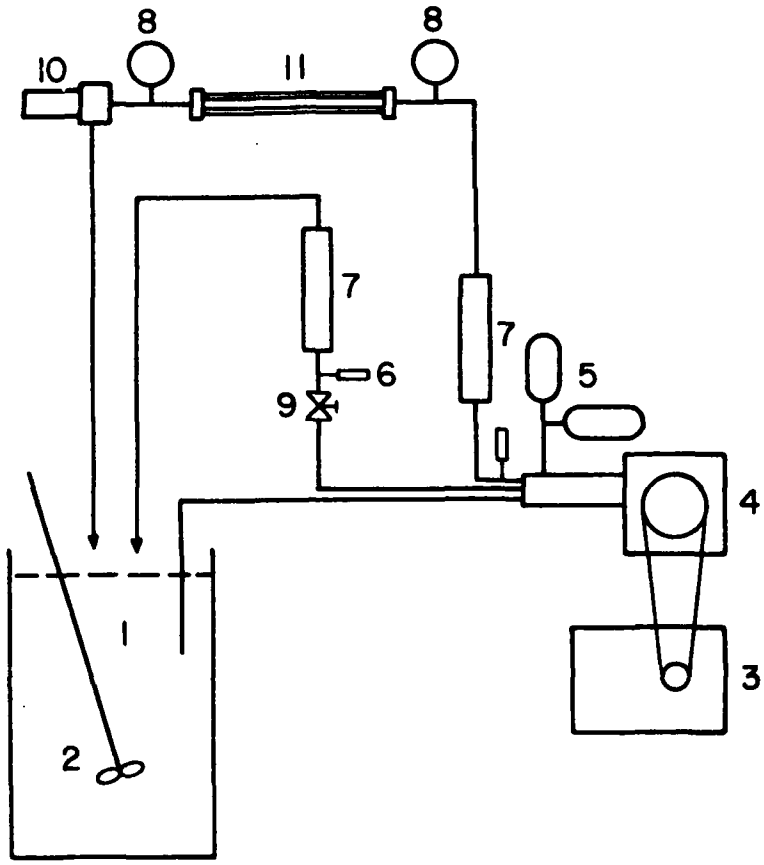
The feed circulation system is shown schematically in Figure 2. The experimental membrane test section was designed to support and encase the polymeric membrane to be tested. Feed solution was circulated and recycled through this tubular section with a 5 gpm CAT pump. This pump is a positive displacement, triplex pump with pumped fluids lubricating and cooling the floating pistons. All wetted parts are type 316 stainless steel or chrome plated stainless steel. Power was provided using a three phase, 220 volt, 5 horsepower electric motor driving the pump at approximately 800 rpm and delivering flows of twenty-two liters per minute at pressures to 68 atmospheres.

Operating pressure in the system was controlled by a Consolidated Controls pressure regulator acting as a back-pressure valve releasing the high pressure feed solution to the feed reservoir at atmospheric pressure. Two one-quart Greer Products accumulators effectively dampened fluid pulsations caused by the positive displacement pump. Operating pressures were monitored at the test section inlet and outlet by two Solfrunt bourdon type gauges with internal parts of 316 stainless steel.

Circulating feed solution flowrate was measured by a SK Instruments high pressure rotameter while by-passed feed solution could be regulated by a Hoke 316 stainless steel needle valve and measured by a Fisher rotameter. To prevent damage to the high pressure pump a Circle Seal relief valve and a Victor relief valve were installed in the feed and by-pass outlets, respectively. A thermoregulator was used for temperature control actuating an electronic relay causing chilled cooling water to circulate through cooling coils immersed in the feed reservoir. Feed temperatures were controlled to 1°C. The system volume is approximately 3 liters.

2.4 Tubular Membrane Test Section

A porous 1.27 cm fiberglass tube was chosen to encase and support the polymeric membranes to be tested. Using commercial grade epoxy, Parker 3/4 inch 316 stainless steel male connector fittings were sealed near the

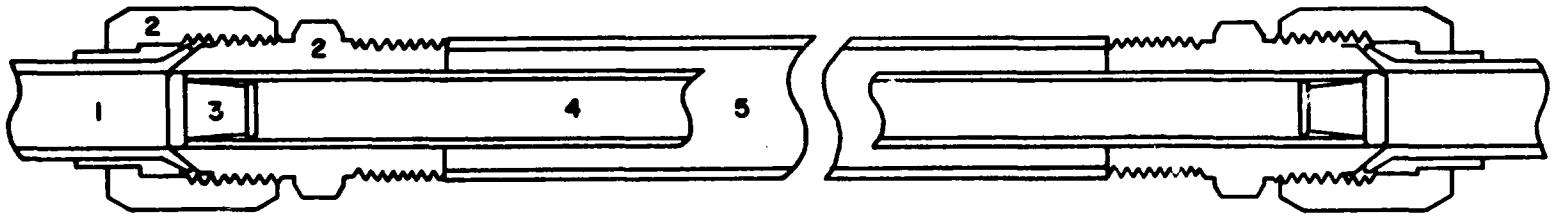


1. Feed Tank
2. Stirrer
3. 5 HP Motor
4. CAT Pump
5. Accumulator
6. Pressure Relief Valve
7. Flowmeter
8. Pressure Gauge
9. Needle Valve
10. Pressure Regulator
11. RO Test Section

Figure 2. Schematic Diagram of the Reverse Osmosis Pumping System

ends of the support tubes carefully allowing space for subsequent insertion of rubber grommets and grommet expanders. A 3/4 inch I.D. by 1 inch O.D. length of Plexiglas tubing was concentrically aligned with the support tube and sealed with epoxy to the Parker fittings. This chamber was used to collect the discharging product. Figure 3 is a detailed drawing of a typical tubular test section.

After a few adjustments in design and assembly, the experimental reverse osmosis test section provided a leak-proof unit allowing easy insertion of precast membranes with convenient hook up to the remainder of the testing apparatus.



1. 316-S.S. Tubing
2. Parker-Hannifin Fitting
3. Rubber Grommet Seal
4. Fiberglass Support Tubing
5. Plexiglass Collection Chamber

Figure 3. Drawing of the Tubular Test Section

3. PERFORMANCE OF NEW MEMBRANES

3.1 Membrane Contributors

Eastman Kodak's KP98 (commercial production had been terminated) was the cellulose acetate membrane being tested before we started casting our own in the third quarter of this study. Extensive effort has been made to collect the membrane samples currently available in the United States. Table 1 lists the type of membranes, their contributors and affiliate organizations. Performance of these candidate membranes tested against model compounds will be shown in the latter sections.

3.2 Selection of Model Organic Compounds

Table 2 lists sixty-two organic compounds, according to results of our literature survey, commonly occurring in hospital wastewaters. Obviously, it would be difficult to test the performance of each new membrane with all the individual compounds listed. Therefore, a screening procedure was established to narrow the list to about one dozen model compounds to be tested in characterizing a new membrane material. The criteria for the selection of these model compounds are given as follows:

1) The model compounds should be listed in Table 2 (with the exception of sodium chloride, which is used as a universal standard compound for testing all membranes, and methyl acetate, which represents the ester group).

2) The model compounds should be either soluble or slightly soluble in water.

3) The model compounds should cover a broad range of various chemical structures and applications.

4) The model compounds selected from each chemical group should be those which were separated poorly by the conventional cellulose acetate membrane.

Fourteen model organic compounds, which represent ten chemical groups and seven types of applications, have been selected. They are given in Table 3.

3.3 Analytical Procedures

The degree of solute separation by each membrane was determined by comparing the solute concentrations in both the permeate and the feed. Concentration of sodium chloride was measured by a Yellow Spring Conductivity Bridge, Model 1485. The Beckman Total Organic Carbon Analyzer, Model 915, was used to measure the concentration of individual organic model compound in its own presence in terms of TOC. Experimental error of the TOC Analyzer is in the range of 1 ppm.

Table 1

Candidate Membranes and Their Contributors

Membranes	Contributors	Organizations
Cellulose acetate Butyrate (CAM)	S. Manjikian	Universal Water 11722 Sorrento Valley Rd. San Diego, California 92121
Cellulose acetate (blend) (CA_{blend})	C. W. Saltonstall, Jr.	Envirogenics 9200 East Flair Drive El Monte, California 91734
NS-1	L. T. Rozelle	North Star 3100 38th Avenue S. Minneapolis, Minnesota 55406
Polyamide (aromatic)	R. McKinney, Jr.	Chemstrand Box 731 Durham, North Carolina 27702
Cellulose acetate membrane in tubular module	D. Furukawa	Universal Oil Products 8133 Aero Drive San Diego, California 92123
NS-1 membrane in tubular module	D. Furukawa	Universal Oil Products 8133 Aero Drive San Diego, California 92123

Table 2: Organic Compounds Commonly Occurring in Hospital Wastewater

Compounds	MW	Solub.	Toxicity	Sources
(1) Alcohols				
Methyl -	32	∞	3	Solvent
Ethyl -	46	∞	2	Solvent
Iso-propyl -	60	∞	3	Rubbing alcohol
Butyl -	74	s	3	Solvent
Amyl -	88	i	3	Solvent
(2) Acids				
Hydrocyanic (HCN)	27	∞	6	Metal polish, insecticide, rotenticide, fungicide
Cyanic (HOCN)	43	s	3	Insecticide, rotenticide
HCOOH	46	∞		Disinfectant
Acetic	60	∞		Disinfectant, stop-bath
Oxalic	90	s	4	Bleach, metal cleaner
Lactic	74	∞		
Stearic	285	i	1	Basic ingredient of cream and lotion
Citric	176			
(3) Aromatic Compounds				
Benzane	78	δ	4	Solvent
Toluene	92	i	4	Solvent
Xylene	106	i	4	Solvent
Anilene	93	s	4	Solvent
Phenol	94	s	4	Disinfectant
Cresol	108	δ	4	Disinfectant
DDT	355		4	Insecticide, rotenticide
4-nitrophenol	139	$\frac{1.6g}{100cc}$	4	Fungicide
2-4 dinitrophenol	184	$\frac{0.6g}{100cc}$	4	Fungicide
Hydroquinone	110	s	4	Photo developer
Alkyl benzene sulfonate				Largest class of anionic surfactant
Naphthalene	128	i		Deoderizer
p-di-Cl-benzene	147	i	3	Moth ball, insecticidal fumigant
Monomethyl-P-amino Phenol Sulfate (Elon)			4	Photo developer
Hexachlorophene			4	Disinfectant

Legend (see Appendix V for definition)
Toxicity 1-6 (6 being highly toxic)
Solubility ∞ All proportion
s Soluble (or vs, very soluble)
i Insoluble
sl Slightly soluble
δ Trace

Table 2: Organic Compounds Commonly Occurring in Hospital Wastewater (Continued)

Compounds	MW	Solub.	Toxicity	Sources
(4) Miscellaneous Solvents				
CCl_4	154	i	4	
CS_2	76	sl	3	
Acetone	58	∞	3	
(5) Others				
Methyl thiocyanate	73	δ		Pesticide, insecticide
Ethyl thiocyanate	87	i		Pesticide, insecticide
I-propyl thiocyanate	101	i		Pesticide, insecticide
BHC	290	i	4	Pesticide, insecticide
QAC			3-4	Pesticide, Insecticide, disinfectant
DEET				Insect repellent
Na diethyl barbiturate	184	δ		Sedative, hypnotic agent
$Na_2C_2O_4$ (oxalate)	134	$\frac{3.7g}{100cc}$	4	Bleach, metal cleaner
Formaldehyde	30	s	3.4	Deoderizer, fumigant, photo-laq-hardner
Urea	60	vs		Cesspool
Chloroform	119	δ	3	Anesthetics, liniment
Ether	74	s	3	Anesthetics, liniment
Alkyl sulfate				Surfactant
2-terpineal	154	δ	3	Pine oil, disinfectant, floor cleaner
d-sorbital (70%)	182	s		Hand lotion
Glycerol	92	∞	1	Shampoo
Na-lauryl sulfate			3	Shampoo
Soap			2	
Phenidone			4	Photo developer
Sulfosalicylic acid			4	
(6) Active ingredients in the following products or materials				
Lysol				
Deodorant				
Hair shampoo				
Mouthwash				
Hair coloring				
Phisohex				
Wright Gremsa stain				
Blood				
Spinal fluid				
Urine				
Mercurochrome				General antiseptics

Table 3: Chemical Structures of Model Compounds and Their Applications in Hospitals

Chemical Structures \ Applications	Solvent	Pepticide Insecticide	Photo-Developers	Disinfectant	Anesthetics	Soap Detergent	Others
Alcohol	methanol ethanol			ethanol		glycerol	i-propanol
Acid			acetic acid				
Aldehyde		formaldehyde	formaldehyde				
Ketone	acetone						
Ether					ethyl ether		
Aromatic	aniline		hydroquinone	phenol			
Amine	aniline						
Amide							urea
Ester							methyl acetate
Miscellaneous							sodium chloride

3.4 Testing of Flat-Sheet Membranes

In addition to the conventional CA membrane, Eastman Kodak's KP98, five other types of new membrane materials representing three completely different chemical structures have been tested. Cellulose acetate butyrate (CAB) and blended cellulose acetate $CA_{(blend)}$ membranes provided by Universal Water and Envirogenics, respectively, are derivatives of cellulose acetate. The nylon base aromatic polyamide membrane was supplied by Chemstrand. The crosslinked polyethylenimine (PEI) membrane, designated as NS-1, was contributed by North Star. NS-1 was later redesignated by OSW as NS-100.

All these membranes were tested at a constant temperature of 24°C, flow rate of 0.30 gpm and at two different pressures, i.e. 600 and 1500 psi., against model organic compounds at a concentration of 1,000 ppm. During the run, each membrane was first tested against deionized water, then a standard 5,000 ppm sodium chloride solution. Following these membrane characterization studies, the model organic compounds were tested one after another. Flux and rejection data were taken after allowing the membrane to equilibrate with the testing solution for at least one hour. The standard sodium chloride solution was again tested half-way through and at the conclusion of testing of all these model compounds. It was believed from these intermittent tests of sodium chloride solutions for the same membrane studied, any fouling and/or compaction of the membrane may be observed. This data in turn can be used if necessary to correct for flux decline. As proposed by Sourirajan (1970), performance data at two different pressures are needed for the complete characterization of membranes.

The performances of all the tested membranes under the aforementioned conditions are shown in Tables 4 and 5.

3.5 Testing of Hollow Fiber Membranes

A duPont's B-9 Permeator, which consists of approximately one million hollow fibers made of aromatic polyamide, was acquired for this study. The module was tested against model compounds under standard testing conditions, i.e. 400 psi, 24°C and 75% conversion. The flux of permeate is strongly dependent on the properties of the solute and the feed flow rate. Therefore, in order to collect three parts of permeate from four parts of feed (i.e. 75% conversion), the flow rate of each feed solution had to be adjusted. Table 6 summarizes the performance of the B-9 permeator. The experimental data reported by the manufacturer are also listed for comparison. It was found that separations of sodium chloride and alcohols were higher than those reported by duPont; however, the rejection of phenol was lower. In general, the performance of B-9 Permeator agreed well with what was claimed by the manufacturer.

TABLE 4
Performance of Candidate Membranes at 600 psi, 24°C and 0.30 gpm Feed Flow Rate

	pH	CA Flux (gfd)	CA Rej (%)	CAB Flux (gfd)	CAB Rej (%)	CA_{blend} Flux (gfd)	CA_{blend} Rej (%)	Polyamide Flux (gfd)	Polyamide Rej (%)	NSI 307-52C(E1) Flux (gfd)	NSI 307-52C(E1) Rej (%)	NSI 307-53J Flux (gfd)	NSI 307-53J Rej (%)
Deionized Water	6.07	9.07		1.94		5.24		3.78				9.73	
Sodium Chloride 5,000 ppm	6.64	7.76	95.7	1.69	99.6	4.68	98.5	3.07	99.13			8.96	99.71
Ethanol 1,000 ppm	5.42	8.32	12.55	1.65	1.9	4.92	24.19	3.31	57.46	13.59	64.78	14.64	65.66
i-Propanol 1,000 ppm	5.91	8.25	43.16	1.62	41.04	4.83	60.35	2.67	88.97	13.61	82.01	15.41	85.10
Acetic Acid 1,000 ppm	3.77	9.07	10.21	1.66	12.38	4.81	17.53	2.71	70.14	13.05	68.70	15.30	48.02
Formaldehyde 1,000 ppm	4.64	7.83	19.68	1.41	41.05	4.56	32.82	2.46	52.10	14.32	37.05	15.32	38.62
Acetone 1,000 ppm	5.48	8.08	4.98	1.53	16.60	4.64	23.29	2.21	71.96	12.70	80.44	13.99	76.03
Ethyl Ether 1,000 ppm	5.59	8.81	12.56	1.08	39.51	5.20	30.21	1.87	89.74	10.17	90.98	11.64	82.18
Glycerol 1,000 ppm	5.97	8.52	80.21	1.02	90.21	5.11	95.15	2.15	88.04	11.21	96.87	13.27	89.15
Sodium Chloride 5,000 ppm	6.64	7.63	87.4	0.85	99.4	4.57	97.4	2.22	99.32	15.53	89.08	17.10	88.75
Hydroquinone 1,000 ppm	5.20	6.24	-0.63	0.85	30.97	3.95	7.03	2.11	84.49	11.95	82.23	13.74	71.93
Phenol 1,000 ppm	6.25	5.87	-13.66	0.69	10.56	3.06	-5.66	2.09	80.06	9.58	68.57	12.64	55.68
Urea 1,000 ppm	7.72	6.51	17.56	0.78	8.00	4.40	38.02	1.93	55.41	7.67	64.15	10.44	55.37
Sodium Chloride 5,000 ppm	6.64	6.47	83.4	0.71	99.5	4.25	97.6	1.72	99.56	9.01	98.91	11.50	93.70
Deionized Water	6.07							2.08		11.80		14.54	
Methanol 1,000 ppm	5.77	8.16	-7.82	2.28	-9.09	6.77	-20.30	2.85	19.10	34.03	-5.98	29.69	18.06
Aniline 1,000 ppm	6.62	6.40	-8.60	1.58	25.51	4.86	22.26	2.64	78.08	28.78	31.36	25.94	51.80
Methyl Acetate 1,000 ppm	5.38	7.57	-3.53	1.68	-25.14	6.41	20.72	2.85	54.31	32.45	36.37	33.16	28.32

TABLE 5

Performance of Candidate Membranes at 1,500 psi, 24°C and 0.30 gpm Feed Flow Rate

	pH	CA		CAB		CA_{blend}		Polyamide		NSI 307-52C(E1)		NSI 307-53J	
		Flux (gfd)	Rej (%)	Flux (gfd)	Rej (%)	Flux (gfd)	Rej (%)	Flux (gfd)	Rej (%)	Flux (gfd)	Rej (%)	Flux (gfd)	Rej (%)
Deionized Water	6.07	20.15		4.87		12.40							
Sodium Chloride	6.64	17.55		3.58		10.53		7.16		20.51		28.95	
5,000 ppm			97.3		99.8		99.1		99.58		99.26		99.24
Ethanol	5.42	18.23		3.57		10.97		7.22		26.53		28.56	
1,000 ppm			17.92		14.43		36.88		70.45		70.01		73.57
i-Propanol	5.91	18.55		3.91		11.20		6.72		44.60		65.50	
1,000 ppm			51.95		57.58		76.57		95.53		56.06		40.16
Acetic Acid	3.77	18.23		3.74		11.24		7.98		403.08		41.75	
1,000 ppm			17.36		26.18		29.67		82.21		9.00		69.86
Formaldehyde	4.64	17.76		3.57		10.92		5.36		27.80		31.66	
1,000 ppm			29.24		50.64		48.37		68.61		49.96		50.65
Acetone	5.48	17.47		3.41		10.80		5.64		25.19		32.65	
1,000 ppm			5.67		6.16		29.89		72.24		78.26		77.32
Ethyl Ether	5.59	19.23		2.71		12.12		5.26		33.27		32.45	
1,000 ppm			9.74		2.01		23.54		91.67		65.62		77.09
Glycerol	5.97	17.76		2.19		11.27		5.91		28.25		33.38	
1,000 ppm			84.60		96.08		98.30		88.14		96.18		91.69
Sodium Chloride	6.64	15.23		1.94		10.48		5.82		39.10		39.10	
5,000 ppm			90.1		99.4		98.30		99.64		83.39		94.34
Hydroquinone	5.20	13.44		2.10		9.07		5.52		25.50		28.48	
1,000 ppm			-8.20		38.15		18.19		98.61		86.29		77.98
Phenol	6.25	11.64		1.46		6.68		5.31		22.35		24.83	
1,000 ppm			-16.09		-12.07		-18.44		88.72		70.21		65.72
Urea	7.72	14.87		1.84		10.53		4.59		17.50		22.68	
1,000 ppm			26.76		31.63		24.37		89.32		74.32		63.38
Sodium Chloride	6.64	13.72		1.68		9.98		4.38		22.11		28.25	
5,000 ppm			88.2		99.5		98.4		99.61		98.54		95.71
Deionized Water	6.07							4.79		23.50		28.48	
Methanol	5.77	17.85		5.10		15.88		8.02		70.34		67.18	
1,000 ppm			-8.32		1.27		-12.42		5.42		1.41		9.87
Aniline	6.62	13.97		3.25		11.50		7.11		57.58		54.02	
1,000 ppm			-4.89		-5.19		17.29		82.19		14.99		31.31
Methyl Acetate	5.38	16.45		3.80		15.14		7.61		90.34		72.78	
1,000 ppm			11.14		-10.78		12.36		44.50		23.02		44.62

Table 6

Summary of the Performance of B-9 Permeator

at 400 psig, 24°C and 75% Conversion

	Experimental		Reported*	
Solute	Conc. (ppm)	Rej. %	Conc. (ppm)	Rej. %
Sodium chloride	3,850	93.06	1,500	90
Ethanol	677	36.49	500-2,000	28
i-propanol	1,174	90.05	500-2,000	75
Acetic acid	682	31.28	500	40
Formaldehyde	1,278	21.19		
Acetone	856	52.93		
Ethyl ether	388	57.67		
Glycerol	765	87.85	500-2,000	90
Hydroquinone	551	60.49		
Phenol	773	44.67	500-2,000	55
Urea	1188	34.45		
Methanol	536	28.01	500-2,000	0
Aniline	440	47.28		
Methyl acetate	370	57.45		

* Perma-Sep Division, duPont Co.

3.6 Testing of Tubular Membranes

Two tubular modules were generously provided free of charge by Universal Oil Products (UOP). One is a MINI-MODULE containing 1.0 sq ft of CA membrane. The other is an 18" long, 1/2" diameter tubular testing unit lined with the crosslinked PEI (NS-1) membrane. Both modules were tested at 600 psi, 24°C and 1.50 gpm as recommended by UOP. Their performances against model compounds are summarized in Table 7 and Figure 4.

3.7 Results and Discussion

Although a great number of aromatic halogenous compounds were found in wastewater, no intention was made to include them as model compounds. According to the separation data published by Matsuura and Sourirajan (1971, 1972), the presence of halogenous groups always tends to increase membrane separation of the polar compounds. For example, the solute separation is 2% for phenol but 22% for p-Cl-phenol and 20% for m-Cl-phenol; 19% for benzoic acid, but 44% for o-Cl-benzoic acid; 5% for aniline, but 19% for m-Cl-aniline, 21% for o-Cl-aniline and 14% for p-Cl-aniline.

It is interesting to note, from Tables 4 and 5, that membranes made of CA and its derivatives, e.g. CAB and $CA_{(blend)}$, show a similar pattern of rejection (Figure 4). The molecular weight of the organic molecule (MW < 150) does not seem to determine the solute separation. Instead, the chemical nature of the solute plays an important role.

Matsuura and Sourirajan (1971, 1972, 1972, 1973) recently published a series of papers studying the relation of the chemical properties of a solute to its separation by CA membrane. Their conclusions are summarized as follows:

1) Solute separation in reverse osmosis is governed by the hydrogen bonding ability of the organic molecule when it is essentially undissociated and by electrostatic repulsion of ions when the molecule is partially or completely dissociated.

2) Solute separation for proton donors, such as alcohols and phenols, increases with increase in $\Delta\nu_{s(acidity)}$, shift in the OH band maximum in the IR spectra of the solute in carbon tetrachloride and ether solution, which is a measure of acidity.

3) Solute separation for proton acceptors including aldehydes, ketones, ethers and esters increases with increase in $\Delta\nu_{s(basicity)}$, shift in the OD band maximum in the IR spectra of CH_3OD in benzene and other solvents used as solutes in reverse osmosis experiments, which is a measure of basicity.

4) Solute separation for the dissociable compounds such as mono-carboxylic acids and amines is a function of the dissociation constant.

TABLE 7

Summary of the Performance of Two

Tubular Modules of Universal Oil Products

Solute	concentration (ppm)	pH	Crosslinked PEI flux (gfd)	Crosslinked PEI separation (%)	Mini-Module (CA) flux (gfd)	Mini-Module (CA) separation (%)
deionized water	-----	6.07	7.33	-----	11.65	-----
sodium chloride	5,000	4.67	6.15	99.62	9.59	97.87
ethanol	1,000	4.20	6.43	21.98	10.87	2.62
i-propanol	1,000	3.21	6.01	98.30	10.37	57.78
acetic acid	1,000	3.09	4.67	65.55	10.56	2.10
formaldehyde	1,000	3.54	6.71	56.45	10.92	23.79
acetone	1,000	5.30	7.18	80.21	10.37	5.78
ethyl ether	1,000	5.41	7.33	91.10	10.87	20.34
glycerol	1,000	4.56	5.06	93.56	10.66	94.70
sodium chloride	5,000	4.91	7.55	99.57	10.97	97.84
hydroquinone	1,000	4.50	6.25	89.66	9.27	-11.89
phenol	1,000	3.56	5.61	88.34	7.76	16.35
urea	1,000	3.88	7.24	59.31	10.56	25.65
methanol	1,000	4.85	7.35	19.14	10.92	- 8.82

Table 7 continued on next page

TABLE 7 (continued)

Solute	concentration (ppm)	pH	Crosslinked PEI flux (gfd)	Crosslinked PEI separation (%)	Mini-Module (CA) flux (gfd)	Mini-Module (CA) separation (%)
amiline	1,000	5.61	7.14	88.10	8.67	-19.56
methyl acetate	1,000	4.37	7.48	81.75	10.42	23.14
sodium chloride	5,000	4.85	7.14	99.50	9.51	97.85
deionized water	-----	6.07	7.24	-----	10.61	-----

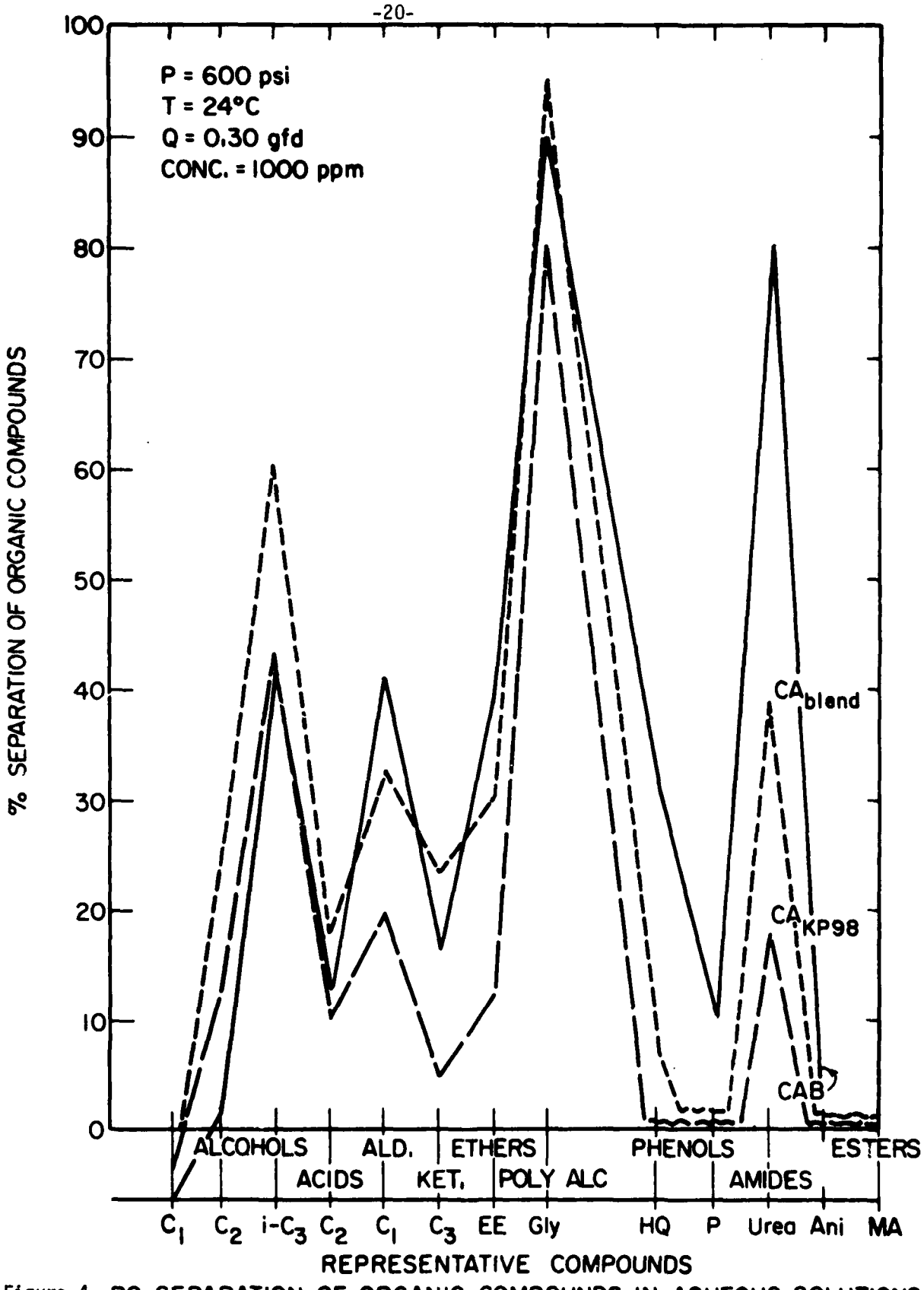


Figure 4. RO SEPARATION OF ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS USING CELLULOSE ACETATE BASE MEMBRANES

5) Solute separation always increases with increase in the degree of dissociation or pH of the solution (Figure 5).

6) Solute separation for compounds having the same functional group increases with increase in the degree of branching of the molecule.

7) Cellulose acetate membrane has a net proton-acceptor character with respect to solute-membrane interactions.

8) Solute separation, as well as $\Delta\nu_{s(acidity)}$, $\Delta\nu_{s(basicity)}$ and dissociation constant may be correlated with Taft number, which represents the effect of the substituent group on the polar effect of the molecule. Such correlation provides a means for predicting membrane performance for each class of solutes.

These conclusions provide a guideline for the prediction of solute separation by the CA membranes. By measuring the shift of OH band maximum in IR spectra, or from the dissociation constant data, or from the estimation of the Taft number the trend of the solute separation may therefore be predicted. Because of the similar pattern in the separation of different classes of solutes and because of the same net proton-acceptor character among the CA, CAB and $CA_{(blend)}$, the above conclusions drawn for the CA membrane should also be applicable to the CAB and $CA_{(blend)}$. Such an assumption is confirmed by the similarities in the curves shown in Figure 6. This figure illustrates the solute separation data found in Table 4 versus the Taft number for all solutes containing hydroxyl groups.

In general, separations of model compounds using this class of membrane are unsatisfactory. Except for isopropanol and glycerol, none of the model compound separations exceed 50%. On the other hand, many of them, including methanol, phenol, hydroquinone and methyl acetate, show negative rejections by the CA membranes.

Figure 7 shows the permeate flux for each model compound. The average fluxes are 10 gfd for CA membrane, 5 gfd for $CA_{(blend)}$ membrane and 1.5 gfd for CAB membrane. Similarity among the shape of flux curves again can also be observed. In general, permeate flux and solute separation tend to decrease with increase in acidity. This effect, based on the analyses of Matsuura and Sourirajan, is due to the formation of induced intermolecular hydrogen bonding between the solute and the CA molecules, which tends to bring the neighboring polymer segments in closer proximity to each other, resulting in a transient densification of the porous structure of the membrane.

Compaction effects of the membranes can be seen from the flux data with the three sodium chloride solutions (open circles shown in Figure 7) tested. Among them, $CA_{(blend)}$ shows the least such effects and CAB the highest.

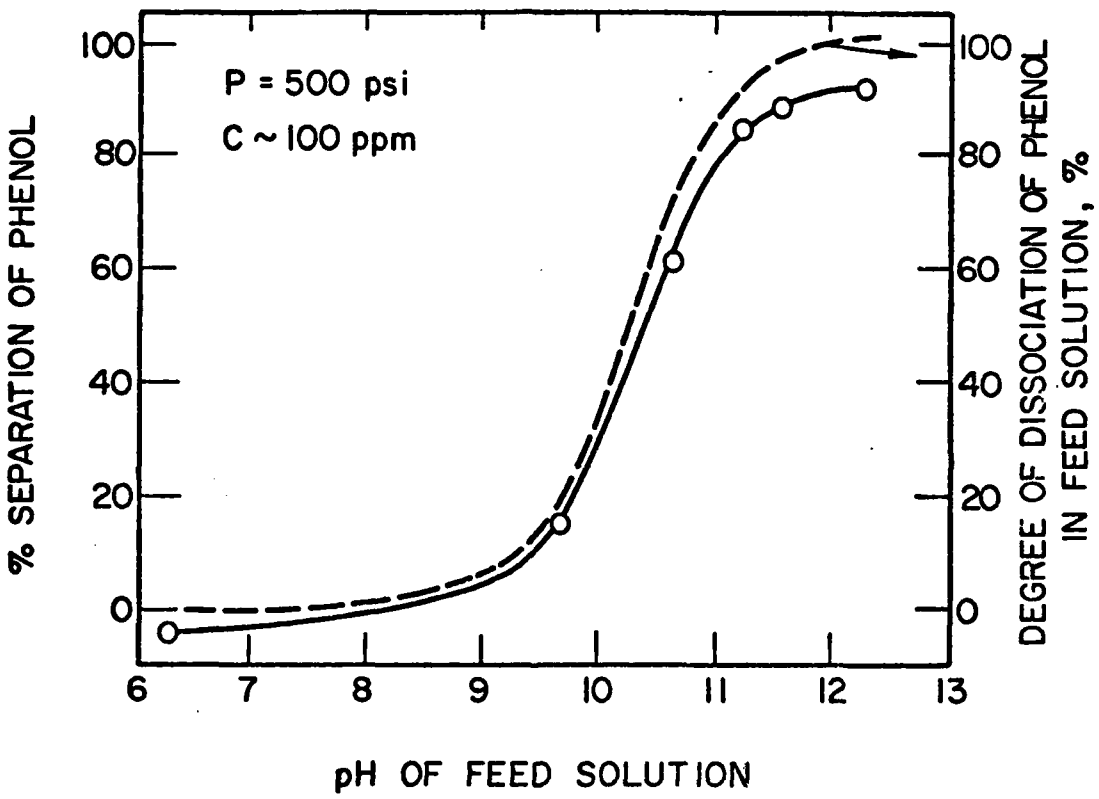


Figure 5. EFFECT OF pH OF FEED SOLUTION AND DEGREE OF DISSOCIATION ON SEPARATION OF PHENOL (MATSUURA AND SOURIRAJAN, 1972)

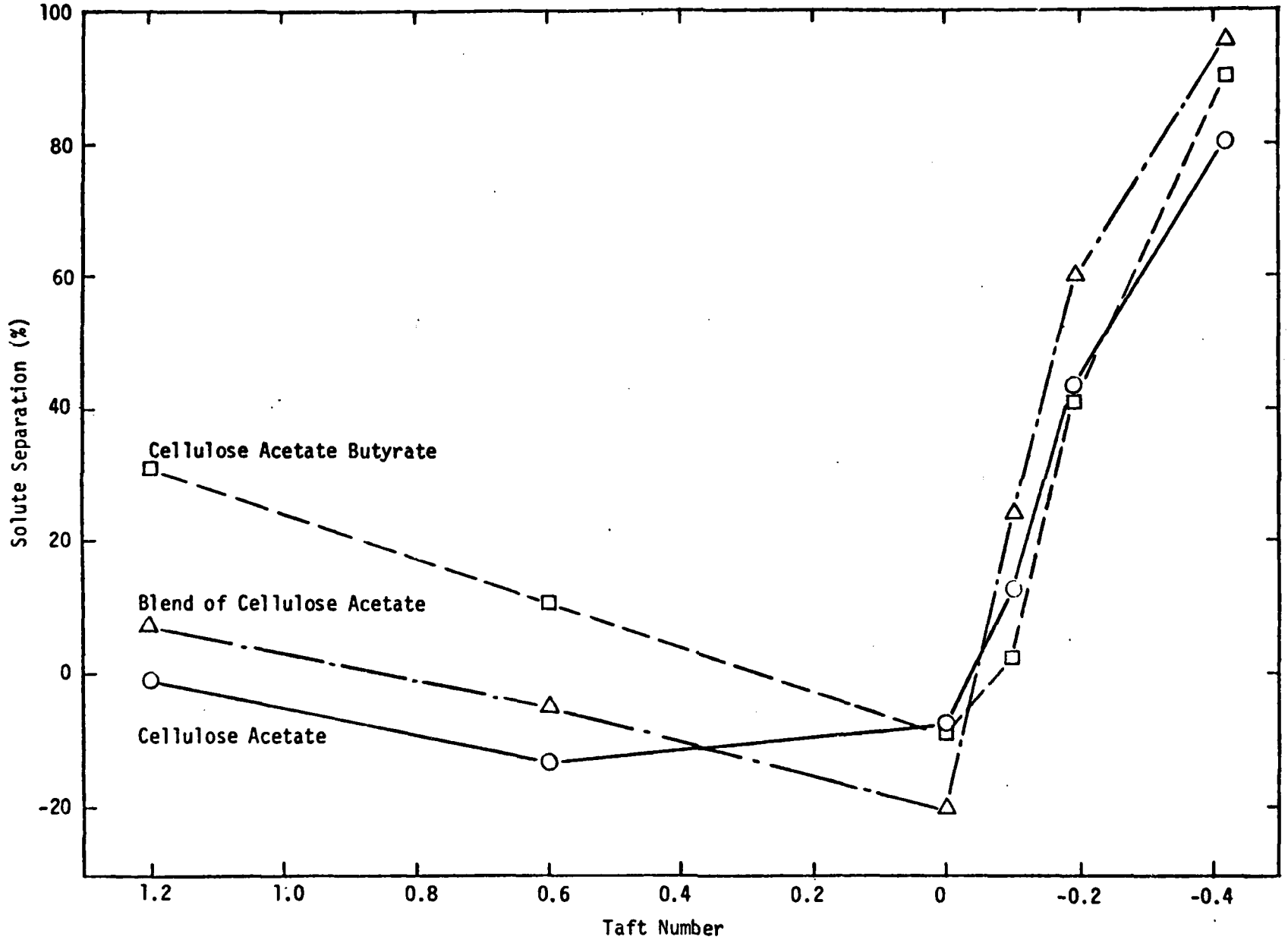


Figure 6. REJECTIONS OF ORGANIC SOLUTES CONSISTING OF HYDROXYL GROUP BY CELLULOSE ACETATE MEMBRANE AND ITS DERIVATIVES

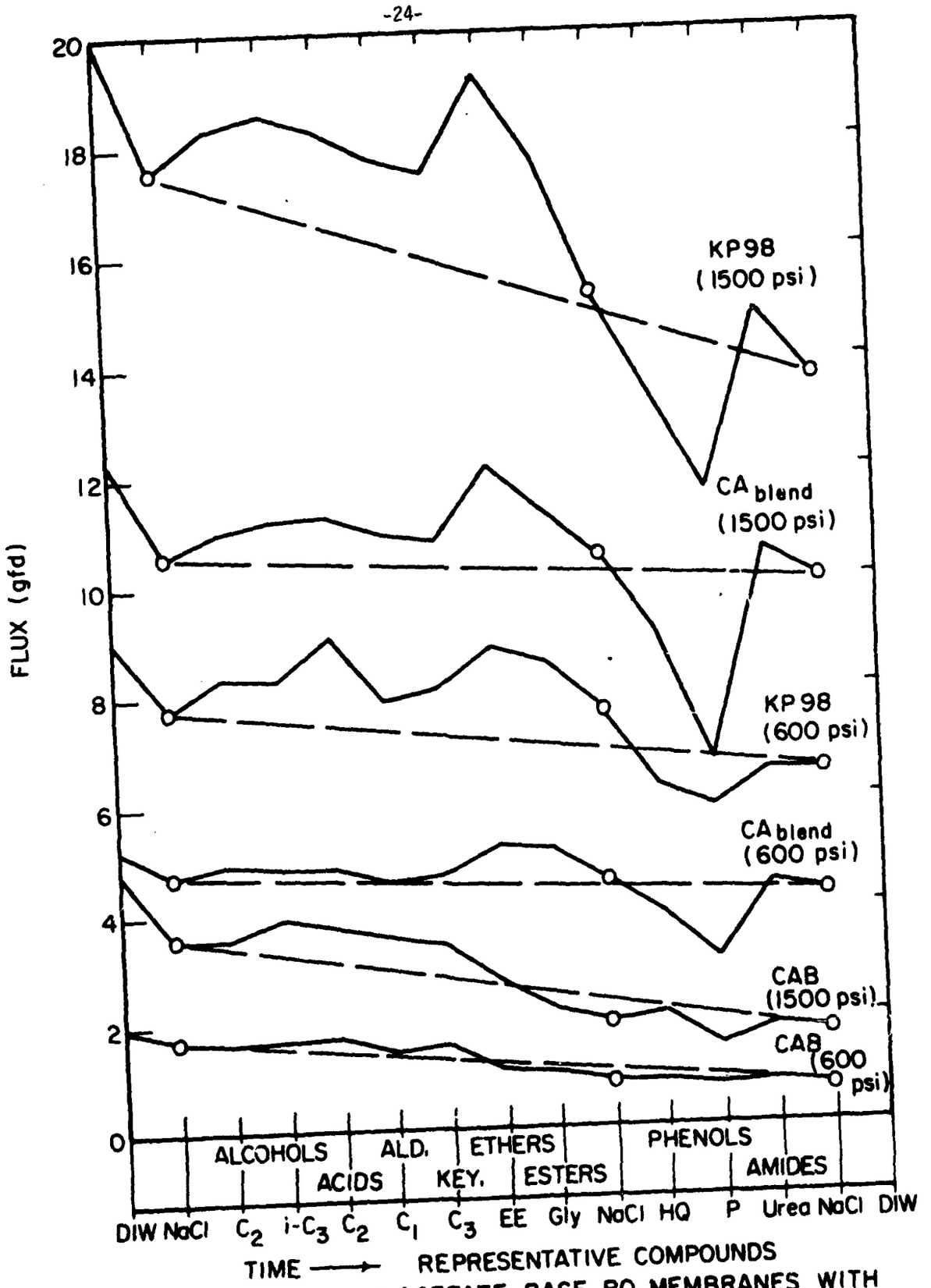


Figure 7. FLUX OF CELLULOSE ACETATE BASE RO MEMBRANES WITH ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS

Although the performance of the MINI-MODULE from UOP, 10 gfd at 97.8% NaCl separation, was the best among all the CA membranes tested, the separation of organic solutes followed the same general pattern as shown in Figures 4 and 11. The separation of acetone and acetic acid was lower than those obtained with the CA membrane in sheet form; on the other hand, the separation of phenol and methyl acetate was found to be somewhat higher.

Because of the unsatisfactory performance of membranes composed of cellulose acetate membrane and its derivatives, it is concluded that the cellulose acetate base membranes are not suitable for the separation of organic compounds. Modification of cellulose acetate, such as changing the acetyl content or introducing more hydrophobic groups, would not drastically improve the performance of this type of membrane.

Figure 8 illustrates solute separations of aromatic polyamide membranes at 400 psi for hollow fiber and 600 and 1,500 psi for flat sheet. Most of the compounds produce 70% or higher separation at 1,500 psi. Most impressively, separations of polar aromatic compounds, such as phenol, hydroquinone and aniline, are higher than 80%. Results of tests agree with the theory that separation increases with increasing pressure.

Crosslinked PEI membrane (NS-1) exhibits good resistance to pH ranging from less than 1 to 13 as claimed by North Star. Two such membranes were tested; solute separations at 600 psi are illustrated in Figure 9. In general, solute separations are comparable to that of aromatic polyamide membranes. Figure 10 shows a comparison of model compound separations by the cellulose acetate, polyamide and NS-1 membranes. The high rejections of polar molecules, by the NS-1 and by the polyamide membranes are extremely interesting when considering wastewater treatment applications.

The performance of the tubular module lined with NS-1 membrane was excellent, > 99.5% salt separation. The permeate flux, however, was much lower, 6-7.5 gfd, than that of NS-1 cast in flat-sheet form. Separations of organic model compounds were similar to that of the flat-sheet with the exception that the tubular membrane provided a lower rejection of ethanol but a higher rejection of aromatic compounds (Figure 11).

Comparison of permeate fluxes among NS-1 and polyamide membranes using CA membrane as a reference is illustrated in Figure 12. At 600 psi the average fluxes are about 12 gfd for NS-1, 8 gfd for CA but only 2.5 gfd for polyamide. With similar ability to separate model compounds, NS-1 shows five-fold higher in flux than polyamide. The advantage of NS-1 is obvious from this point of view.

According to the preceeding discussion, NS-1 appears to be the most promising candidate membrane for organic removal among those that have been tested. Besides its high flux and good rejection toward most of the model compounds, its resistance to acid and base adds an exceptional asset. Although its flux appears to be somewhat unsteady, we believe that this poses a minor problem.

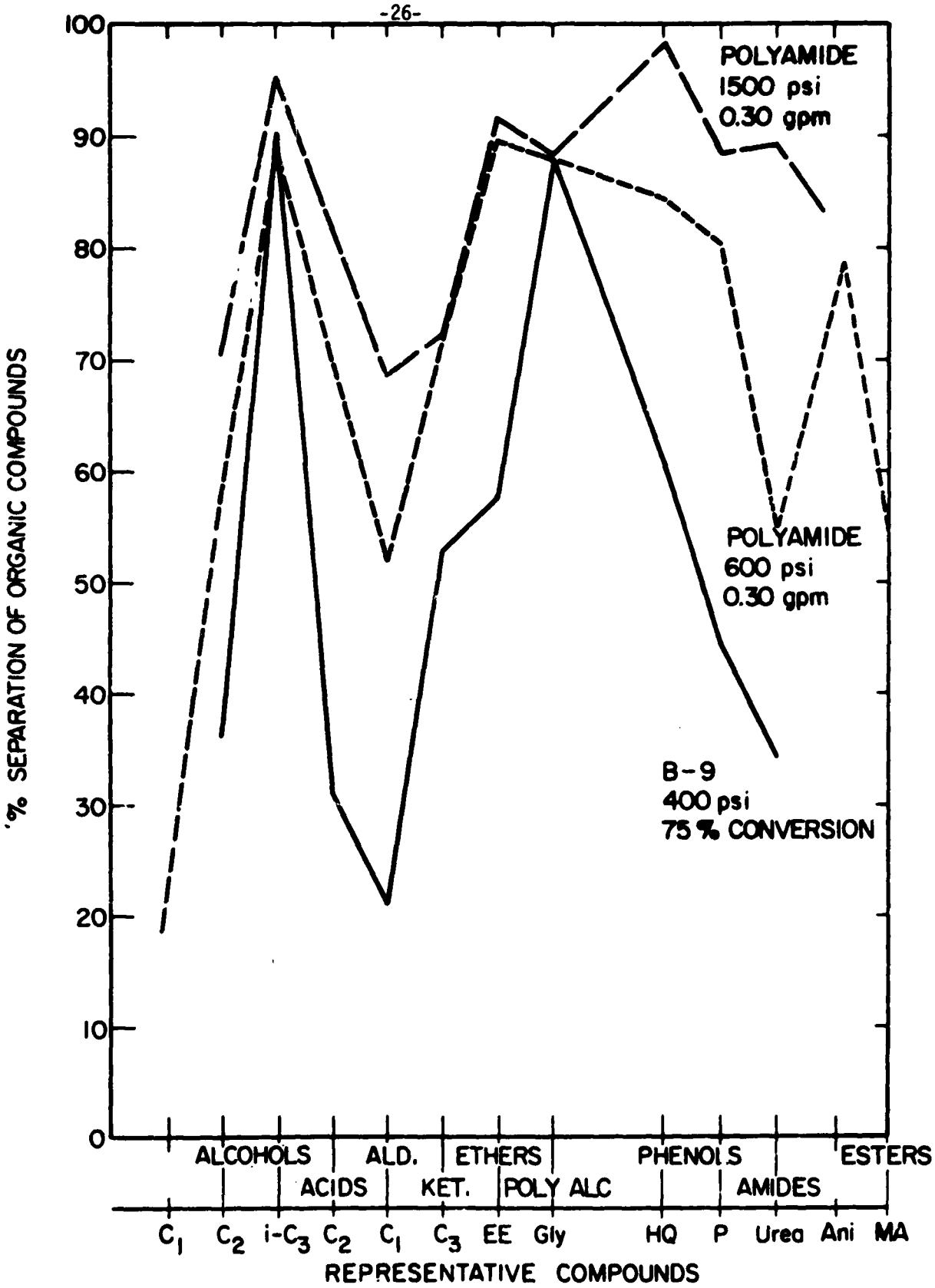


FIG. 8 RO SEPARATION OF ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS USING POLYAMIDE MEMBRANES

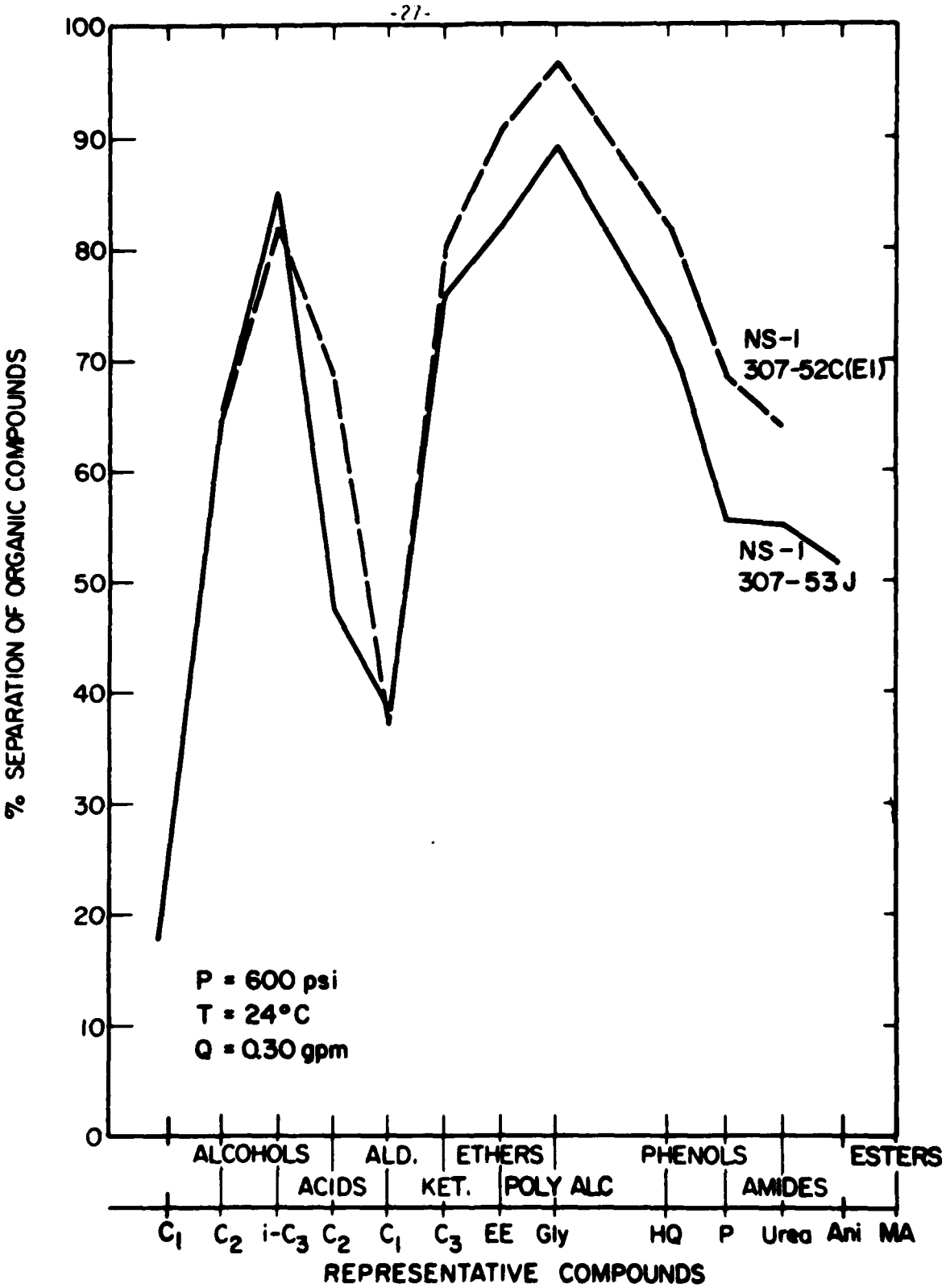


Figure 9. RO Separation of Organic Compounds in Aqueous Solutions Using Ultrathin Membranes

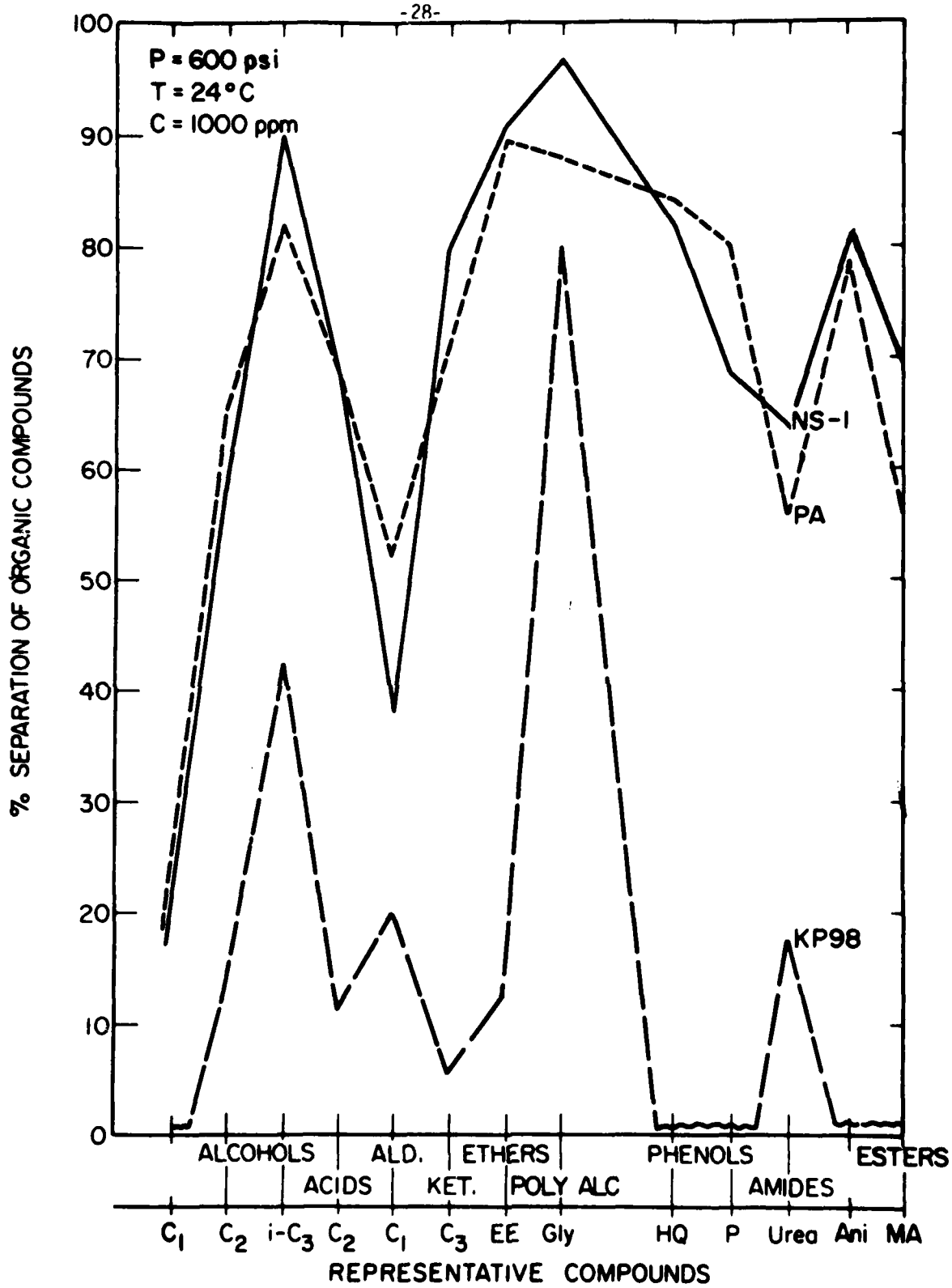


Figure 10. Comparison of RO Separation of Organic Compounds Using Different Types of Membranes

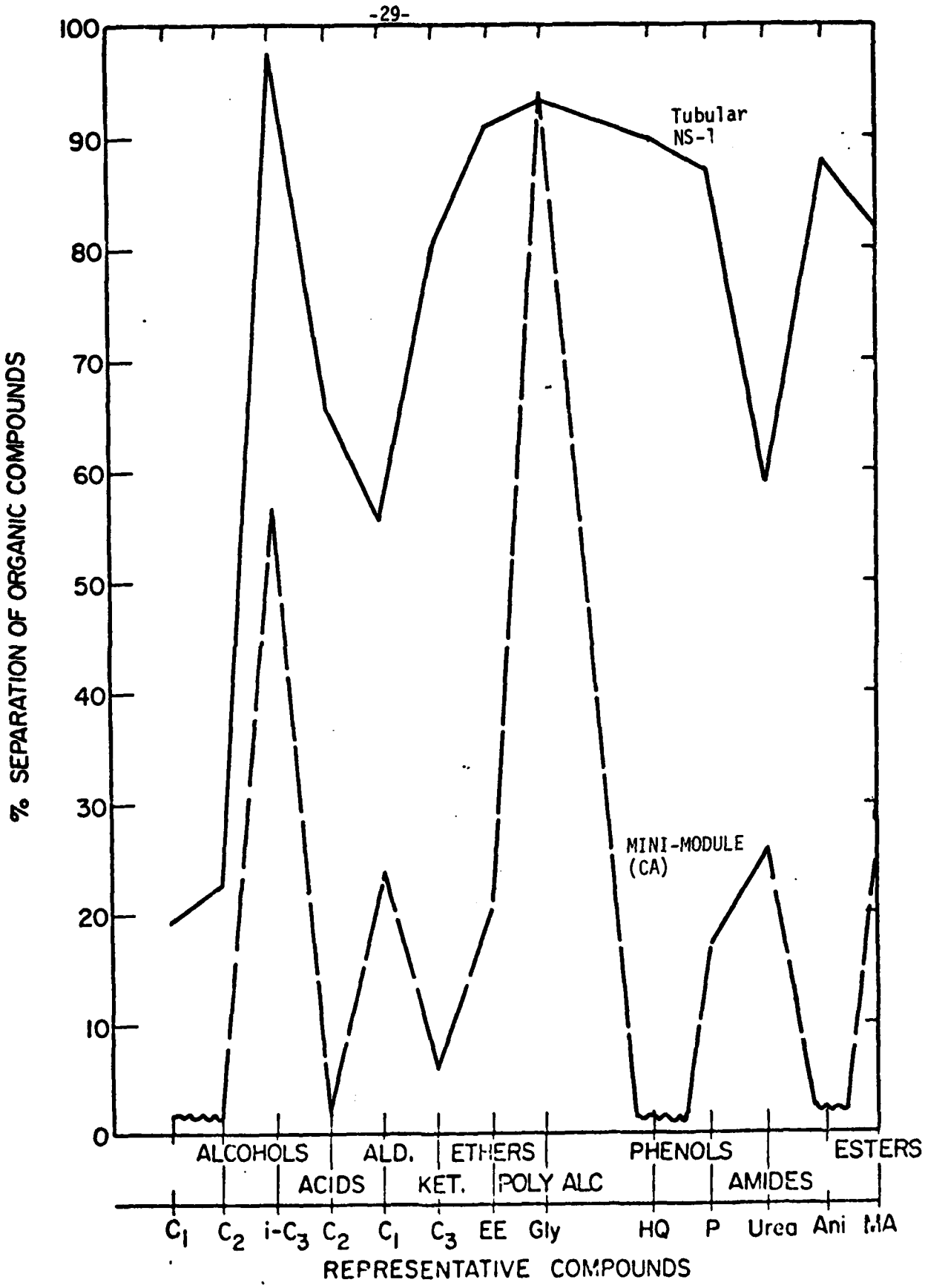


Figure 11. COMPARISON OF SEPARATION OF ORGANIC COMPOUNDS BY THE TUBULAR NS-1 AND MINI-MODULE (CA) FROM UOP FLUID SYSTEM

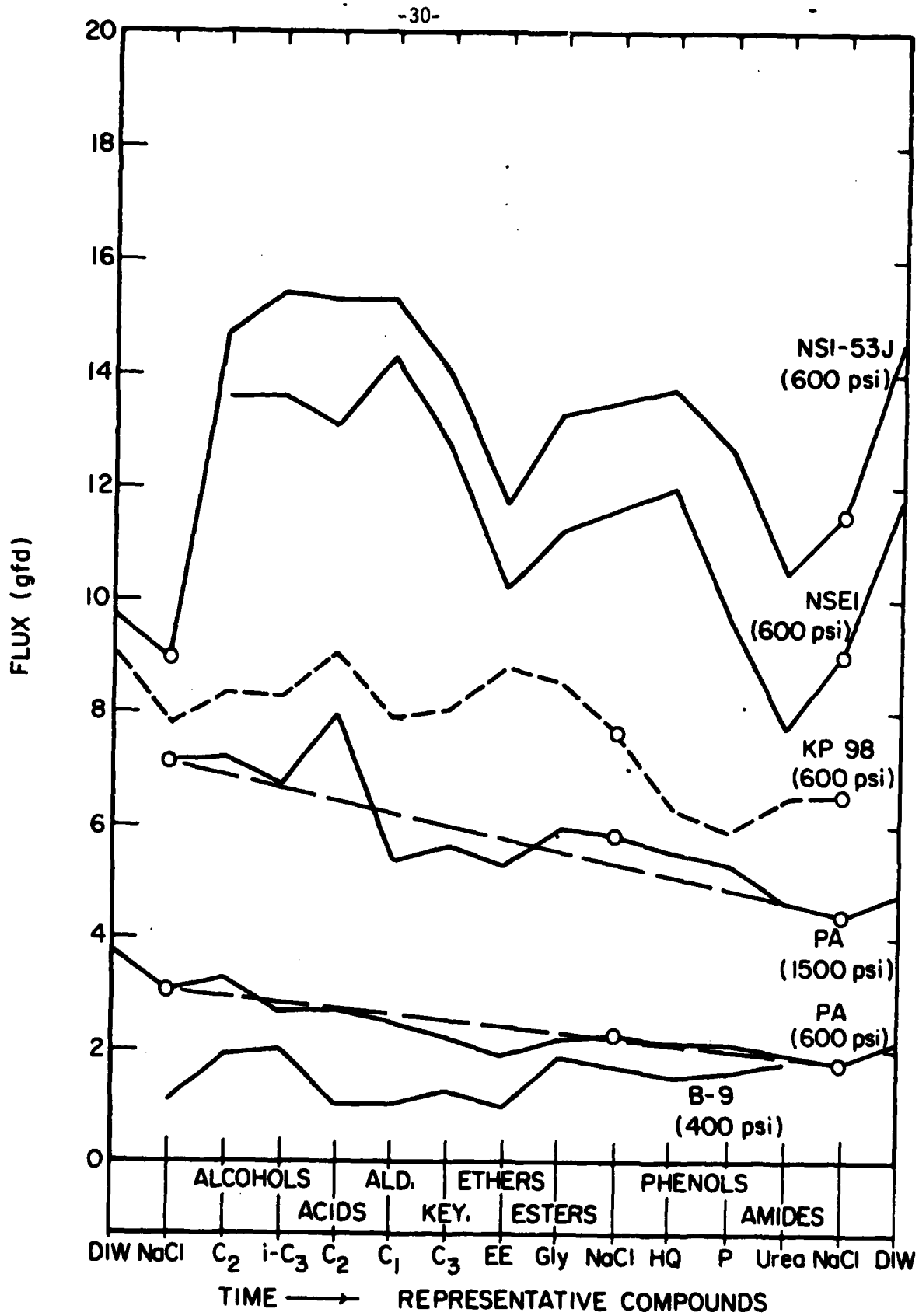


Figure 12. FLUX OF NEW RO MEMBRANES WITH ORGANIC COMPOUND IN AQUEOUS SOLUTIONS

Part of the experimental results and discussion given here was presented at the 75th National Meeting of AIChE in Detroit, June, 1973, and has been accepted for publication in "Water-1973", edited by Dr. G. F. Bennett. Also, we have received quite favorable comments from Dr. S. Sourirajan, (Appendix I), the international authority in the RO area, in terms of both the nature and the results of this study. A part of his letter of August 3, 1973 is quoted as follows:

"I regard your paper as a very valuable and timely contribution both to the science of reverse osmosis and to its application for wastewater treatment. I would appreciate receiving further reprints of your publications in the field."

4. CASTING OF NEW MEMBRANES

4.1 CA Membrane

Prior to studying the membrane performance, the reproducibility of casting the CA membranes was examined in our lab. A Manjikian-Loeb-McCutchan type (1965) of cellulose acetate casting solution was first prepared having the following composition:

cellulose acetate E-398-10 (Eastman Kodak)	25%
formamide	35%
acetone	40%

Three sheets were then cast and annealed under these identical conditions:

Thickness	= 8 mils
casting speed	= 5 in/sec
$t_{evaporation}$	= 4 sec
T_{room}	= 24°C
T_{gel}	= 2.0°C
T_{anneal}	= 87.9°C
t_{gel}	= 60 min
t_{anneal}	= 20 min

Finally, two to three membranes were cut from each sheet and were tested against deionized water and a 5,000 ppm sodium chloride solution at 600 psi, 24°C and 0.30 gpm. Table 8 summarizes the experimental results.

The average permeate flux of seven membranes for deionized water was 8.42 gfd with 0.73 gfd the standard deviation. For a 5,000 ppm sodium chloride solution the average permeate flux and salt rejection were 7.49 gfd and 98.73% with 0.52 gfd and 0.12% their respective standard deviations. Reproducibility was found to be satisfactory, especially when compared to the results of others, e.g. Loeb (1965) reported a reproducibility test which gave a 12.72 gfd flux and 80.7% salt rejection with standard deviations of 1.59 gfd and 19.3%, respectively.

4.2 CAB and $CA_{(blend)}$ Membranes

Since the performance of the CA membranes cast in our lab was quite satisfactory in terms of flux, salt separation and reproducibility, membranes made of other polymeric materials were prepared. Both CAB and $CA_{(blend)}$ membranes were cast under the identical conditions reported by their respective original investigators, Manjikian (1970) and King (1972). For the CAB (36-25-A) membrane, its composition and casting conditions are given as follows:

TABLE 8

*Test of the Reproducibility of the Cast CA Membranes

Membrane	**deionized water	***sodium chloride solution 5,000 ppm	
	flux (gfd)	flux (gfd)	rejection (%)
A1	8.03	7.32	98.63
A2	9.48	8.73	98.51
B1	9.32	7.38	98.82
B2	7.97	7.24	98.97
C1	8.12	7.38	98.80
C2	7.30	7.06	98.69
C3	8.70	7.32	98.71

*Test conditions; P = 600 psi

T = 24° C

Q = 0.30 gpm

**Samples of deionized water collected after continous flow at the test condition for 60 min.

***Samples of 5,000 ppm NaCl solution collected after 90 min of deionized water flow followed by 30 min of NaCl solution at the test condition.

Composition:	EAB-171-15 (Eastman Kodak)	22%
	Acetone	45%
	Triethyl Phosphate	25%
	Glycerol	2%
	n-propanol	6%
Cast Conditions:	t_{evap}	70 sec.
	thickness	7 mil.
	t_{gel}	40 min
	T_{gel}	2.5°C
	no heat treatment	

whereas for $CA_{(blend)}$(36-30-A) membrane

Composition:	dioxane	60 parts
	acetone	30 parts
	methanol	9 parts
	maleic acid	6 parts
	Cellulose di-acetate E-398-3 (Eastman Kodak)	10 parts
	Cellulose tri-acetate A-432-130B (Eastman Kodak)	10 parts
Cast Conditions:	t_{evap}	5 sec.
	thickness	7 mil.
	T_{gel}	3°C
	t_{gel}	40 min.
	T_{anneal}	90°C
	t_{anneal}	5 min

Performances of these two membranes compared to those provided by the original investigators are shown in Table 9.

Fluxes of both membranes cast in our lab were higher than those prepared by the original investigators. However, the separation of sodium chloride using cast membranes was lower, and the separation of organic solutes by the cast membranes was either comparable or in some cases higher. At 600 psi, no compaction or fouling effect was observed during the test period.

4.3 Crosslinked-PEI Membrane

Since the performance of the NS-1 membrane is extremely outstanding in terms of both flux and organic solute separation, effort was made to cast the crosslinked PEI membrane (NS-1) in our lab. Furthermore, it was of interest to us also to determine various casting procedures that govern the performance of the NS-1 membrane. Effort was first made to duplicate the NS-1 membrane and test its reproducibility based on North Star's Annual Progress Report (1972) sent to us by Dr. Kinley of OSW.

Table 9

Preliminary Comparison between the Performances

of the Cast and the Contributed Membranes

at 600 psi, 24°C and 0.30 gpm

Solute	Conc. (ppm)	Cast CAB		Contributed CAB		Cast $CA_{(blend)}$		Contributed $CA_{(blend)}$	
		gfd	%	gfd	%	gfd	%	gfd	%
deionized water	-----	3.56	----	1.94	----	8.91	----	5.24	----
sodium chloride	5,000	3.01	98.1	1.69	99.6	8.26	93.6	4.68	98.5
urea	1,000	3.03	71.45	0.78	80.01	8.64	58.35	4.92	24.19
ethanol	1,000	3.04	24.6	1.65	1.90	8.45	32.80	4.40	38.02

NS-1 is essentially a membrane made from polyethylenimine (PEI) coated on a microporous polysulfone (PS) support and crosslinked with m-tolylene 2,4-diisocyanate (TDI). Therefore, four major steps are involved in its preparation: (1) preparation of the polysulfone (PS) support; (2) PEI coating; (3) TDI reaction; and (4) heat curing.

A PS supporting film of 7 mils in thickness was cast from a 15% solution of PS in dimethylformamide. The film was drawn out on a glass plate and gelled by immersion in deionized water for 60 min. Prior to drying, the film was treated by a surfactant (0.1% dodecyl sodium sulfate). A 2% aqueous PEI solution was used to coat the dried PS film. After 60 sec. of soaking the film was held in a vertical position to drain the excess PEI solution from the surface. Then a 0.5% solution of TDI in hexane was allowed to react with the PEI coated surface. After a 60 sec reaction period, the film was again held in a vertical position to drain the excess solution from the surface. The coated membrane was afterwards baked in a convection oven at 115°C for 600 sec. The structure of the crosslinked PEI active layer is illustrated in Figure 13. The thickness of this crosslinked structure is dependent upon the concentration of PEI solution. Using a 2% aqueous solution of PEI a membrane of approximately 6000 Å thick active layer will result. The active side of the membrane can be easily distinguished by its shiny surface.

Three membranes were prepared following these procedures reported by North Star. Results of preliminary tests showed poor reproducibility of North Star's. Only one out of three membranes showed similar performance to those made by North Star. Table 10 summarizes the experimental results.

In general, the performance of the crosslinked PEI membrane prepared by us was able to reproduce that of the two NS-1 membranes received from North Star. Solute separations were nearly equal but the flux of our membrane was generally higher. In addition, no compaction or fouling of membrane was observed during this period of testing, and the flux was found strongly dependent on the properties of the solute as concluded in the previous section.

The performance of the NS-1 membrane was impressive enough to warrant the further investigation described in Section 7.

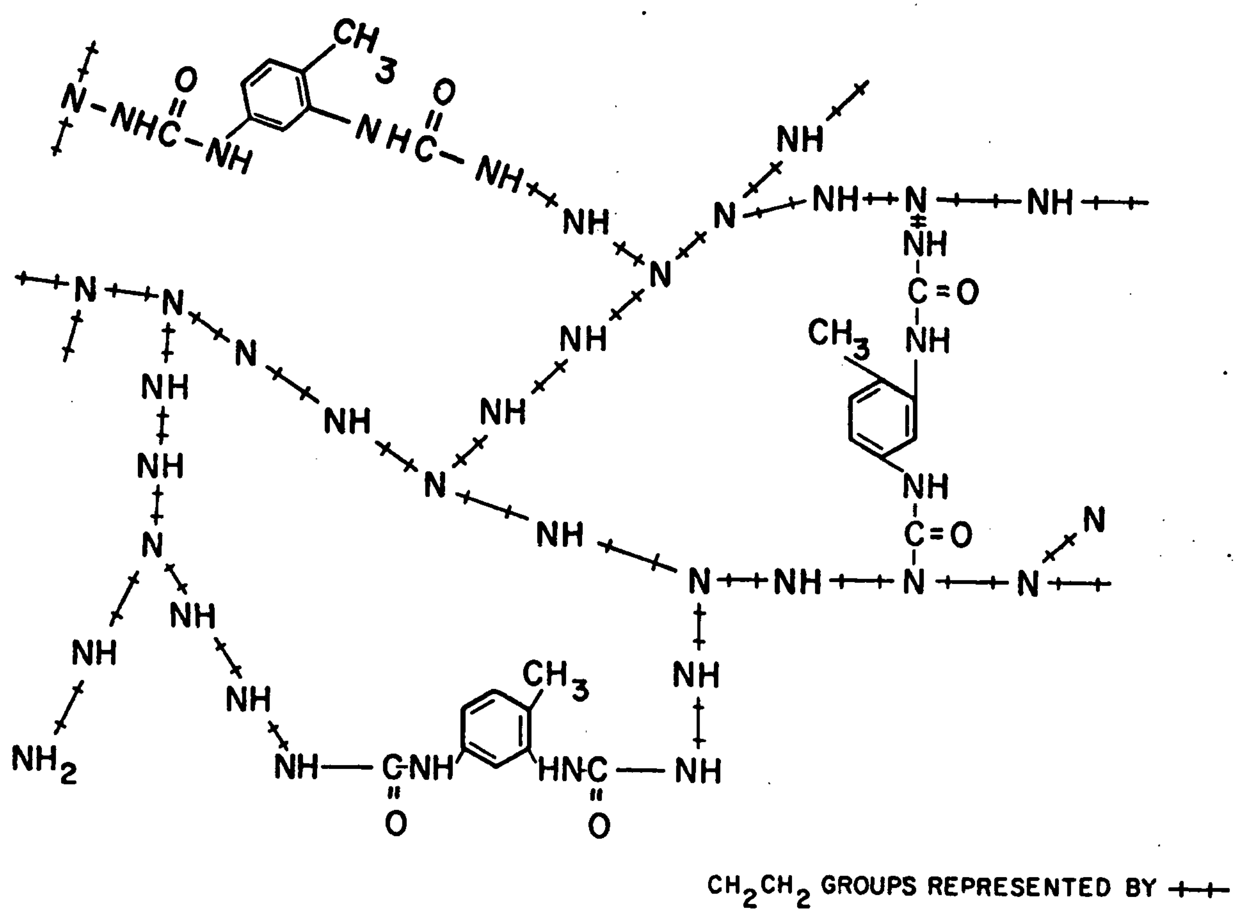


Figure 13 Partial Reaction Product of Polyethylenimine with m-Tolylene 2,4-Diisocyanate

Table 10

Preliminary Comparison of the Performance of the Crosslinked-PEI Membranes at 600 psi, 24° C and 0.30 gpm

Solute	Conc. (ppm)	Cast (F2)		NS-1 Contributed 307-52C		NS-1 Contributed 307-53J	
		flux (gfd)	sprtn (%)	gfd	%	gfd	%
deionized water	-----	11.43	-----	-----	-----	9.73	-----
sodium chloride	5,000	10.88	99.26	-----	-----	8.96	99.71
urea	1,000	14.36	60.40	7.67	64.15	10.44	55.37
ethanol	1,000	16.53	71.43	13.59	64.78	14.64	65.66
phenol	1,000	12.02	72.60	9.58	68.57	12.64	55.68
sodium chloride	5,000	17.61	95.85	9.01	98.91	11.50	93.70

5. CRITERION OF ION SEPARATION

Although the physico-chemical criteria of organic removal by reverse osmosis have been studied extensively by Chian *et al.* (1974, 1975) and Matsuura and Sourirajan (1971, 1972, 1973), there is only limited theoretical work being done regarding the separation of inorganic salts.

Glueckauf (1967) has analyzed the repulsive forces between ions and a porous membrane material using the reverse osmosis operating conditions. Beam, (1969) on the other hand, has analyzed the diffusion of ions through pores, and the electrostatic force which causes ions to avoid a region of low dielectric constant. Solute separation conducted in these studies was expressed as a function of molecular parameters, such as pore size, dielectric constant, ionic radius, ionic charge, etc. Although both of these analyses were based on sound physical parameters of the membrane material and the ions under study and even though both studies generally agreed qualitatively in their experimental results, their final equations were too complicated to have much practical use.

Sourirajan (1970) has also shown that separation of inorganic ions by cellulose acetate membrane is in the order of the lyotropic series of ions. However, this criterion of separation has a few exceptions. In addition, the lyotropic number cannot be used as a parameter to predict quantitatively the ion separation with cellulose acetate membranes.

A crosslinked polyethylenimine membrane, commonly known as NS-100, was employed in this study. The NS-100 membrane was first developed by Cadotte and Rozelle (1972) and subsequently studied extensively by Chian and Fang (1974 a,b,c, 1975). This is a composite membrane consisting of a microporous polysulfone support coated with an ultra-thin layer of polyethylenimine. The latter is further crosslinked with m-tolylene, 2,4-diisocyanate. This membrane gives an excellent separation of salts as well as low molecular weight polar organic compounds, and has a good stability over a wide range of pH (2-12).

The objective of this work was to study the criterion for the separation of inorganic ions with the NS-100 membrane. Hopefully, it can be used to predict the separation of other salts from data obtained with a reference salt solution of sodium chloride.

Three NS-100 membranes were fabricated and tested with a number of inorganic salts. The procedures of NS-100 fabrication will be discussed in detail in Section 7. The stainless steel test cells based upon Manjikian's design (1967, Appendix III) were used for this study. The effective area of each membrane was 3.14 in.^{2}.

Each test solution was prepared by dissolving the specific inorganic salt of interest in deionized water at a concentration of 0.1 mole per liter. The testing conditions for each solution were 600 psig and 25°C at a feed flow rate of 0.3 gal/min. The membranes were first tested with a sodium chloride

solution followed by eight different salts of chloride and three additional sodium halides. Finally, each membrane was tested another time with the sodium chloride solution in order to examine the reproducibility of the solute separation and any possible deterioration of the membrane material.

The concentration of individual salt in an aqueous solution containing a single solute was measured with a Yellow Spring Conductivity Bridge, Model 1485 (Cole-Parmer, Chicago, IL). The concentrations of individual cations in an aqueous solution containing multiple solutes were measured by a Beckman Atomic Absorption unit, Model 485 (Fullerton, CA).

5.1 Results and Discussion

All of the membranes tested gave satisfactory reproducibility and showed no sign of deterioration, according to both the initial and the final tests with the sodium chloride solution.

Similar to the cellulose acetate membranes, the NS-100 gave better separation of the bi-valent ions than the uni-valent ions. Nevertheless, for ions having the same valence, the separation with the NS-100 membrane increased with the decrease of ionic radius, i.e. $Li^+ > Na^+ > K^+ > NH_4^+$; $F^- > Cl^- > Br^- > I^-$; $Mg^{++} = Co^{++} > Ca^{++} > Sr^{++} > Ba^{++}$. This general rule, however, was not followed with the cellulose acetate membrane, which showed that the order of separation for the bi-valent cation was $Mg^{++} = Ba^{++} > Sr^{++} > Ca^{++}$. The discrepancy in the separation order of ions between these two membranes may be due to the weak anion-exchange properties of the NS-100 membrane.

A single ionic parameter which can be used to show these orders of separation for the NS-100 membrane is the enthalpy of hydration. Figure 14 illustrates a plot of the relative permeability of cations against the enthalpy of hydration of these ions. The relative permeability, P, of an ion is defined as

$$P = \frac{C_p}{C_f} \times 100\%$$

where C represents concentration of an ion, subscripts p and f represent permeate and feed solutions, respectively. The separation S, is hence defined as

$$S = 100\% - P \qquad (1)$$

The data of relative permeability for the nine cations tested, including both uni- and bi-valent ions, fall nicely on a smooth curve. A similar plot for the four anions tested is illustrated in Figure 15.

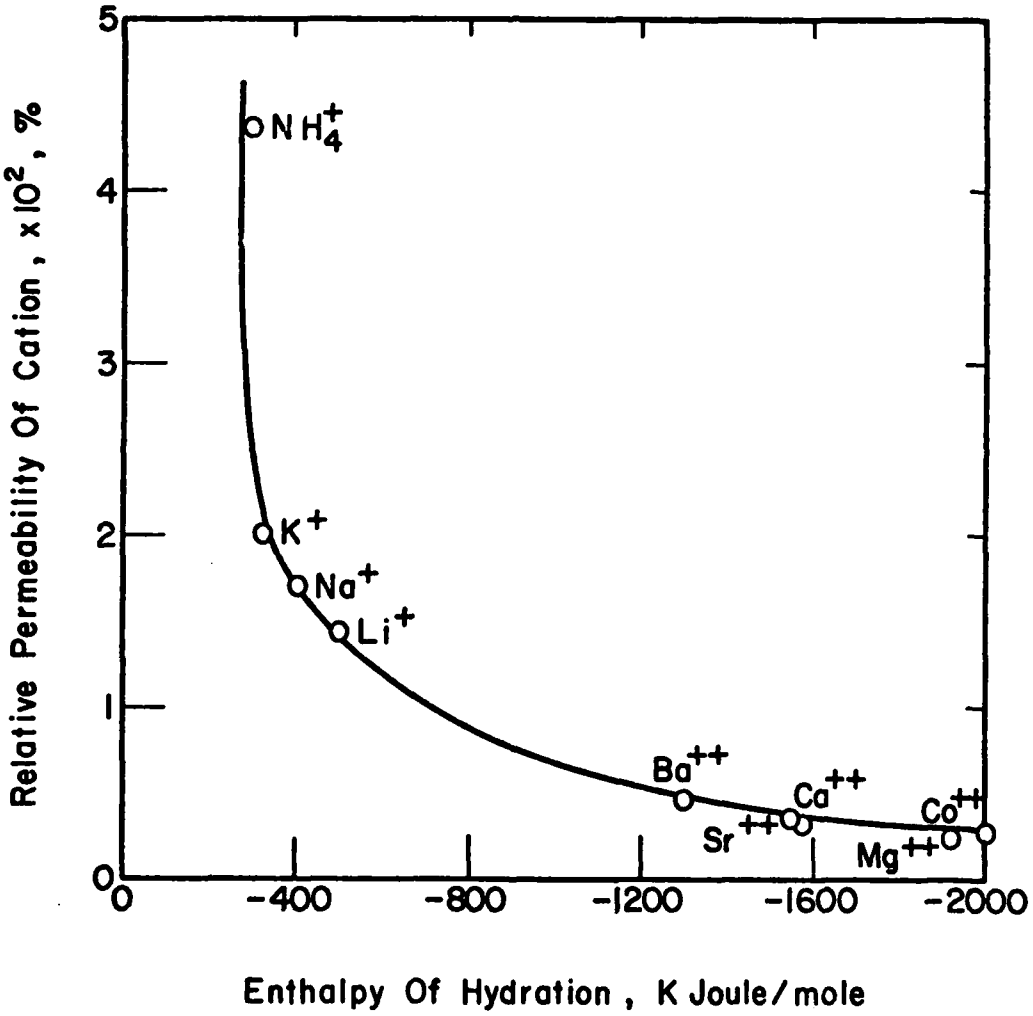

Relative Permeability Of Cation, x10², %
5
4
3
2
1
0
NH4+
K+
Na+
Li+
Ba++
Ca++
Sr++
Co++
Mg++
0
-400
-800
-1200
-1600
-2000
Enthalpy Of Hydration, K Joule/mole

Figure 14

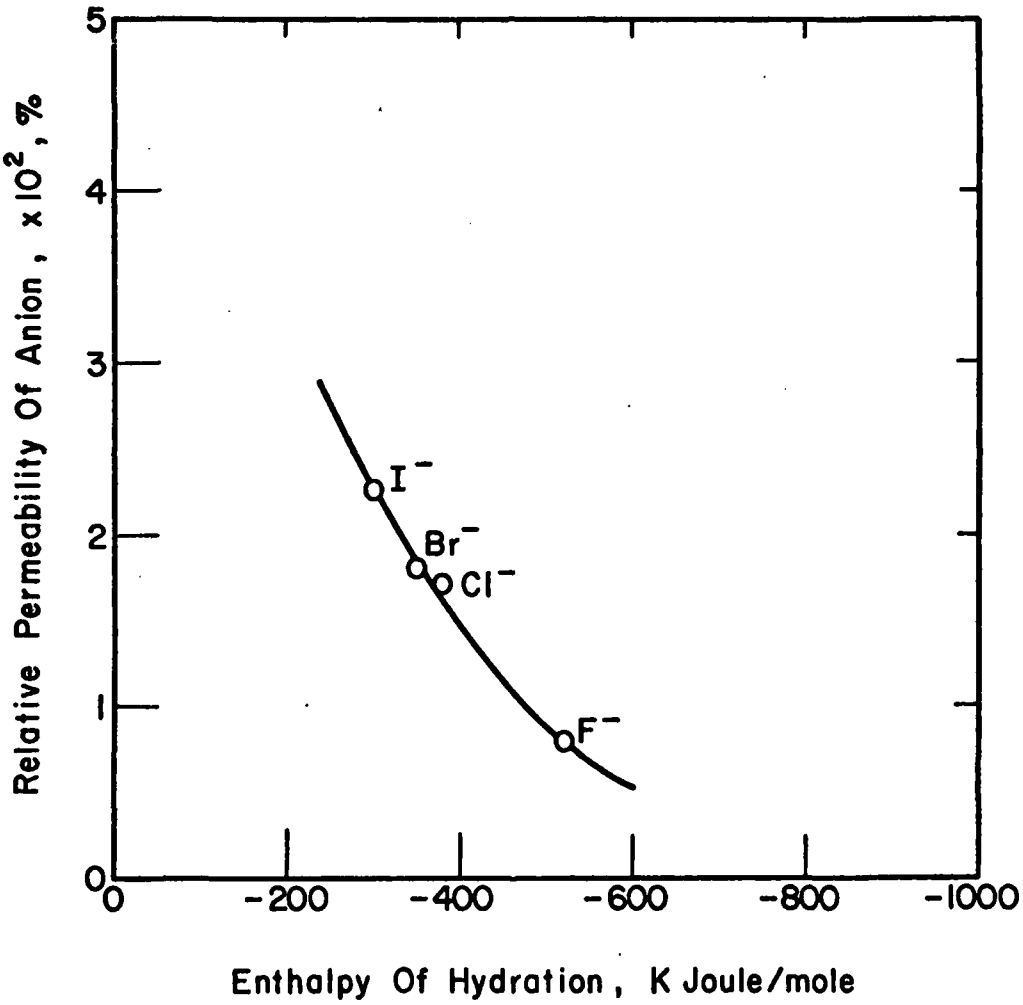

Relative Permeability Of Anion, x10², %
5
4
3
2
1
0
I⁻
Br⁻
Cl⁻
F⁻
0
-200
-400
-600
-800
-1000
Enthalpy Of Hydration, K Joule/mole

Figure 15

The enthalpy of hydration of an ion is defined as the enthalpy released in the following process:

$$Z^{\pm x}\ (g) + \infty\ H_2O(\ell) \xrightarrow{\Delta H_h} Z^{\pm x}(aq)$$

The higher the enthalpy of hydration of an ion, the more the water molecules will form a hydrated complex with the ion in aqueous solution. Better separation of the ion with the NS-100 membrane is attributable to the bulkiness of the hydrated ion. The smooth curves shown in Figures 14 and 15 indicate that the enthalpy of hydration is the sole criterion determining the order of separation of ions, either uni- or bi-valent, with a given NS-100 membrane.

By arbitrarily choosing sodium ion as a cation reference, the reduced permeability, $\bar{P}_c$, and the reduced enthalpy of hydration, $\overline{\Delta H}_{ch}$, of a cation are defined as follows:

$$\bar{P}_c = P_c/P^\circ_c$$

and

$$\overline{\Delta H}_{ch} = \Delta H_{ch}/\Delta H^\circ_{ch}$$

where the superscript ° represents a property of reference ion; subscripts c and h represent cation and hydration, respectively. A plot of reciprocal of $\bar{P}_c$ versus $\overline{\Delta H}_{ch}$ for various cations falls on a straight line as shown in Figure 16. The linear regression equation for the cations can be given as follows:

$$\bar{P}_c^{-1} = 1.44\ \overline{\Delta H}_{ch} - 0.44 \qquad (2)$$

or

$$P_c = \frac{P^\circ_c}{1.44\ \dfrac{\Delta H_{ch}}{\Delta H^\circ_{ch}} - 0.44} \qquad (3)$$

Similarly, by choosing chloride ion as a reference anion, the reduced properties of an anion are defined as

$$\bar{P}_a = P_a/P^\circ_a$$

and

$$\overline{\Delta H}_{ah} = \Delta H_{ah}/\Delta H^\circ_{ah}$$

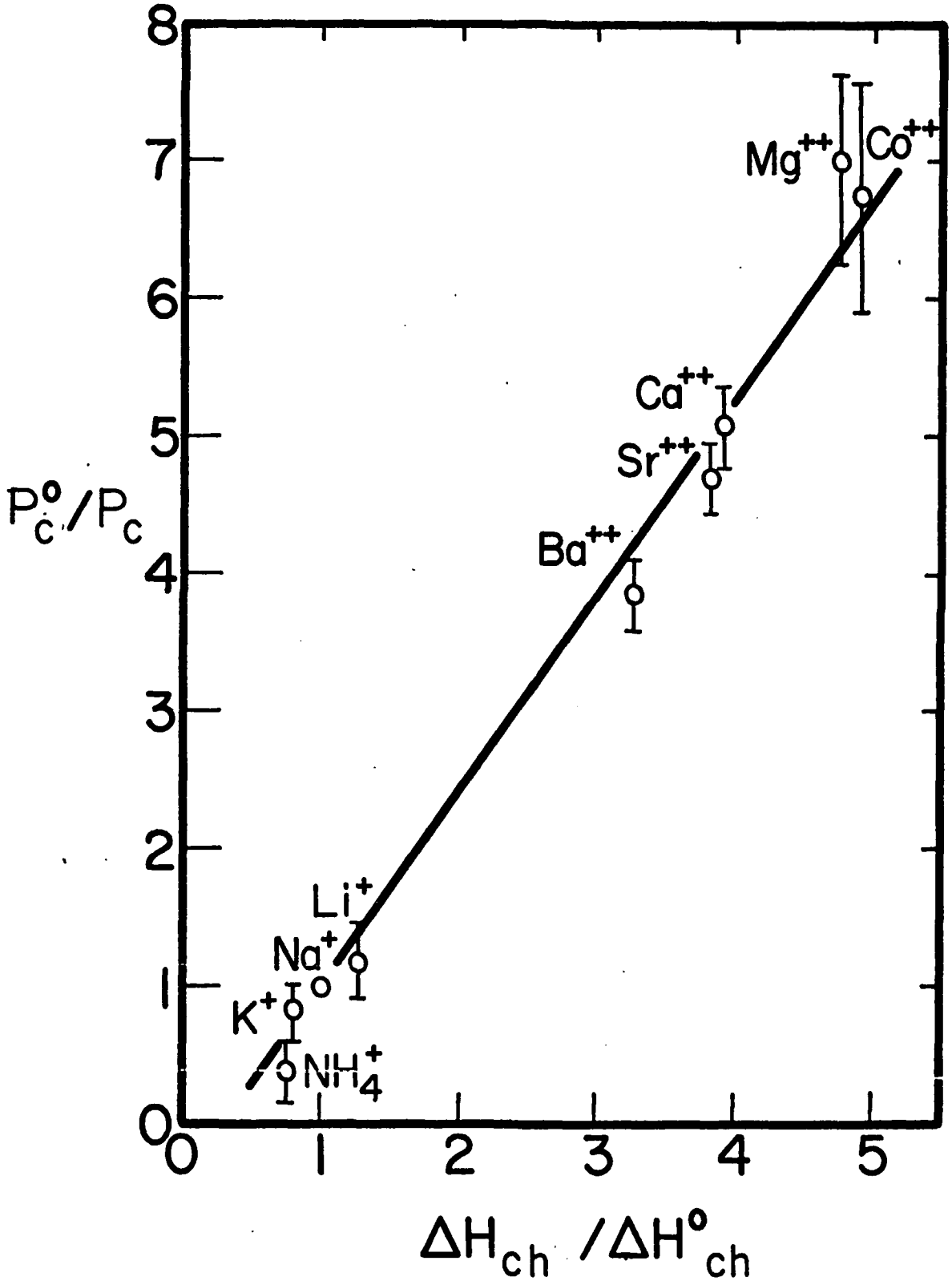

8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
P_c^o/P_c
$\Delta H_{ch}/\Delta H^o_{ch}$
Mg^{++}
Co^{++}
Ca^{++}
Sr^{++}
Ba^{++}
Li^+
Na^+
K^+
NH_4^+

Figure 16

where subscript a represents a property of anion. Figure 17 again illustrates the linear relationship between $\bar{P}_a^{-1}$ and $\overline{\Delta H}_{ah}$ which can be expressed as

$$\bar{P}_a^{-1} = 2.85\ \overline{\Delta H}_{ah} - 1.85 \tag{4}$$

or

$$P_a = \frac{P_a^{\circ}}{2.85\ \frac{\Delta H_{ah}}{\Delta H_{ah}^{\circ}} - 1.85} \tag{5}$$

The simple function as shown in Equations 3 and 5 provides a basis for predicting the permeability of a salt through a given NS-100 membrane. By testing with a sodium chloride solution, the relative permeabilities of both references, i.e. P_c° and P_a°, can be determined. Therefore, the relative permeabilities of both cation and anion of another salt, i.e. P_c and P_a, can be calculated from their respective enthalpies of hydration using Equations 3 and 5.

In a feed solution containing a mixture of salts, the permeability of an ion depends not only on its concentration in the feed solution but also on the presence of other ions. In a neutral pH solution, in which the concentrations of both hydronium and hydroxide ions are relatively low, the concentration of individual cation and anion in the permeate solution can be estimated by the following equations:

$$C_{pi} = A_{ci} C_{fi} P_{ci} \tag{6}$$

$$C_{pj} = A_{ai} C_{fj} P_{aj} \tag{7}$$

where subscripts i and j represent ith cation and jth anion, respectively. The parameters A_c and A_a in Equations 6 and 7 are governed by the electroneutrality of the permeate solution as given in the following equation:

$$\Sigma\ n_i C_{pi} = \Sigma\ n_j C_{pj} \tag{8}$$

where n is the valence of the respective cation or anion.

By substituting Equations 6 and 7 into Equation 8 and assuming the parameters A_c and A_a to be identical respectively for all species of cations and anions, the following equation is obtained:

$$A_c = \left(\frac{\Sigma\ n_j C_{fj} P_{aj}}{\Sigma\ n_i C_{fi} P_{ci}}\right) A_a \tag{9}$$

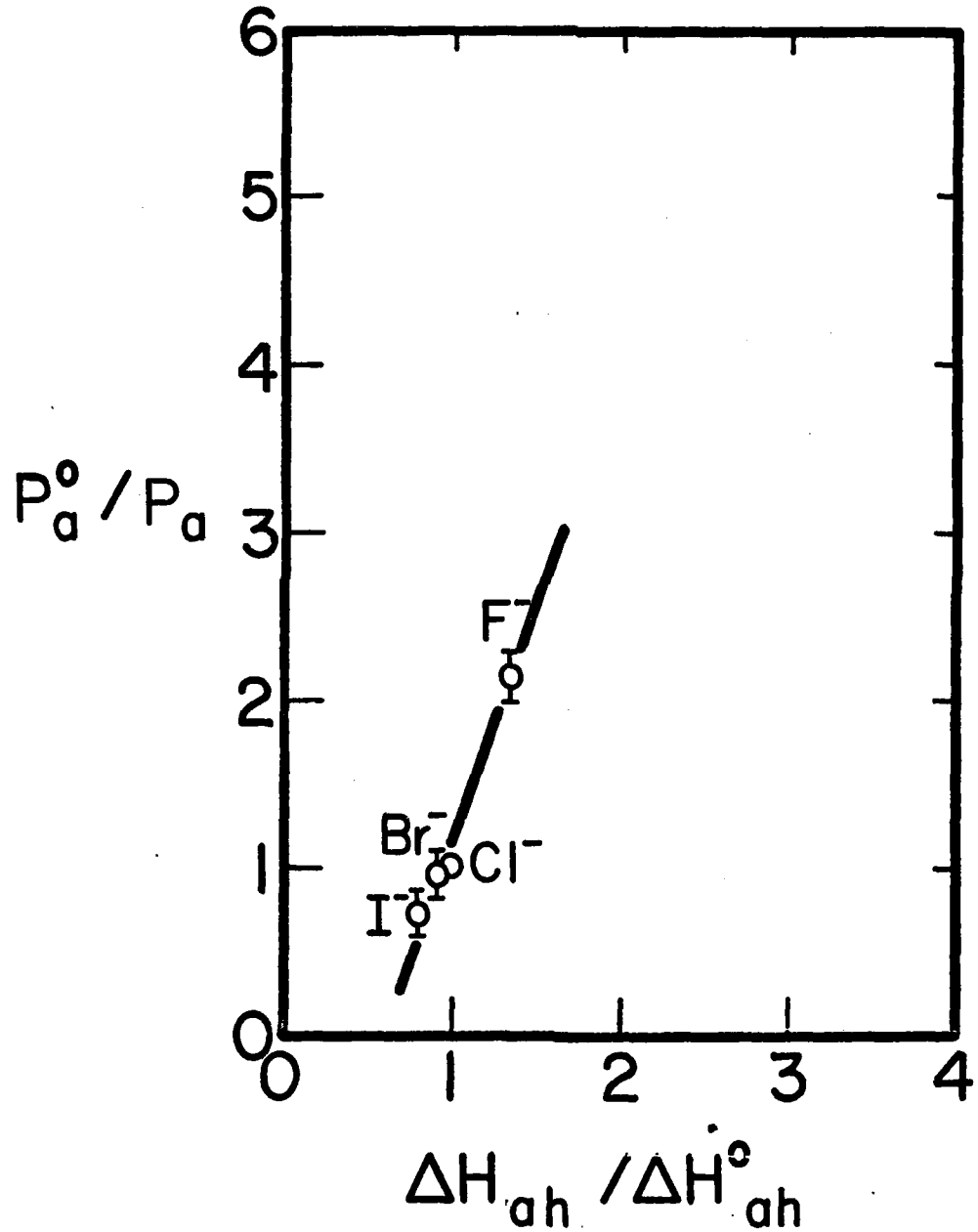


Figure 17

The parameter A_a can be estimated from Equation 7 by measuring the concentration of an anion in both the feed and the permeate solutions and its relative permeability, P_a, determined from Equation 5; the parameter A_c is hence calculated from Equation 9. Accordingly, the concentrations of other ions in the permeate solution can be estimated from Equations 3, 5, 6 and 7 with the known feed concentrations.

The validity of Equations 6, 7 and 9 was examined by the following experiments. Two NS-100 membranes were first tested with a 0.1 M sodium chloride solution followed by a solution containing a mixture of salts, including sodium chloride, potassium chloride, barium chloride and magnesium chloride at a concentration of 0.025 M for each salt. Since chloride was the common anion employed in this experiment, the permeability of chloride ion was assumed constant in both the sodium chloride solution and the solution containing a mixture of these salts. As a result, parameter A_a is equal to unity; the separation of individual cations of known concentration in the feed solution can then be estimated from Equations 3, 6 and 9. The experimental results and the predicted values are given in Table 11. It is seen that close agreement is obtainable between the observed and the predicted values at two levels of salt separation under study.

Agrawal and Sourirajan (1970) have developed a model for predicting the separation of individual cations in aqueous solution containing two solute systems with the cellulose acetate membrane. They have also successfully extended their model developed for the two solute systems for the prediction of separation of individual cations from an aqueous solution containing four solutes, such as those employed in this study. This study, however, offers another approach in predicting separation of individual ions from a mixture of multiple solutes in aqueous solution with the newly developed NS-100 membrane. Results of this study have shown that the enthalpy of hydration of ions appears to be a simpler criterion for use in predicting the separation of salts in aqueous solution with the NS-100 membrane.

The simple relation between the relative permeability of an ion and its enthalpy of hydration enables one to predict the separation of an individual ion in aqueous solution based upon a single test with sodium chloride solution.

TABLE 11

Prediction of Separation of Individual Cations in Aqueous Solution Containing a Mixture of Metallic Chloride

cation	Membrane 1 observed (%)	Membrane 1 calculated (%)	Membrane 2 observed (%)	Membrane 2 calculated (%)
sodium	97.56	97.29	95.25	92.02
potassium	97.50	96.15	88.67	88.77
barium	99.18	99.35	98.97	98.09
magnesium	99.28	99.59	99.10	98.79

6. REMOVAL OF ORGANIC COMPOUNDS WITH NEW POLYMERIC MEMBRANES

6.1 Removal of Thirteen Model Compounds

The objective of this section was to examine the effectiveness of various reverse osmosis membranes for the separation of polar organic compounds in water. The tested membranes included eight different types of flat-sheet membranes made of various materials as well as four types of modules manufactured in either tubular or hollow-fiber form.

It has been reported by Chian and Fang (1974a), Fang and Chian (1975), Matsuura and Sourirajan (1971) and Duval and Helfgott (1975) that the separation of a specific polar organic compound by a given reverse osmosis membrane depends largely on the functional group of the compound, whereas the separation of compounds having the same functional group depends on the size and branching of the molecules. Accordingly, in this study only the low-molecular-weight compounds were selected for membrane testing from each functional group, including acid, aldehyde, amide, amine, ester, ether, ketone and phenol. Three alcoholic compounds i.e., methanol, ethanol, and i-propanol, were tested by each membrane for the examination of the steric effect of the solute.

The membranes tested in this study, their abbreviations, configurations and suppliers, are shown in Table 12. Flat-sheet membranes were tested at 600 pounds per square inch (psig) and a flow rate of 0.30 gallon per minute (gpm) using stainless steel test cells based upon Manjikian's design (1967). As suggested by the suppliers, the tubular modules made of CA and NS-100 membranes were tested at 600 psig and 1.5 gpm while the hollow fiber B-9 and B-10 modules were tested at 400 psig and 2.5 gpm, and 750 psig and 4.0 gpm, respectively.

Each membrane was first characterized with a 5,000 parts per million (ppm) sodium chloride solution followed by testing with thirteen solutions each containing a single organic compound at a constant concentration of 1,000 ppm at zero product water recovery. However, with the B-9 and B-10 permeators, a product water recovery of 75 percent was employed. No pH adjustment was made for these test solutions. At the end of each series of testings, the membrane was again tested with a 5,000 ppm sodium chloride solution. By comparing both tests against sodium chloride, the deterioration of a membrane, if any, could be identified. The organic compounds selected for membrane testing, their chemical classifications and toxicities (Gleason *et al.* (1969)) are shown in Table 13.

A Yellow Springs Conductivity Bridge, Model 1485, (Yellow Springs, OH) was used to measure the concentration of sodium chloride. At dilute concentration (<100 ppm), the conductivity is proportional to the concentration of the salt solution. A Beckman Total Carbon Analyzer, Model 9.5, (Fullerton, CA) was used to measure the concentration of organic solutes. The carbon content of a dilute solution (total organic carbon < 100 ppm) was proportional to the peak height shown in the recorder of the Analyzer. Three to

TABLE 12

Reverse Osmosis Membranes, Their Abbreviations, Configurations, and Suppliers

Membrane Material	Abbreviation	Configuration	Supplier
cellulose acetate	CA	flat-sheet	University of Illinois
cellulose acetate	CA-T	tube	Universal Oil Products
cellulose acetate butyrate	CAB	flat-sheet	Universal Water
cellulose triacetate	CA3	flat-sheet	Envirogenics
crosslinked polyethylenimine	NS-100	flat-sheet	University of Illinois
crosslinked polyethylenimine	NS-100-T	tube	Universal Oil Products
NS-200	NS-200	flat-sheet	North Star
poly-2,2'-(m-phenylene)-5,5' bibenzimidazole	PBI	flat-sheet	Celanese
sulfonated polyphenylene oxide	SPPO	flat-sheet	General Electric
aromatic polyamide	AP	flat-sheet	Chemstrand
aromatic polyamide	B-9	hollow-fiber	duPont
aromatic polyamide	B-10	hollow-fiber	duPont

TABLE 13

Organic Compounds for Membrane Testing

Compound	Chemical Classification	Toxicity*
methanol	alcohol	3
ethanol	alcohol	2
i-propanol	alcohol	3
acetic acid	acid	-
formaldehyde	aldehyde	3,4
acetone	ketone	3
ethyl ether	ether	3
urea	amide	-
glycerol	polyhydric alcohol	1
phenol	phenol	4
hydroquinone	dihydric phenol	4
aniline	amine	4
methyl acetate	ester	-

*Toxicity scale is from 1, relatively nontoxic, to 6, highly toxic (Gleason *et al.*, 1969).

five injections were made for each sample in order to confirm the reproducibility of the analysis. The accuracy of the analysis was ± 1 ppm of organic carbon content when diluted to a concentration of less than 100 ppm for analysis.

The solute separation by each membrane is defined as follows:

$$\text{Solute Separation} = \left[1 - \frac{\text{solute concentration in permeate solution}}{\text{solute concentration in test solution}}\right] \times 100\%$$

6.1.1 Results and Discussion

Figure 18 illustrates the separation of sodium chloride with all of the membranes tested. Most of the membranes gave better than 93 percent separation of salt with the exception of PBI and SPPO, which separated less than 75 percent of salt. According to Laconti *et al.* (1972) and Modeland Lee (1972) the latter two membranes did not perform as well as was claimed by their respective suppliers. However, comparison of the salt separations of each membrane before and after each series of tests indicates that none of the tested membranes yielded any sign of deterioration during the testing period.

Figures 19, 20, 21, 22, 23 and 24 illustrate respectively the separations of methanol, ethanol and i-propanol, acetic acid and formaldehyde, acetone and ethyl ether, urea and glycerol, phenol and hydroquinone, as well as aniline and methyl acetate. The permeate flux was found to be insensitive to the type of organic solute present in the test concentration at a level of 1,000 ppm. The average permeate flux and the overall separation of the thirteen polar organic compounds (see definition in Table 14) with each membrane are shown in Table 14. Although the overall separation of solute is meaningless while relating to the separation of other unknown organic compounds, it however provides a basis for the comparison of the overall effectiveness of each membrane towards the separation of these thirteen compounds tested in this study.

In general, the specific PBI and SPPO membranes evaluated in this study showed poor separation toward both organic and inorganic compounds. Membranes made of cellulose acetate and its derivatives, including CA, CA-T, CAB and CA3, separated inorganic salt between 97 to 99.5 percent, but yielded a very low degree of separation for the polar organic compounds. In the cases of methanol, phenol, hydroquinone and aniline, these membranes yielded negative separation, i.e., the solute concentration was higher in the permeate than that in the test solution. The concentration of such highly polar compounds in the permeate was due to the high polarity of cellulose acetate (Matsuura and Sourirajan, 1971). Efforts have been made by various investigators (Lonsdale and Podall, 1972) to reduce the polarity of the cellulose acetate membrane material by substituting a free hydroxyl group of cellulose acetate with additional acetyl group, e.g. CA3, or with butyl group, e.g. CAB. However, membranes made of CA derivative performed only slightly better than the CA and CA-T in their separation of polar organic compounds. For

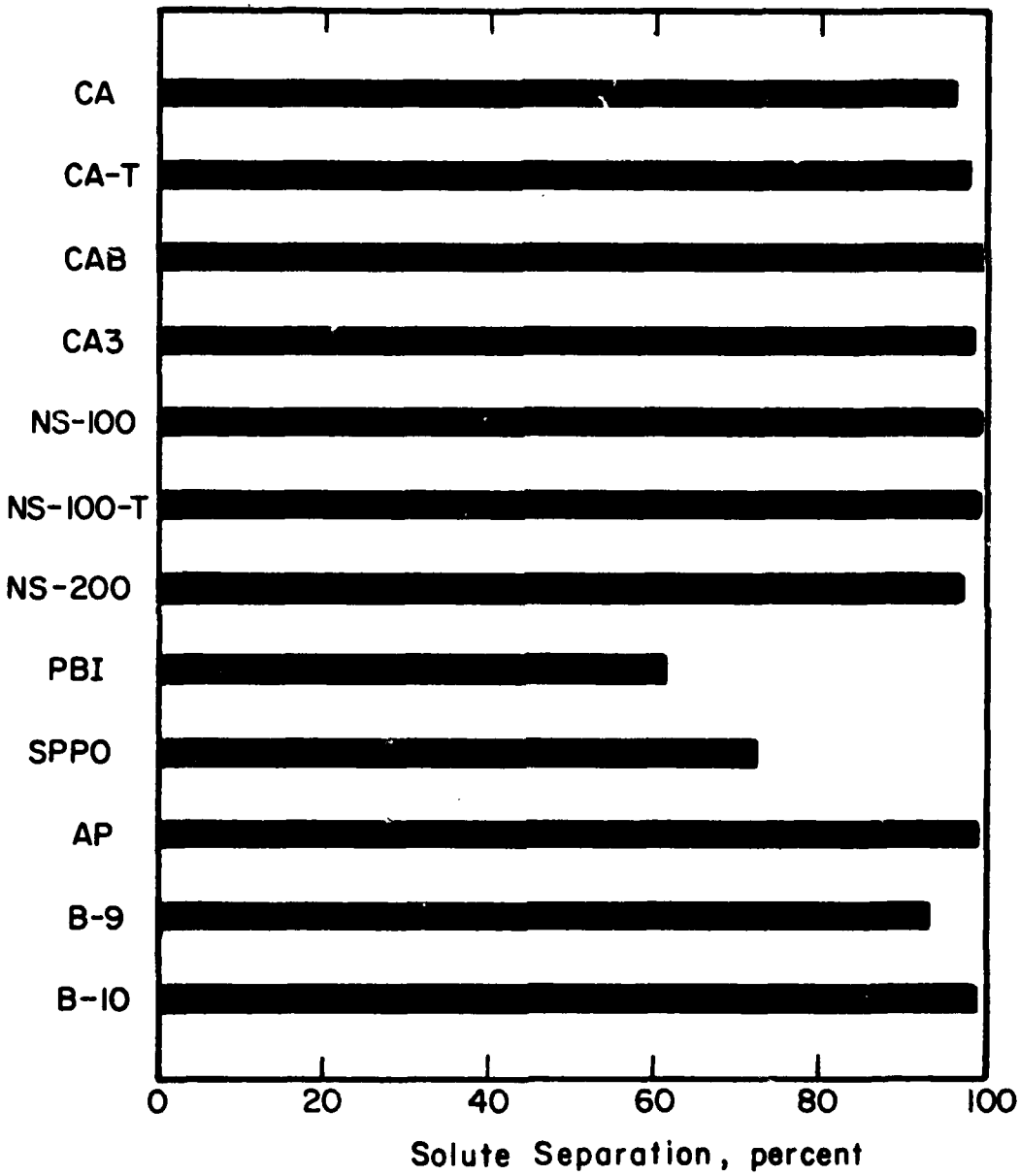


Figure 18

Separation of Sodium Chloride

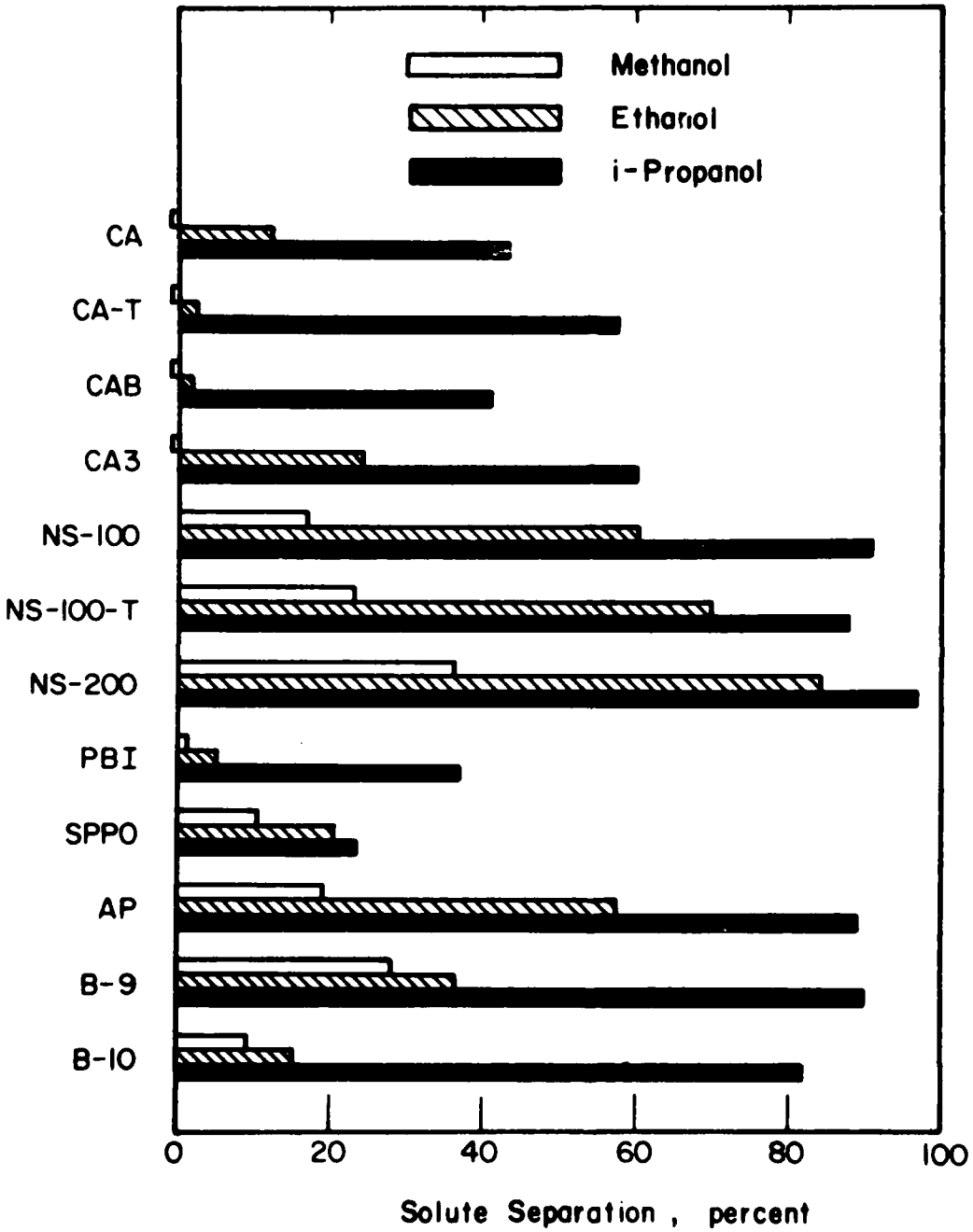


Figure 19. Separation of Methanol, Ethanol and i-Propanol

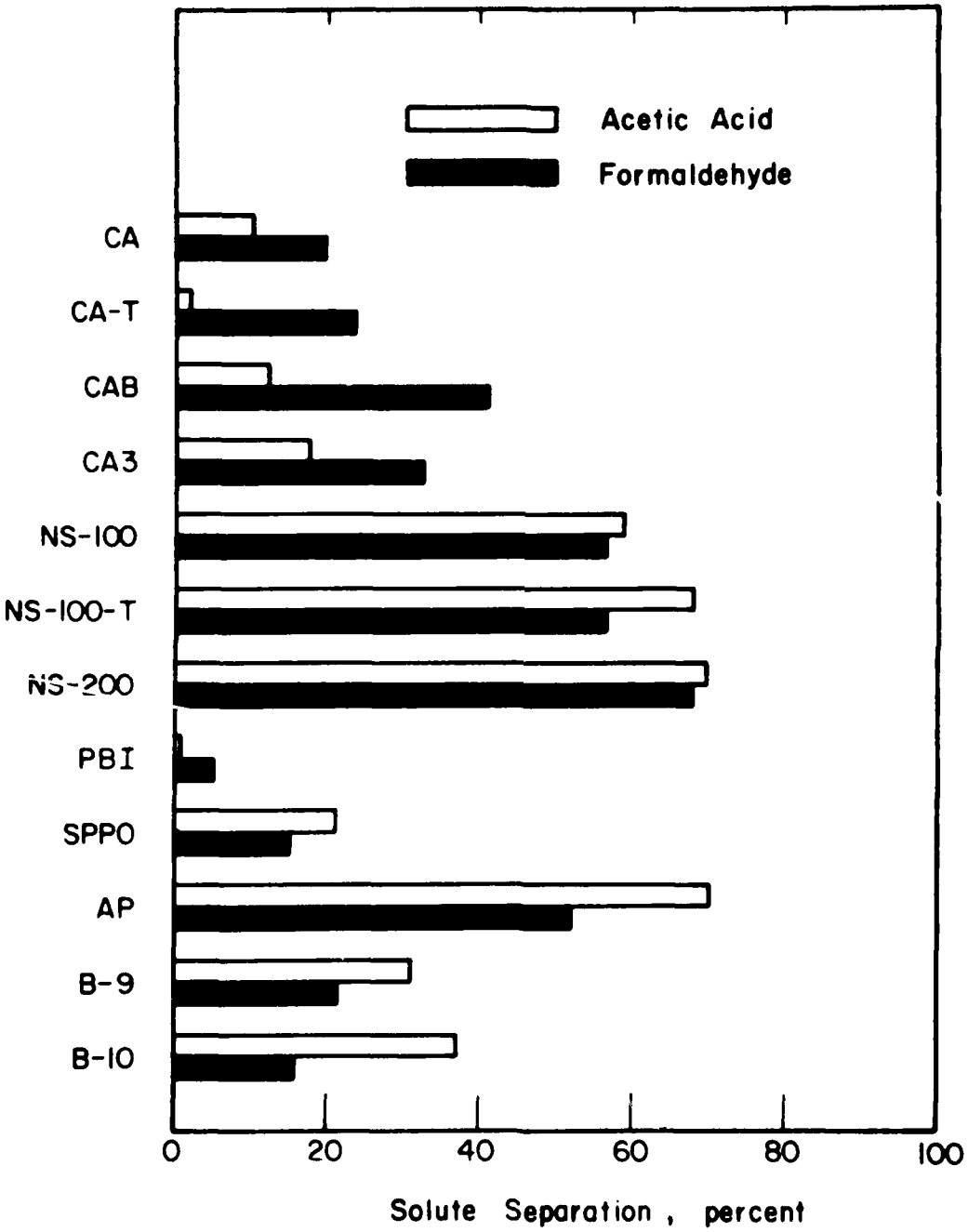


Figure 20. Separation of Acetic Acid and Formaldehyde

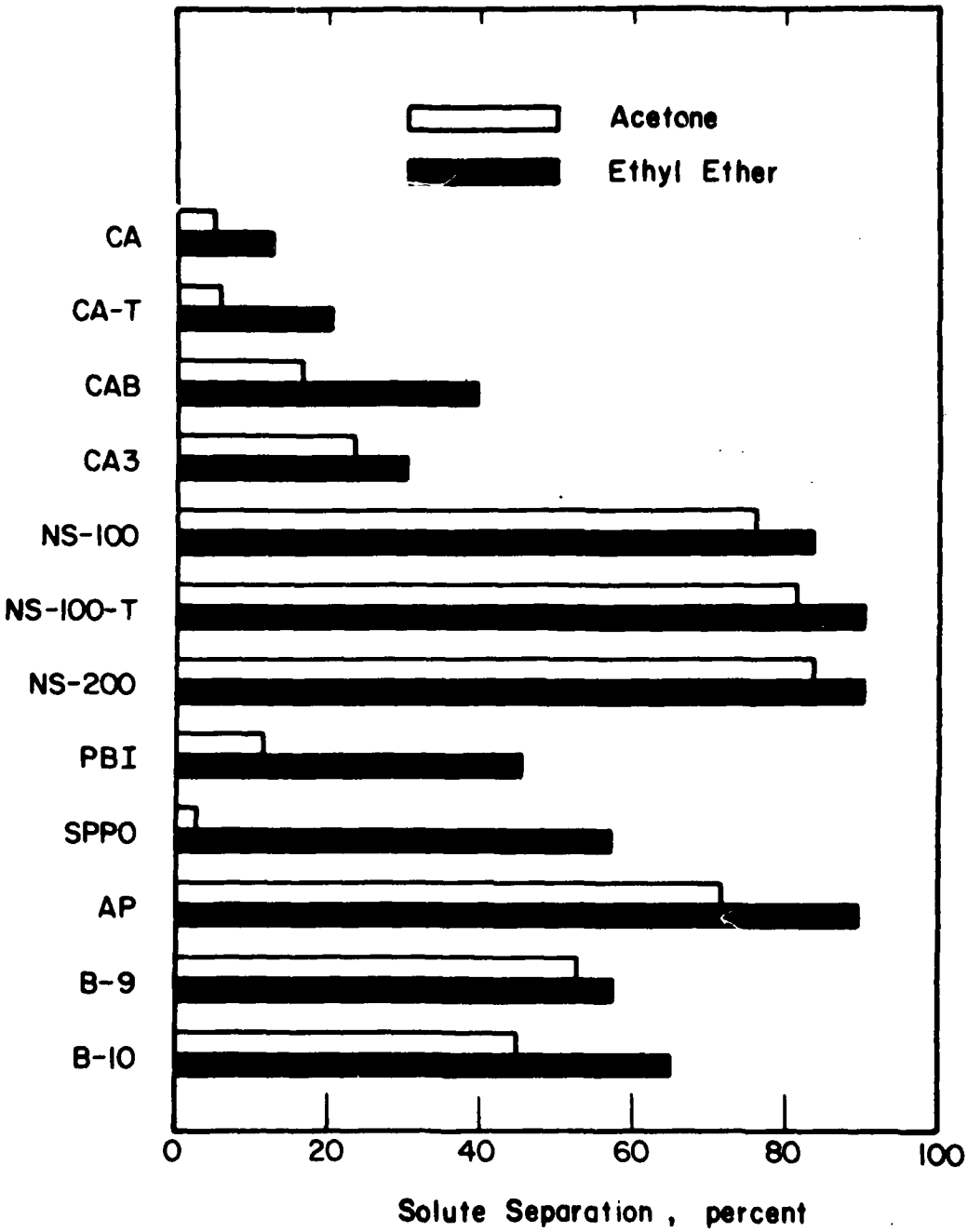


Figure 21. Separation of Acetone and Ethyl Ether

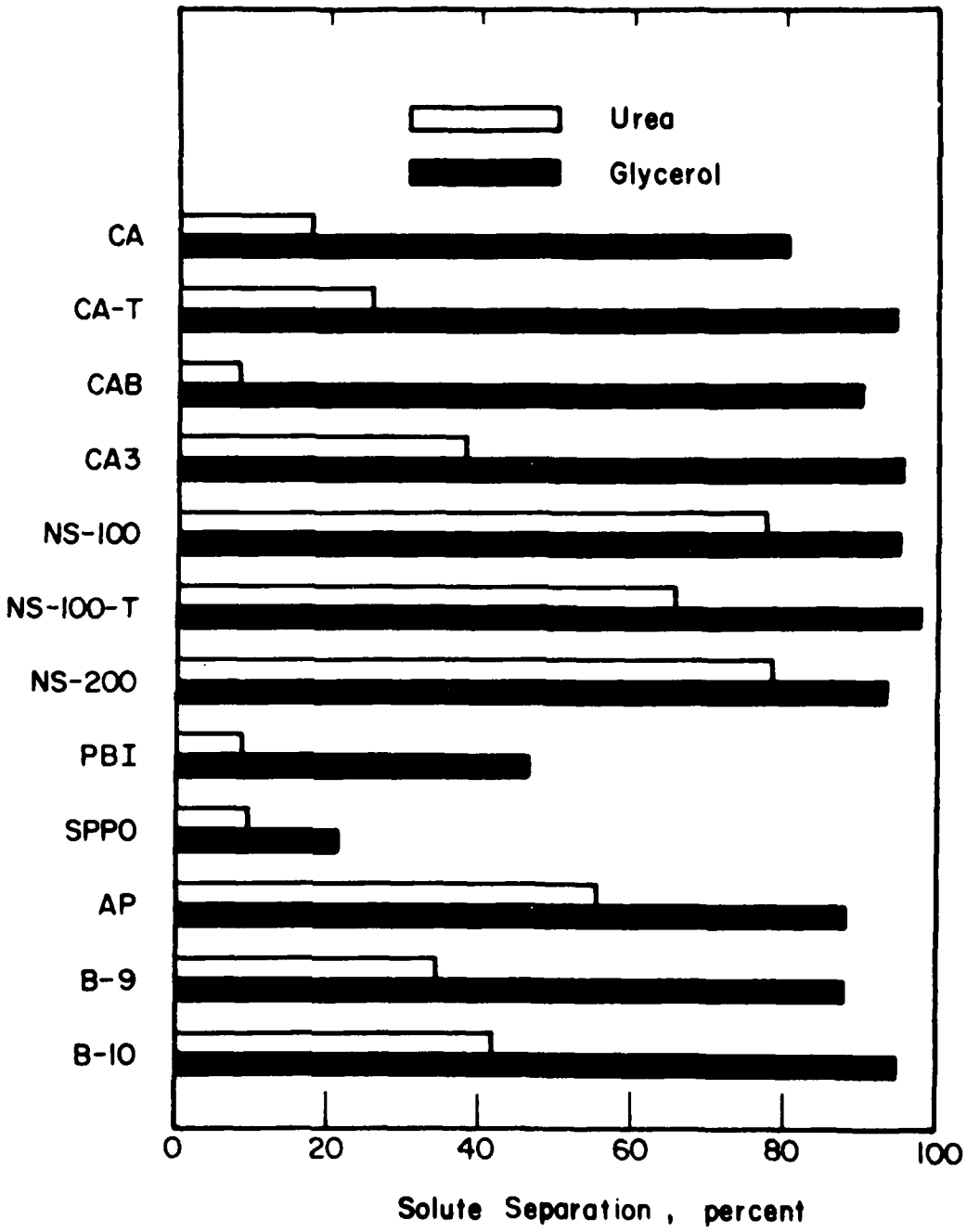


Figure 22. Separation of Urea and Glycerol

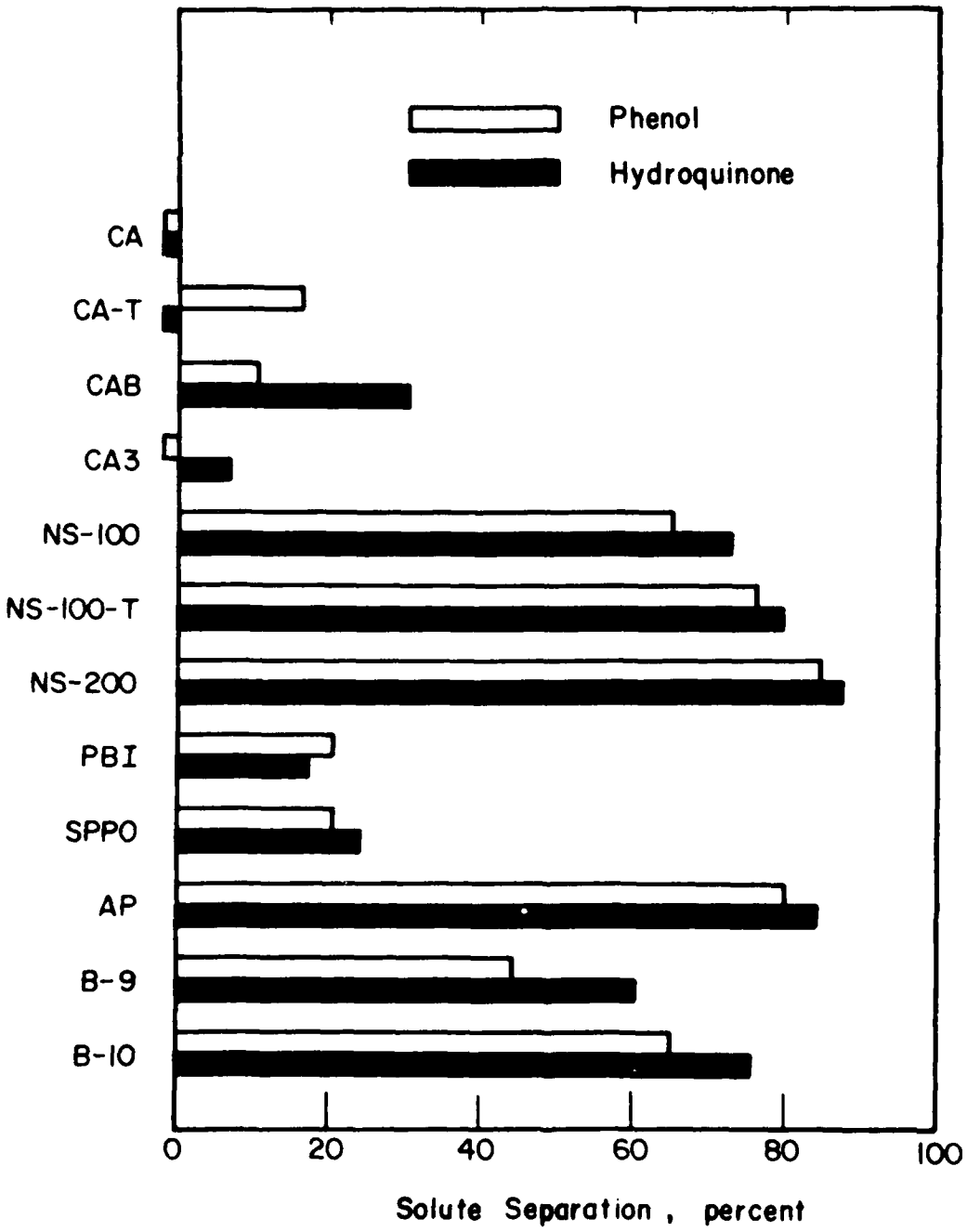


Figure 23. Separation of Phenol and Hydroquinone

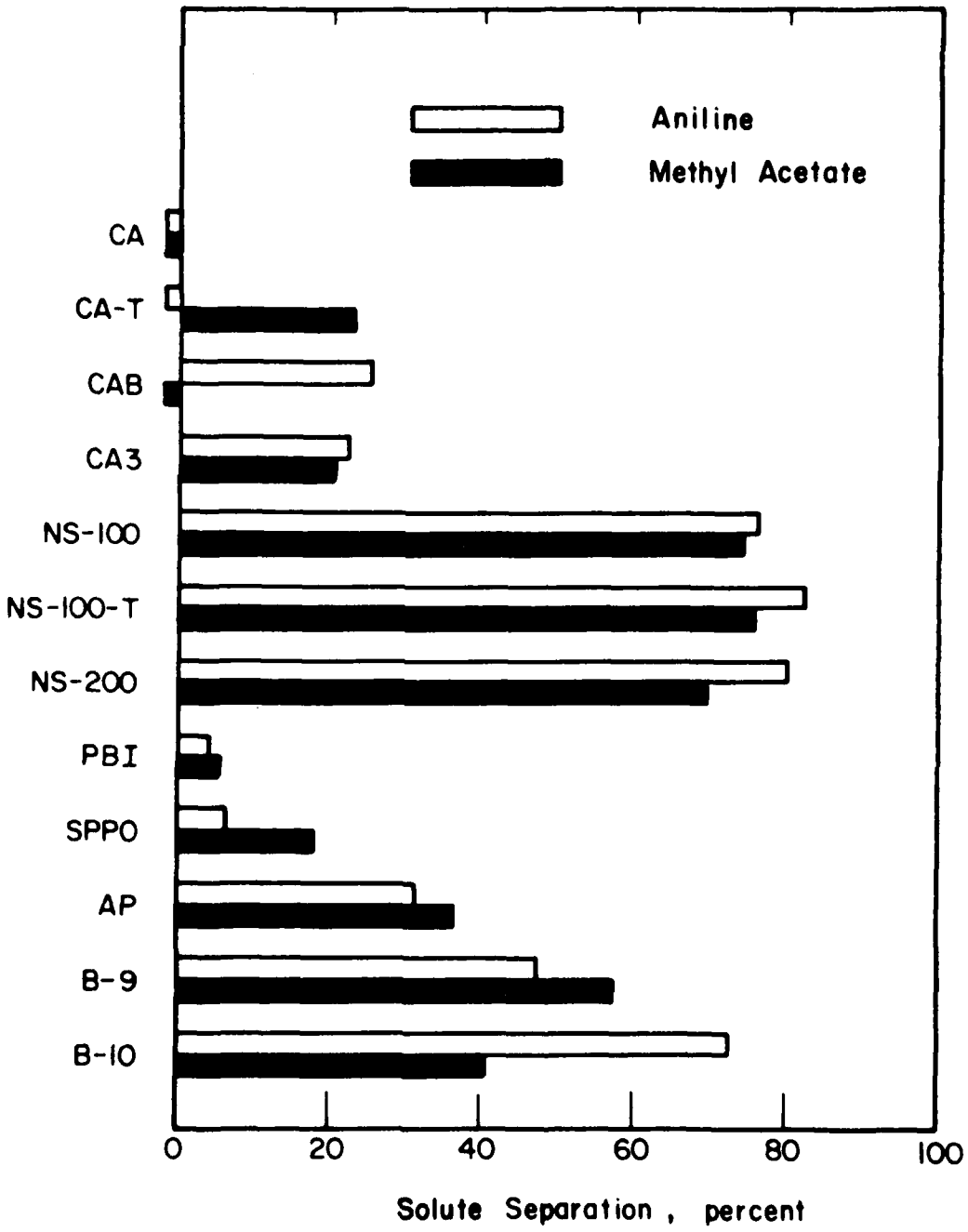


Figure 24. Separation of Aniline and Methyl Acetate

TABLE 14

Average Permeate Fluxes and Overall Solute Separations of Reverse Osmosis Membranes

Membrane	Average Flux (gfd)	Overall Separation of** 13 Model Compounds (percent)
CA	7.66	12.82
CA-T	10.17	17.84
CAB	1.37	21.81
CA3	4.89	26.61
NS-100	9.71	69.83
NS-100-T	6.50	73.65
NS-200	6.69	78.92
PBI	36.03	16.12
SPPO	17.39	19.36
AP	2.45	63.48
B-9 (2' x 5" diam.)	1,250 gpd*	50.00
B-10 (4' x 5" diam.)	4,500 gpd*	50.81
B-10 (4' x 5" diam.)	4,500 gpd*	52.11***

*Since the total surface area of hollow-fiber module is unknown, the permeate capacity, in terms of gallons/day, is shown.

**The overall separation of solutes shown here indicates that the anticipated separation of a mixture having a concentration of 1000 ppm of TOC contributed on equal weight basis by each of the thirteen test compounds.

***Actual separation of mixture of solutes on equal weight basis having a final TOC of 1000 ppm

instance, all of these membranes, i.e., CA, CA-T, CAB and CA3, yielded good separation of i-propanol and glycerol; on the other hand, all yielded negative separation of methanol. Besides, the relatively nonpolar nature of CAB and CA3 reduces greatly the affinity of these membranes to water; as such, both CAB and CA3 show a drastic reduction in permeate flux (see Table 14) as compared to CA and CA-T.

The NS membranes were originally developed by the North Star R & D Institute (Minneapolis, MN) and subsequently studied extensively by Fang and Chian (1975a, 1975b) and Chian and Fang (1974a, 1975c). Although they were prepared in different laboratories, the NS-100, NS-100-T and NS-200 yielded comparable membrane performances. At the same level of permeate flux, these membranes yielded 98-99.5 percent separation of salt as compared to 96-98 percent by CA. Table 14 shows that the overall separation of polar organic compounds by NS membranes is much higher than that of CA.

Three membranes made of aromatic polyamide, including AP, B-9 and B-10, also yielded similar separation of these model compounds. They separated better than 90 percent of salt and 50 percent of the test compounds. Although the permeate flux of membranes made of polyamide is low, the capacity of permeation flow can be increased by increasing the active membrane surface area per unit module volume, such as the hollow-fiber module of B-9 and B-10. For all the compounds tested, the AP membrane gave better separation than B-9 and B-10. This is due to the higher average feed concentration as well as polarization effect at the membrane surface encountered with the hollow fibers in both B-9 and B-10. These effects were reduced by the invariant feed concentration and the existence of highly turbulent flow near the flat sheet AP membrane surface. The B-10 yielded 304 times higher permeate rate than the B-9 (see Table 14), because of having larger active surface area (approximately twice) and higher operating pressure.

Although the mechanism by which the membrane separates solutes from solutions is still a subject of much controversy, any theory of separation mechanism is, however, intimately concerned with the physicochemical properties of both the membrane and the solutes under study. The most widely accepted theory on reverse osmosis separation of solutes so far is the preferential sorption - capillary flow mechanism proposed by Sourirajan (1970). It states that an appropriate chemical nature of the membrane surface in contact with the solution, together with the existence of pores of appropriate size on the skin layer at the interface, is an indispensable twin requirement for the success of solute separation.

In this study, the pore size of each membrane evaluated was controlled by its separation of sodium chloride tested under standard conditions as given in the previous section. With the exception of PBI and SPPO membranes, all other membranes studied here yielded the most optimal separation of sodium chloride and flux under the standard testing conditions as shown in Figure 18. The lower than the desired level of separation of sodium chloride with the PBI and SPPO membranes (see Figure 18) may account for their poor separation of the test compounds as shown in Table 14. Based on the mechanism of

capillary flow (Klein and Smith, 1972), for a given solute, any degree of reverse osmosis separation is possible with a given membrane material if the porous structure of the surface of the membrane is allowed to vary. Therefore, the separation of these test compounds with both PBI and SPPO membranes can be improved appreciably, if the surface porosities of these membranes are brought to a point which would separate sodium chloride comparable to those obtained with the other membranes tested, i.e. 95-99% (see Figure 18).

Once the physical properties of the membrane, such as the surface structure and porosity, are determined as characterized by their separation of sodium chloride (see Figure 18) and fluxes (see Table 14), the relationship between the physicochemical properties of solute in aqueous solutions and the chemical nature of the membrane materials can then be established to interpret the separation data of these organic compounds with various membranes tested.

According to the analysis of Matsuura and Sourirajan (1971), for a given membrane material and structure, one of the most important physicochemical criteria governing reverse osmosis separation of organic solute in aqueous solution is the "Polar Effect" of the solute molecule which includes both the functional group and the substituent groups. Both acidity and basicity of the functional groups are considered to be the relevant expression of polar effect. A measure of acidity and basicity is given by the ease of hydrogen bond formation and/or degree of dissociation of the molecule in aqueous solution. The former can be quantitatively expressed by the shift of the OH- and OD- band maximum in the IR spectra whereas the latter by the dissociation constant, pKa, with both carboxylic acids and amines. A measure of the effect of the substituent groups on the polar effect of the molecule can be quantitatively expressed by Taft and Hammelt numbers. Other less quantitative measures of solute separation include the use of solubility parameters between the organic solutes and the membrane materials (Klein 2nd Smith, 1972) and the steric effect of the molecule.

Whereas the quantitative analysis of separation data of a large number of organic compounds with a limited number of membranes, such as CA and NS-100, has been reported by Matsuura and Sourirajan (1971) and Fang and Chian (1975a), respectively, only qualitative analysis is given here in relating the solute separation data of polar organic compounds with the chemical nature of a large number of membrane materials.

Many investigators (Fang and Chian, 1975a; Matsuura and Sourirajan, 1971; Duval and Helfgott, 1975) have reported that the separation of aqueous solution of organic compounds with membranes depends greatly on their degree of ionization. For instance, the separation of formic acid by the NS-100 membrane varied from approximately 6 percent when partially undissociated to 98 percent when dissociated completely (Fang and Chian, 1975a). In the case of inorganic salts, it has also been reported that the separation of an ion with a given membrane depends on its enthalpy of hydration (Fang and Chian, 1975b); the larger the extent of the enthalpy of hydration of the

ion, the higher the degree of separation resulted. This is due to the formation of hydrated complex of the dissociated ion which is bulky in size and hence is difficult to diffuse through the membrane. Comparisons of Figures 18-24 indicate that the separations of the low-molecular-weight polar organic compounds were not as effective as those of sodium chloride for all the membranes tested. This is attributable to the lesser degrees of dissociation of organic molecules under the pH of testing as compared to the bulkier hydrated inorganic ion.

According to the preferential-sorption mechanism (Sourirajan, 1970), solute molecule is first adsorbed on the membrane surface and then transported through the membrane because of the gradient of its chemical activity. Therefore, in addition to the steric effect as discussed above, the solute separation is also dependent on the characteristics of the membrane and the functional group of the molecule to be separated. Figures 19 to 24 show results of solutes separation with different membrane materials.

Salome (1961) has developed a molecular parameter, permachor, from the study of permeability of organic vapors through polyethylene film. The parameter permachor increases with increasing size, branch and polarity of the molecule. A molecule having a high permachor has a lesser degree of permeability through the polyethylene film. However, it is known commonly that the non-polar hydrocarbons have a lower degree of permeability through the reverse osmosis membranes as compared to those molecules having a more polar functional group. This is due to the nature of the membranes selected for the reverse osmosis process differs from that of polyethylene film. Certain degrees of polar characteristics are required in order to have an affinity to water molecules and thus good water permeation flow. Hence it is not a surprise to find that the experimental results of this study indicate that the permachor parameter was not applicable to the solute separation of reverse osmosis. Nor was a quantitative relation found between the solute separation and any single molecular parameters of organic solute, such as dipole moment or solubility parameter.

Fang and Chian (1975a), and Duvel and Helfgott (1975) have reported that the separation of solutes having the same functional group depends on the size and shape of the solutes. Those solutes having a longer chain and/or more branches yield a higher degree of separation. This general rule is confirmed from the tests of three alcoholic compounds using different membrane materials as shown in Figure 19. All the membranes tested, without a single exception, separated a greater extent of i-propanol than ethanol, which in turn separated better than methanol. This can be attributable to the steric effect of the solute while diffusing through the membrane.

The ultimate goal of this section is to assess the effectiveness of various reverse osmosis membranes for the separation of organic contaminants in wastes. However, in the real world of waste treatment, the membrane process is to be applied to separate complex mixtures of molecules rather than single solute solutions. Therefore, the possible effect of solute interaction on its separation in mixtures, along with results of actual reverse osmosis separation of various wastewaters, is discussed here.

Since the organic compounds selected for this study consist of some of the lowest molecular-weight homologs in each of the functional groups, results of solute separation with various membrane materials represent the most conservative data as compared with the actual organic contaminants in wastewaters based on the mechanism of the steric and polar effect of the solute as discussed previously. Whereas the individual effect of solute interaction between each pair of the test compounds is unknown, a limited experiment of the combined effect of solute interaction among all the test compounds has been conducted with the B-10 module. A slightly higher separation of total solutes in a mixture of these thirteen test compounds was observed as shown in the bottom line of Table 14. This discrepancy is well within the combined experimental errors of both the reverse osmosis runs and the analytical procedures. This slight increase in the separation of a mixture of test compounds can also be explained by the neutralization effect of the acid and the basic molecules in the test compounds, resulting in somewhat higher dissociable neutral compounds. However, in the case of separating dissociable compounds, solute separation is closely related to the concentration of solutes and pH and ionic strength of the solutions. For a mixture consisting of dissociable compounds from the same functional group, such as the carboxylic group, the solute separation of mixtures was found to be lower than that calculated from data obtained from single solute solutions (Chian *et al.*, 1975). This is due to the depression of solute dissociation.

Fortunately, in waste treatment, the organic compounds present in wastewaters were found to have higher molecular weight, and thus lower polarity, than those tested in this study (DeWalle and Chian, 1974). Chian *et al.* (1975) have studied the effect of biological treatment of municipal sewage on the removal of organics with the reverse osmosis process. Table 15 shows that membrane separation of TOC increases with the increase in the degree of treatment of sewage with the activated sludge system. It is seen from Table 15 that membrane separation of soluble TOC increases from 70.1 percent for raw sewage to 82.8 and 93.7 percent, respectively, for effluents from the high and the low loading units. The decrease in loading implies that sewage is treated more intensively. As such, a higher percentage of biologically refractory materials is expected in the treated effluent from a low loading system (Chian and DeWalle, 1975). These materials are mainly high molecular weight humic substances formed as a result of biological activities.

The specific membrane studied by Chian *et al.* (1975) is a B-10 permeator which has an overall separation of 50 percent for the test compounds (see Table 14). This is much lower than that obtained with the worst case while separating soluble organics from raw sewage. Therefore, the overall separation of solutes with various membranes as given in Table 14 can be considered to be the lowest limit that one can expect while treating sewage wastewaters.

With the exception of PBI and SSPO, most of the twelve membranes evaluated showed a high degree of separating sodium chloride. When tested thirteen low molecular-weight polar organic compounds consisting of various functional

TABLE 15

Separation of Soluble Organics* in Sewage and Secondary Effluents by Reverse Osmosis(18)

	TOC mg/ℓ Feed	TOC, mg/ℓ RO Effluent**	Percent Separation
Sewage	32.8	9.8	70.1
High Loading Secondary Effluent ($F/M=0.69\ day^{-1}$)	18.0	3.1	82.8
Low Loading Secondary Effluent ($F/M=0.33\ day^{-1}$)	11.1	0.7	93.7

*Soluble organics in the filtrate of the 0.45μ Millipore Membrane (Bedford, MA)

**B-10 Permeator (DuPont Wilmington Delaware)
Operating Conditions: Product Water Recovery 80%
Pressure 800 psig
Feed Flow Rate 4 gal/min
Temperature 25°C

groups, the NS series membranes yielded the highest overall separation of 70 percent of these compounds, while the AP and the CA series membranes yield somewhat better than 50 and 10 percent, respectively. The overall separation of these compounds with various membranes can be considered to be the lowest possible ones while applying reverse osmosis to treatment of wastewaters, especially sewage.

6.2 Removal of Pesticides

Pesticides have been widely used to increase not only the production of food and fiber but also the freedom from epidemic diseases and obnoxious plant and animal life. In 1971, a total of 1.34 billion pounds of pesticides were manufactured (Lawless, 1972) in the United States. The estimated annual growth rate of poundage manufactured now approaches 16 percent (Atkins, 1972). It is obvious that the use of pesticides has become indispensible to many in the struggle to improve man's life.

Nevertheless, the side-effects resulting from the use of pesticides have become increasingly severe (Environmental Protection Agency, 1973). Pesticide residues have been reported to impart an unpleasant odor and taste to water (Robeck *et al.*, 1965). Pesticide residues not only kill noxious pests and weeds but also kill various microorganisms, fish, birds and wildlife. Moreover, because of their resistance to decomposition, the pesticide residues have appeared in man's immediate food supply through natural food chains. Since 1945, pesticide residues have been reported in milk, tissues of fish and wildlife and all types of waters, such as municipal drinking, irrigational and recreational waters. The amount of residues found in the wastewater of pesticide manufacturers is stunning. In spite of the extensive treatment of pesticide wastewater generated by pesticide manufacturers, a recent investigation (Lawless, 1972) showed that a large amount of pesticide ranging from a few pounds per day to over a thousand pounds per day was found in their effluents. All of these facts clearly show the need for an in-depth study of the removal of pesticide residues from water.

Numerous studies have been conducted on processes for removal of all types of pesticides from aqueous solution (Atkins, 1972). Several treatment processes, such as activated sludge treatment, chemical oxidation, coagulation and filtration, adsorption (activated carbon, ion-exchange, saturated clay systems, hydrous aluminum silicate), liquid-liquid extraction and photo-chemical degradation have been developed as a result of these studies. Hindin and his coworkers (1969) have studied the removal of a few chlorinated pesticides, including DDT, TDE, BHC and lindane, by reverse osmosis using a cellulose acetate (CA) membrane. The initial results of their findings have shown that reverse osmosis seems to be a promising treatment process for removing pesticides from water.

In Section 6.1 it was reported that a number of noncellulosic base membranes, such as aromatic polyamide and cross-linked-polyethylenimine (NS-100) membranes, exhibited far better properties of removal of organic compounds and resistance to pH as compared to the conventional CA membrane. Because of this advancement in membrane technology, reverse osmosis has been gradually finding application in the treatment of a variety of domestic, industrial and hospital wastewaters. This section gives an in-depth study of pesticide removal with reverse osmosis which is needed for fully assessing the potential of this process.

Thirteen major pesticides and two metabolites of pesticides were selected for this study. The selections of pesticides were based upon their chemical compositions, applications and occurrences in water. The trade and chemical names, molecular weights, classifications, solubilities, toxicities as well as annual productions of pesticides are summarized in Table 16. Samples of pesticides were provided by the Pesticides and Toxic Substances Effects Laboratory of the Environmental Protection Agency, North Carolina. The metabolite samples were provided by Illinois State Natural History Survey. All pesticides studied here were of analytical grade.

Nanograde solvents, such as acetone, hexane, ether, ethanol, dichloromethane and benzene, were used for dissolution and extraction of pesticides in this study. Demineralized water was used to prepare the aqueous solution of pesticides.

Conventional CA membrane and a newly-developed cross-linked-polyethylenimine membrane were employed in this work. The CA membrane, designated as KP-98, was a product of Eastman Kodak Co. (Kingsport, Tenn.). It possesses an asymmetric structure, which is composed of dense active layer of approximately 2000 Å in thickness supported by a porous layer about 0.25-0.5 mm in thickness. It is the dense active layer which dominates the permeate flux and the solute separation.

The cross-linked-polyethlenimine membrane, designated as NS-100 by the Office of Saline Water (OSW), was provided by North Star Research and Development Institute (Minneapolis, MN). Previous study has shown that the NS-100 membrane is the most promising membrane ever developed with respect to pH stability, permeate flux and the removal of solutes, especially small polar organic compounds.

While testing an aqueous solution containing 5,000 parts per million (ppm) of sodium chloride at room temperature and under a pressure of 40.8 atmospheres (600 psig), a flux of 32 $ml/cm^2/day$ (8 gallons per square foot per day, gfd) with 96.5 percent rejection of sodium chloride was obtained with the CA membrane. Under the same testing conditions, the NS-100 membrane yielded a flux of 49 $ml/cm^2/day$ (12 gfd) and a rejection of 99.5 percent of sodium chloride.

TABLE 16
Classification and Properties of Tested Pesticides

Trade Name	Chemical Name	Molecular Weight	Chemical Classification	Type	Solubility (Atkins, 1972; Gunther, 1968) (ppm)	Oral Toxicity (Atkins, 1972; Melinikov, 197[illegible]) LD_{50} (mg/Kg)	Estimated Annual Sales in 1971 (Lawless, 1972) (million pounds)
diazinon	0,0 diethyl 0-(2-isopropyl -6-methyl-4- pyrimidinyl) phosphorothioate	304	organophosphorus	insecticide	40	76-108	10
malathion	0,0-dimethyl phosphorodithioate of diethyl mercaptosuccinate	330	organophosphorus	insecticide	145	2800	35
parathion	0,0-diethyl 0-p-nitrophenyl phosphorothioate	291	organophosphorus	insecticide	20-25	6-15	15
methyl-parathion	0,0-dimethyl 0-p-nitrophenyl phosphorothioate	263	organophosphorus	insecticide	50	9.4	45
aldrin	1,2,3,4,10,10-hexachloro-1,4,4a, 5,8,8a-hexahydro-1,4-endo, exo-5,8-dimethanonaphthalene	365	halogeneous cyclodiene	insecticide	0.20	55	10
dieldrin	1,2,3,4,10,10-hexachloro-6,7- epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene	381	halogeneous cyclodiene	insecticide	0.25	60	<1
heptachlor	1,4,5,6,7,8,8a-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	373	halogeneous cyclodiene	insecticide	0.056	130-135	6
heptachlor-epoxide	1,4,5,6,7,8,8a-heptachloro-3a, 2,3-expoxy-3a,4,7,7a-tetraphyd -4,7-methanoindene	389	halogeneous cyclodiene	metabolite of heptachor	-	-	-
lindane	1,2,3,4,5,6-hexachloro-cyclohexane	291	halogeneous aliphatics	insecticide	7.3-10	90	<1

TABLE 16(continued)

Trade Name	Chemical Name	Molecular Weight	Chemical Classification	Type	Solubility (Atkins, 1972; Gunther, 1968) (ppm)	Oral Toxicity (Atkins, 1972; Melinikov, 1971) LD_{50}(mg/Kg)	Estimated Annual Sales in 1971 (Lawless, 1972) (million pounds)
DDE	1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene	318	halogeneous aromatics	metabolite of DDT	-		-
DDT	1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane	354.5	halogeneous aromatics	insecticide	0.0012-1	113	45
trifluralin	α,α,α-trifluro-2,6-dinitro-N,N-dipropyl-p-toluidine	335.3	salt of quantarnary ammonium bases	herbicide	24	>10,000	25
randox	diallylchloroacetamide	174	derivative of aliphatic carboxylic acids	herbicide	19,700	700	10
atrazine	2-chloro-4-ethylamino-6-isopropyl amino-s-triazine	216	s-triazines	herbicide	70	1750-3080	90
captan	N-trichloromethyl thiotetrahydrophthalimide	301	mercaptanes	fungicide	insoluble	9 000	18

The pesticides investigated in this study can be divided into three groups: (1) chlorinated hydrocarbons, including aldrin, lindane, dieldrin, heptachlor, heptachlor epoxide, DDT and DDE; (2) organophosphorus, including diazinon, parathion, methyl-parathion and malathion; (3) miscellaneous pesticides, including randox, trifluralin, atrazine and captan. Because of their low solubility in water, each group of the pesticides was first dissolved in acetone as stock solutions. Three different aqueous solutions, each containing a specific group of the pesticides, were prepared by dissolving in water a given amount of the acetone stock solution of pesticide mixtures. The final concentrations were adjusted to a level within the solubility limits for each of the pesticides in the groups given above.

The removal of each of the above pesticide solutions with CA and NS-100 membranes was tested using a stainless steel static test cell. Figure 25 depicts the static test cell manufactured by Abcor, Inc. (Cambridge, MA). Each of these tests was conducted at room temperature and at a pressure of 40.8 atmospheres (600 psig). The latter was controlled by the pressure regulator on the nitrogen tank. The membrane, with its active surface facing the solution, was supported on a sintered stainless steel plate. During the run, the pesticide solution was agitated by a magnetic stirring bar suspended close to the surface of the membrane. Such circulation is necessary to minimize the effect of concentration polarization on the membrane surface which in turn governs the performance of the membrane process. Due to the limitation of the test cell employed in this study, only a narrow range of agitation rate is allowed to be varied. This makes it difficult to evaluate the adequacy of agitation in avoiding concentration polarization. However, the normal agitation rate was maintained throughout the experiment so that results can be related meaningfully to the characteristics of the membranes which were tested under identical conditions with 5000 ppm of aqueous solution of sodium chloride.

A fresh membrane was used for each test. The test cell was filled with 150 milliliters (ml) of pesticide solution. After adjusting the nitrogen pressure and stirring speed, the permeate was collected from the low-pressure side of the cell. At the amount when 40 percent of the original solution was collected, the pressure of the cell was reduced to atmospheric. Both the retentate and the permeate were weighed. The test cell was then filled with 50 ml of extracting solvent. A 50:50 by volume of acetone and water was used for extracting the NS-100 membrane while ethanol was used for extracting the CA membrane. The extraction process was carried out under a pressure of 13.6 atmospheres. The pesticides extracted from the membrane were collected in the permeate. The test cell was cleaned and rinsed thoroughly with acetone and demineralized water between experiments.

Pesticides in feed, retentate, permeate and the membrane extract were quantitatively and qualitatively analyzed by a Tracor Gas Chromatograph Model 550 (Tracor Lane, Austin, TX). For all the pesticides studied here, a N_i^{63} high-temperature electron capture detector (ECD) using nitrogen as carrier gas was used. Two 4 mm ID Pyrex glass columns were used for the analysis. A 183 cm (6 ft) column packed with 100-120 mesh Supelcoport

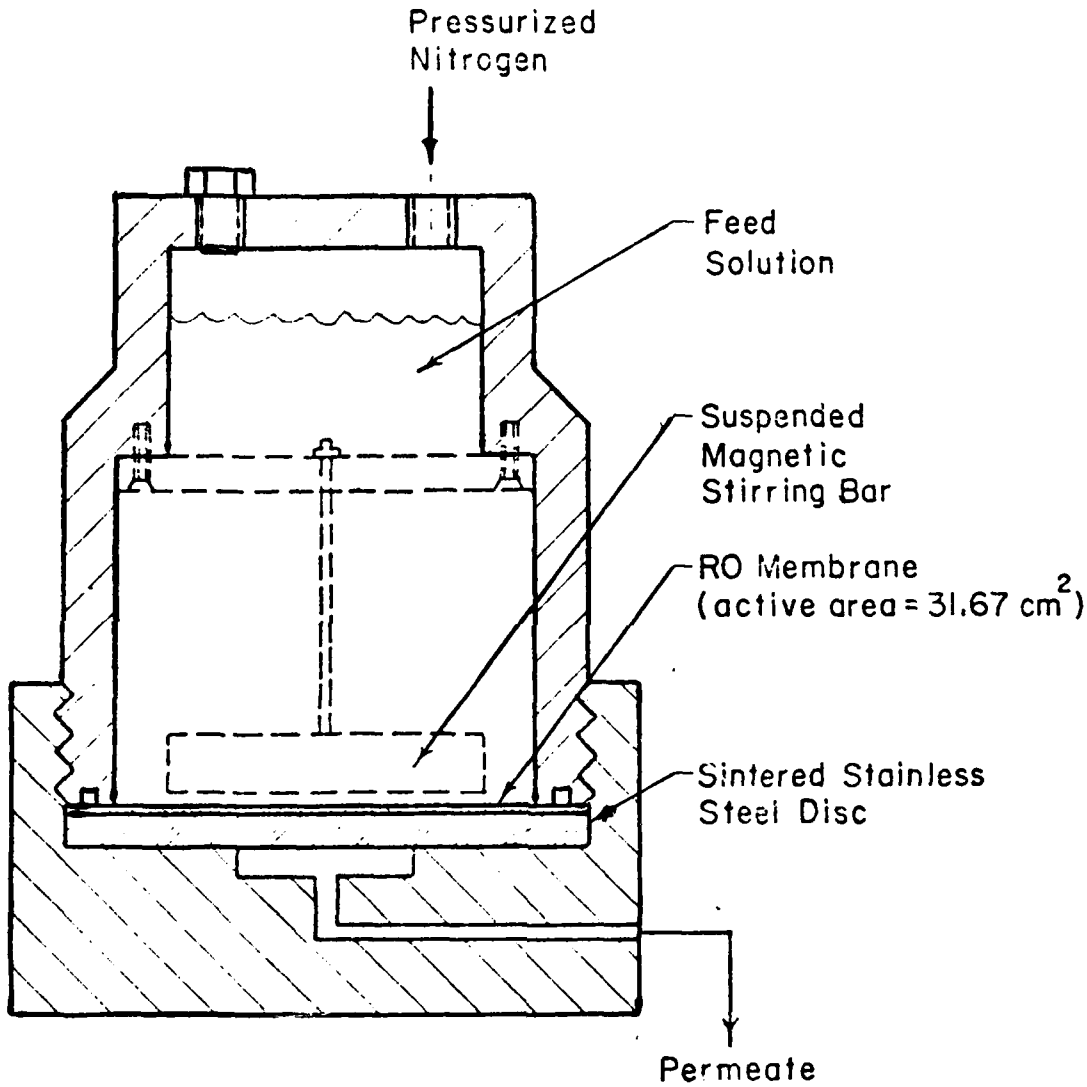


FIGURE 25 STATIC TEST CELL FOR REVERSE OSMOSIS MEMBRANE (Manufactured by Abcor, Inc.)

(Bellefonte, PA) containing 1 percent OV-17 and 3 percent QF-1 was employed for non-polar pesticides such as chlorinated hydrocarbons. For organophosphorus and other pesticides, a 61 cm (2 ft) column packed with 100-120 mesh Supelcoport containing 2 percent OV-17 and 4 percent QF-1 was used.

Chlorinated hydrocarbons in each sample were extracted with a mixture of ether and hexane in a proportion of 1 to 9. Other pesticides were extracted with dichloromethane. After two consecutive extractions for each sample, the extracted solution was transferred to a 250 ml Erlenmeyer flask equipped with a Snyder condenser; 25 ml of benzene was added to the extracted solution. The mixture was evaporated on a steam batch until 5 ml of benzene solution remained. The content of the flask was then transferred and made up to 10 ml, 100 ml or other volumes to a concentration suitable for injection into the GC column for analysis of pesticides.

6.2.1 Results and Discussion

The average permeate fluxes were found to be 32 and 49 ml/cm^2/day (8 and 12 gfd) for CA and NS-100 membranes, respectively. Because of the low concentration of the pesticides (ranging from 0.28 ppm of DDT to 10.53 ppm of trifluralin in the original feed solution), the flux of permeated water was found to be independent of the pesticides tested and remained constant throughout the run. In actual cases, membrane fluxes will depend more upon the concentration of the total dissolved solids (TDS) than on the amount of pesticides in water.

The efficiency of the membranes for removing certain pesticides was determined as follows:

$$R = [1 - \frac{C_p V_p}{C_f V_f}] \times 100\% \qquad (10)$$

where R represents the percentage of pesticide being removed; C and V represent the concentration of pesticide and volume of aqueous solution, respectively; subscripts p and f represent permeate and feed solution, respectively. Tables 17, 18 and 19 show the percentage removal of each group of pesticides with both CA and NS-100 membranes as determined by using Equation 10. Percentages of pesticide removal were calculated when 40 percent of the volume of the original feed solution was removed in the form of permeate.

From a simple material balance made among pesticides present in the original feed, with membrane retentate and permeate as shown in Tables 17, 18 and 19, it was found that an appreciable amount of pesticides was lost after the tests. The possibility of decomposition and hydrolysis of pesticides that might occur within a period of a few days between sample collection and analysis was not eliminated but seems unlikely in view of the relatively short time involved. This is especially true with the more

TABLE 17

Removal of Chlorinated Pesticides by Reverse Osmosis

	Membrane	amount of pesticides (μg) in solutions				%	% ***
		Original feed	Retentate	Permeate	adsorbed** (calc.)	removal	adsorption (calc.)
aldrin	NS-100	142.3	6.9	N.D.*	135.4	100	95.15
	CA		29.1	N.D.	113.2	100	79.55
lindane	NS-100	506.4	440.2	5.3	60.9	98.95	12.03
	CA		157.5	2.5	346.4	99.51	68.40
heptachlor	NS-100	145.1	5.4	N.D.	139.7	100	96.28
	CA		28.1	N.D.	117.0	100	80.63
heptachlor epoxide	NS-100	306.9	25.6	0.5	280.8	99.84	91.50
	CA		71.5	0.7	234.7	99.77	76.47
DDE	NS-100	69.0	4.2	N.D.	64.9	100	94.06
	CA		13.6	N.D.	55.4	100	80.29
DDT	NS-100	42.0	2.4	N.D.	39.6	100	94.29
	CA		N.D.	N.D.	42.0	100	100
dieldrin	NS-100	321.3	14.9	N.D.	306.4	100	95.36
	CA		75.7	0.4	245.2	99.88	76.31

* N.D.= non-detectable

** Adsorbed (Calc.) = pesticides present in the original feed less that determined in the retentate and permeate

*** $\frac{\text{Pesticides adsorbed (calc.)}}{\text{Pesticides in original feed}} \times 100\%$

TABLE 18

Removal of Organophosphorus Pesticides by Reverse Osmosis

pesticide	Membrane	amount of pesticides (μg) in solutions: Original feed	Retentate	Permeate	adsorbed (calc.)	% removal	% adsorption (calc.) **
diazinon	NS-100	473.7	273.5	56.6	143.6	98.05	30.31
	CA		334.7	8.3	130.7	98.25	27.59
methyl-parathion	NS-100	913.1	542.1	4.0	370.6	99.56	40.59
	CA		496.9	4.1	412.1	99.55	45.13
malathion	NS-100	1,057.8	647.0	3.7	407.1	99.65	38.49
	CA		739.9	8.9	309.1	99.16	29.22
parathion	NS-100	747.3	363.2	1.3	382.8	99.83	51.22
	CA		412.5	0.9	333.9	99.88	44.68

TABLE 19

Removal of Miscellaneous Pesticides by Reverse Osmosis

pesticide	Membrane	amount of pesticides (μg) in solutions: Original feed	Retentate	Permeate	adsorbed (calc.)	% removal	% adsorption (calc.) **
randox	NS-100	326.8	286.0	4.7	36.1	98.56	11.05
	CA		253.7	91.4	18.3	72.03	5.60
trifluralin	NS-100	1,578.9	530.0	0.1	1,048.8	99.99	66.43
	CA		560.1	4.1	1,014.7	99.74	64.27
atrazine	NS-100	1,101.7	956.5	24.0	121.2	97.82	11.00
	CA		851.4	176.0	74.3	84.02	6.74
captan	NS-100	688.9	437.0	N.D.*	252.4	100	36.64
	CA		314.7	8.4	440.1	97.78	63.88

* N.D. = non-detectable

** $\frac{\text{Pesticides adsorbed (calc.)}}{\text{Pesticides in original feed}} \times 100\%$

persistent chlorinated pesticides. The only other possibility which might account for the loss of pesticides would be adsorption of pesticides onto either the wall of the stainless steel (type 316) test cell or the polymeric membrane materials. While results of analysis of the acetone rinse from the compartment of the test cell wetted by the feed solution showed trace to nondetectable amounts of pesticides, an appreciable amount of pesticides was, however, detected in the membrane extract.

Quantitative recovery of pesticides was not attained from membrane extracts due to either lack of adequate solvent for extraction, i.e. solvent having a favorable distribution coefficient for extraction, or not enough time to reach equilibrium. Partial recovery of pesticides from the adsorbates, such as soils and clays, is frequently reported (Hamaker and Thompson, 1972). However, in some cases, recovery was larger than 100 percent apparently due to experimental error. In spite of this inability to determine quantitatively the amount of pesticides adsorbed by the membrane material, detection of pesticides in appreciable amounts from the membrane extract strongly supports the notion that the loss of pesticides is mainly due to adsorption onto the membrane material.

Attempt was made to calculate the percentage of pesticides adsorbed by the membrane materials in order to give an insight into the basic mechanisms involved in the adsorption and rejection of pesticides by the membranes. It was believed that understanding of these mechanisms would provide a basis for predicting the performance of the membranes tested toward the removal of pesticides other than those tested. In addition, knowledge of the relationship between the chemical nature of the membrane and the individual pesticide will lead to establishing useful criteria for the choice of membrane best suited for the removal of pesticides by reverse osmosis.

Tables 17, 18 and 19 show the percentage of each group of pesticides adsorbed by both CA and NS-100 membranes. The percentage of pesticide adsorbed was calculated based upon a material balance given below:

$$A = [1 - \frac{C_p V_p + C_r V_r}{C_f V_f}] \times 100\% \qquad (11)$$

where A represents the percentage of pesticide being adsorbed; C and V represent, respectively, the concentration of pesticides and the volume of the aqueous solution; and subscripts r, p and f represent the retentate, permeate and feed, respectively.

It is seen from these tables that, with the exception of lindane, the percentage adsorption is the highest for the chlorinated hydrocarbons (see Table 17). This is followed by trifluralin and captan in the miscellaneous group (see Table 18), and all of the organophosphorus pesticides tested (see Table 19). The poorest adsorption is observed with randox and atrazine as shown in Table 18. It should be noted that adsorption data reported here

are not indicative of the equilibrium data as would normally be required for establishing the empirical Freundlich isotherms. The average contact time of the pesticide solutions with NS-100 was only 40 minutes and with CA 55 minutes. In view of the relatively short equilibrium time involved, the adsorption process was by no means in true equilibrium. However, the relative degree of adsorption of various pesticides by the membranes does give an indication of the relative magnitudes of the distribution adsorption coefficient of pesticides between the two phases of membrane materials tested and aqueous solution. The distribution coefficient is defined by the expression of $(x/m)/C_{eq}$ obtained from the Freundlich isotherms in which x/m represents the weight of material being adsorbed per unit weight of adsorbent and C_{eq} represents the equilibrium concentration of adsorbate in the solution.

The distribution adsorption coefficient is naturally related to the intermolecular interactions of the adsorbate between the solid phase of adsorbent and the liquid phase of aqueous solution. In view of this, the chemical nature of pesticides and membrane materials should be discussed to further explain the degree of adsorption of pesticides by membranes. On the basis of the preferential sorption-capillary flow mechanism (Sourirajan, 1970), solute separation in reverse osmosis is thought to depend upon the chemical nature of solute and membrane. In order to obtain optimal performance of the membrane, proper balance between the hydrophobic and hydrophilic groups on the backbone of the membrane polymeric structure is essential. For example, the hydrophobic acetyl groups on the cellulose molecule are necessary for reverse osmosis separation of salts. On the other hand, however, the hydrophilic hydroxyl groups are needed for greater passage of solvent water. The widely used cellulose membrane, such as the one employed in this study, contains 2.5 acetyl groups on the average out of the maximum of 3.0 per repeating β-glucoside unit of the polymer. The polar hydroxyl group is responsible for the poor rejection of the highly polar organic compounds (Chian and Fang, 1974). In Figure 13 it is shown that the ethylene backbone and the cross-linked benzene groups are the nonpolar regions, and the urea peptide bond and amines are the polar region of the NS-100 membrane. Chian and Fang (1974) have concluded that NS-100 is more apolar than the CA membrane due to its better rejection of the highly polar organic solutes.

By the same token, pesticide molecules also comprise polar and nonpolar regions. With the exception of the highly substituted lindane, most of the chlorinated pesticides have nonpolar regions of significant size in proportion to polar regions. They are likely to adsorb onto the hydrophobic region of membrane materials (e.g. acetyl, ethylene and benzene groups) by means of the van der Waals-London forces. The interaction between the hydrocarbon (nonpolar) regions of pesticides and membranes is amplified further by the tendency of water to form a partial cage of ice-like hydrogen-bonded clusters of water molecules around nonpolar regions of both adsorbate and absorbent (Poland and Scheraga, 1967). This type of interaction derived from the structure changes of water molecules around nonpolar molecules is called hydrophobic bonding, and the interaction force involved is related

to entropy generation. In other words, hydrocarbon groups tend to associate with one another and with hydrophobic surfaces in order not to cause additional structuring in the water which involves a decrease in the entropy of the total system, and is thermodynamically rather unfavorable (Birshtein, 1969; Franks and Quickenden, 1970).

Table 17 also shows that the NS-100 membrane has a higher percentage adsorption of the nonpolar chlorinated pesticides than the CA membrane. This indicates that the former membrane is somewhat more nonpolar as compared with CA. It agrees with the conclusion drawn by Chian and Fang (1974) that better separation of the polar organic compounds with the NS-100 membrane is attributable to the apolarity of the membrane material relative to CA. Therefore, poor adsorption of lindane, along with somewhat poor separation of this highly chlorinated hydrocarbon with these membranes, suggests that the lindane molecule is relatively polar as compared with the rest of the chloropesticides tested. This is indeed the case. The lindane molecule has a polar region of larger size than the hydrocarbon nonpolar region as shown in Table 16. By the same token, poor adsorption of atrazine and randox, along with poor separation of these pesticides by membranes as shown in Table 19, also suggests the polar nature of these pesticides. Hydrogen bonding has actually been indicated for adsorption of s-triazine herbicides to clay surfaces from the study of infrared spectra of adsorbed material (Bellamy, 1968). The electron-rich π-cloud donor of s-triazine and alkenes, and the lone-pair electron donor of secondary amines (see Table 16) are responsible for the polar nature of atrazine and randox which in turn leads to formation of hydrogen bonding.

All of the organophosphorus pesticides tested (see Table 18), along with trifluralin and captan (see Table 19), show intermediate adsorption of pesticides as compared with the nonpolar chloropesticides and the relative polar atrazine, randox and lindane. It is interesting to note that the percentage adsorption of organophosphorous pesticides average around 40 percent. This corresponded to the amount of permeate removed from the test cell, i.e. 40 percent of the feed removed. Therefore, adsorption of organophosphorous appears to result from the direct flow of solution through the microporous structure of the membrane material rather than from adsorption onto the skin layer of the membranes. Strong adsorption of chloropesticides onto the skin layer of the membranes is evidenced by the greater percentage of adsorption, e.g. 75 to 100 percent, relative to the amount of solution passing through the membranes, i.e. 40 percent.

As postulated by Matsuura and Sourirajan (1973) one of the most important physicochemical criteria governing reverse osmosis separation of organic solute in aqueous solution is the "Polar Effect" of the solute molecule. A measure of the hydrogen bonding ability and the dissociation constants gives relevant expression of polarity of the organic solutes. In general, poor removal of solutes by the CA membrane corresponded to solutes having greater tendency to form hydrogen bonding. Results of this study on solute separation by membranes agree well with the separation

mechanism proposed by Matsuura and Sourirajan (1973), i.e., poor removal of pesticides was observed with the relatively polar ones, e.g. atrazine, randox and lindane, which are also adsorbed poorly by the membranes tested. Within this group of somewhat more polar pesticides, the differences in rejection by membranes may be attributable to the size of the molecules which in turn governs the rate of diffusion of solutes across the membranes. This explains high rejection of lindane over atrazine and randox (see Table 16, 17 and 19).

From these findings, it provides a general criterion in selecting membrane material for efficient separation of pesticides. That is, the more the apolarity of the membrane material is, the better the pesticides removal will be, mainly through the mechanisms of adsorption according to this study. Therefore, the relatively nonpolar aromatic polyamide (e.g. duPont's B-9 permeator, Wilmington, DE), PBI (polybenzimidiazole, Celanese, Summit, NJ) and furfural alcohol (NS-200, North Star R&D Inst.) membranes should all be comparable in performance, as compared with the NS-100, according to results of their removal of the model compounds reported by Chian and Fang (1974). This, however, would be at the expense of decreasing water flux, an important engineering parameter of the reverse osmosis process, according to Sourirajan's model of preferential sorption of water. Remedies for overcoming the low water flux due to the use of more nonpolar membrane material would be either employing reverse osmosis module configuration that will provide a large specific surface area to compensate for the low flux, such as the use of hollow-fiber module; or controlling the thickness of the effective skin layer to enhance water flux according to Darcy's Law, such as the use of ultra-thin membranes.

The effect of pressure, temperature and concentration of solutes on the performance of the reverse osmosis process has been discussed in great detail by numerous authors (Sourirajan, 1970; Ballou *et al.*, 1971; Merten and Bray, 1966; Michelsen and Harriot, 1970; Michaels, 1968), and will not be the subject of this study. However, attempts have been made to discuss the effect of the above operating variables on membrane performance toward aqueous solutions of pesticides.

In general, solute separation has usually been observed to increase with feed pressure to either an asymptotic maximum (Shor *et al.*, 1968) or to approach 100 percent rejection as in the case of cellulose acetate (Merten and Bray, 1966), although observation of an inverse relationship between separation and pressure with porous glass membranes (Ballou *et al.*, 1971) and polyvinyl alcohol films (Michelsen and Harriott, 1970) are not unknown.

The membranes employed in the present study have been tested regarding solute separation versus applied pressure with a 0.5% sodium chloride aqueous solution. It was found that increase in solute separation with pressure was more pronounced with the partial salt rejection membrane, such as CA. With the high salt rejection membrane, such as NS-100 having a rejection of 99.5 percent sodium chloride, the effect of pressure on solute separation becomes negligible probably due to approaching the asymtotic maximum of 100

percent rejection. In view of the excellent removal of the chloropesticides, organophosphorous pesticides and triafuralin and captan with both CA and NS-100 membranes, increase in pressure within a practical range would have little or no effect on improving removal of these pesticides. However, it is anticipated that rejection of the more polar atrazine and randox would increase somewhat with increasing pressure. This will be especially true with the CA membrane due to poorer rejection toward these pesticides. Removal of 72 percent and 84 percent of randox and atrazine, respectively, was obtained with the CA membrane as compared with 98.6 percent and 97.8 percent removal of these pesticides with NS-100 membrane.

Increase in temperature within an allowable range for the reverse osmosis process normally would result in flux increases in direct proportion to the decrease in solution viscosity according to Darcey's Law for viscous flow in pores. Again, with membranes having poor rejection of solutes, the increase in permeate flux with increasing temperature tends to improve membrane rejection of solutes. Solute transport through the membrane will increase with temperature to a lesser extent when compared to increase in permeate flow. On this basis, rejection of the more polar pesticides, such as atrazine and randox, will increase with temperature especially with the CA membrane due to its poorer rejection of these pesticides. However, no apparent increase in rejection of the nonpolar and lesser polar pesticides, such as chlorinated hydrocarbons and organophosphorus,would be expected because of their efficient removal of these pesticides in the first place, e.g. an average of better than 99.5 percent removal. With the strongly adsorbed pesticides, such as most of the chlorinated hydrocarbons, some increase in rejection may be anticipated since the hydrophobic interactions partially responsible for the adsorption of nonpolar pesticides become stronger with increasing temperature (Birshtein, 1969).

Higher feed concentrations generally result in lower flux, since the solvent flow follows the relationship:

$$J_1 = K\ (\Delta P - \Delta\pi) \tag{12}$$

where J_1 is the flux of solvent; ΔP is the applied driving force; K is the membrane permeability; and $\Delta\pi$ is the osmotic pressure of solutions across the membrane. Since the solubility of pesticides is so low and the molecular weight is so high, the effect of increase in concentration of pesticides on solvent flux is almost negligible because of extremely small changes of osmotic pressure, $\Delta\pi$, involved. However, high feed concentration results in high flux for solute transport across the membrane due to the increased concentration driving force for solute diffusion as given by the following equation

$$J_2 = \frac{K_2}{D_2 M\delta}\ \Delta C \tag{13}$$

where J_2 is the diffusional flux of solute across the membrane; K_2 is the distribution coefficient of solutes between the membrane and the solution; D_2M is the diffusivity of solute in membrane; δ is the thickness of the active skin layer; and ΔC is the concentration driving force.

Therefore, high solute flux, associated with the increase in pesticide concentration, would result in poorer rejection.

In natural water, persistent pesticides, such as chlorinated hydrocarbons, are normally complexed with humic and fulvic acids (Khan, 1973; McNamara, 1968). These humic substances have been found to be effectively rejected with the reverse osmosis membrane mainly because of their high molecular weight (DeWalle and Chian, 1974), on the order of a few thousands to tens of thousands; the removal of pesticides from natural water is thus expected to be even higher than those data shown in Tables 17, 18 and 19. This is especially important with the poorly rejected polar pesticides, such as atrazine and randox, which tend to form hydrogen bonding and complex with the humic substances.

In view of the strong sorptive characteristics onto the membrane materials with most of the pesticides tested, one would expect a leakage of pesticides when the adsorption capacity of membranes is exhausted. Although there is no experimental result to show actual exhaustion of the adsorption capacity of membranes, this is, however, a matter of real concern when long term tests are conducted. Tardiff and Deinzer (1973) have employed reverse osmosis to concentrate river water for organic analysis. With the evidence found in this study regarding strong sorptive characteristics of the persistent chloropesticides onto reverse osmosis membrane materials, effort should be directed toward development of procedures for extracting either pesticides or other trace organics that might adsorb onto the membranes without deleterious effect on the membrane.

Excellent performance of CA and NS-100 membranes in removing a wide variety of pesticides, including chlorinated hydrocarbons, organophosphorus and miscellaneous pesticides, was observed. A considerable amount of pesticides was, however, found to be adsorbed onto the membrane materials. The extent of adsorption was shown to be governed by the van der Waals-London forces and hydrophobic bonding between pesticide molecules and the polymeric membrane materials.

Several conclusions can be drawn concerning mechanisms of pesticide removal by the reverse osmosis membranes. Whereas better than 99.5 percent removal of the nonpolar pesticides, such as chlorinated hydrocarbons and organophosphorus, was observed with both membranes tested, the removal of the more polar pesticides, such as randox and atrazine was, however, less satisfactory. This is especially true with the more polar CA membrane. The mechanisms of pesticide removal from aqueous solution can be explained partially by the polar effect of the solute molecule and partially by the extent of adsorption of the pesticide onto the membrane materials. The former mechanism of pesticide rejection is in accord with the theory advanced by Sourirajan.

The effect of pressure, temperature, concentration of solutes and organic matter commonly found in water, e.g., humic substances, on the performance of the reverse osmosis process has been discussed. It is concluded that the above operating variables have little or no effect on membrane performance with pesticides that are rejected efficiently by the membrane. However, with the membrane rejecting pesticides partially, high pressure, temperature and organic content are expected to improve the performance of the membrane on pesticides removal, whereas higher concentrations of pesticides in the feed is expected to have adverse effects.

6.3 Removal of Alcohols, Aliphatic Acids and Amines by NS-100 Membranes

Removal of alcohols, amines and aliphatic acids in single-solute aqueous solution in the concentration range from 0.001 to 0.1 M have been studied using the NS-100 membrane. All the tests were conducted at 600 psig, 25°C and a flow rate of 0.30 gpm. The mechanism of solute separation by the NS-100 membrane differs from that of the cellulose acetate membrane. There was no significant correlation between the removal and the hydrogen bonding ability of the organic solute. Instead, for a given organic solute, its removal increases with the increase in the degree of crosslinkage of the skin layer of NS-100 membrane, and is proportional to its degree of ionization (or degree of dissociation). For organic compounds having the same functional group, the removal of a compound increases with the increase in molecular weight and/or molecular branching. All of these are attributable to the relative non-polarity and the anion exchanger characteristics of the membrane as well as to the steric resistance of the solute to permeate through the membrane.

Three stainless steel 316 test cells based upon Manjikian's design (1967) were used for the reverse osmosis experiments. The effective diameter of each circular membrane was 2 in. All tests were conducted at 600 psig, 25°C and a flow rate of 0.30 gallons per minute (gpm). Prior to testing the organic solutes, each membrane was subjected to a test of 5000 ppm of sodium chloride solution for 2 hours. The performance of each membrane used in this study is shown in Table 20. The percent solute removal is defined as follows:

$$\text{Solute removal} = \frac{\text{solute in feed (ppm)} - \text{solute in permeate (ppm)}}{\text{solute in feed (ppm)}} \times 100\%$$

All membranes were tested with single-solute solutions. The concentration of each organic solute in test solution ranged from 0.01 to 0.001 M. Each test solution was circulated on the membrane surface under testing conditions for 1 hour prior to collecting the permeate samples.

Table 20

Performance of NS-100 Membranes When Tested With 5000 ppm Sodium Chloride Solution at 600 psig and 25°C

Membrane	Permeate Flux (gfd)	Solute Removal (%)
0316A	7.15	98.20
0316B	16.00	97.62
0906A	11.00	98.98
0906B	8.11	99.08
0710A	13.50	98.40
0710B	22.68	97.80
0514C	12.19	99.17
0514D	24.89	97.73
0425A	9.85	98.39
0425B	9.57	96.27
0517A	10.13	98.41
0517B	21.17	97.56
0517C	11.52	98.32
1008A	30.22	96.28
1008B	33.42	97.36
1008C	27.85	98.12
0508A	26.78	98.46
0508B	9.45	99.29

A Yellow Springs Conductivity Bridge, Model 1485 was used to measure the concentration of sodium chloride. With dilute concentration (<100 ppm), the conductivity is proportional to the concentration of the salt solution. Therefore, by comparing the relative conductivity of the permeate and the diluted feed solutions, the salt removal of each membrane could be determined.

A Beckman Total Carbon Analyzer, Model 915, was used to measure the concentration of organic solute in both permeate and feed solutions. In this apparatus, the solution sample was injected and swept by an air stream into a high-temperature (950°C) catalytic combustion tube where the total carbon in the sample was oxidized to carbon dioxide which was then analyzed by a Beckman nondispersive infrared analyzer, Model IR-215B. A sample size of 20 microliters and an air flow rate of 150 cc/min were used for the analysis. The carbon content of a dilute solution (total carbon < 100 ppm) was proportional to the peak height shown on the recorder. Three to five injections were made for each sample in order to confirm the reproducibility of the analysis. The accuracy of the analysis was ± 1 ppm in terms of carbon content.

6.3.1 Results and Discussion

Two NS-100 membranes, 0316A and 0316B, were used to test the aqueous solutions containing single alcohol in a concentration of 100 ppm. Normal alkyl alcohols (from C_1 to C_6) and their isomers were tested. The dissociation constants of alcohols are extremely small; consequently, the alcohols exist as molecules in test solution. Figure 26 illustrates the correlations between the removal and the number of carbon atoms of n-alkyl alcohols. It clearly indicates that the removal of n-alkyl alcohols increases with the number of carbon atoms, or in other words, with the molecular weight of the alcohol.

Chian and Fang (1974) and Matsuura and Sourirajan (1972a), however, found that there was no necessary correlation between the molecular weight and the removal of n-alkyl alcohols by cellulose acetate membrane. Chian and Fang found that the removal of n-hexane by cellulose acetate membrane was -8.2 percent as compared to 9.2 percent for n-pentanol, 19.8 percent for n-butanol and 30.5 percent for n-propanol. According to their study on the removal of numerous organic compounds, Matsuura and Sourirajan (1972a, 1972b, 1972c, 1973) have concluded that cellulose acetate has the characteristics of a proton acceptor. As a consequence, the removal of an organic solute is strongly dependent on its hydrogen bonding ability. For an alcohol, the hydrogen bonding ability can be expressed as the $\Delta\nu_s$ (acidity), which represents the shift in the OH band maximum in the infrared spectra. An alcohol with a higher $\Delta\nu_s$ (acidity) forms a stronger hydrogen bond with the membrane; thus, as a result it is poorly removed by the cellulose acetate membrane.

The data of NS-100 membranes indicate no such correlation between the removal of the $\Delta\nu_s$ (acidity) of alcohols. This is partially attributed to the apolar characteristics of the NS-100 membranes. These characteristics

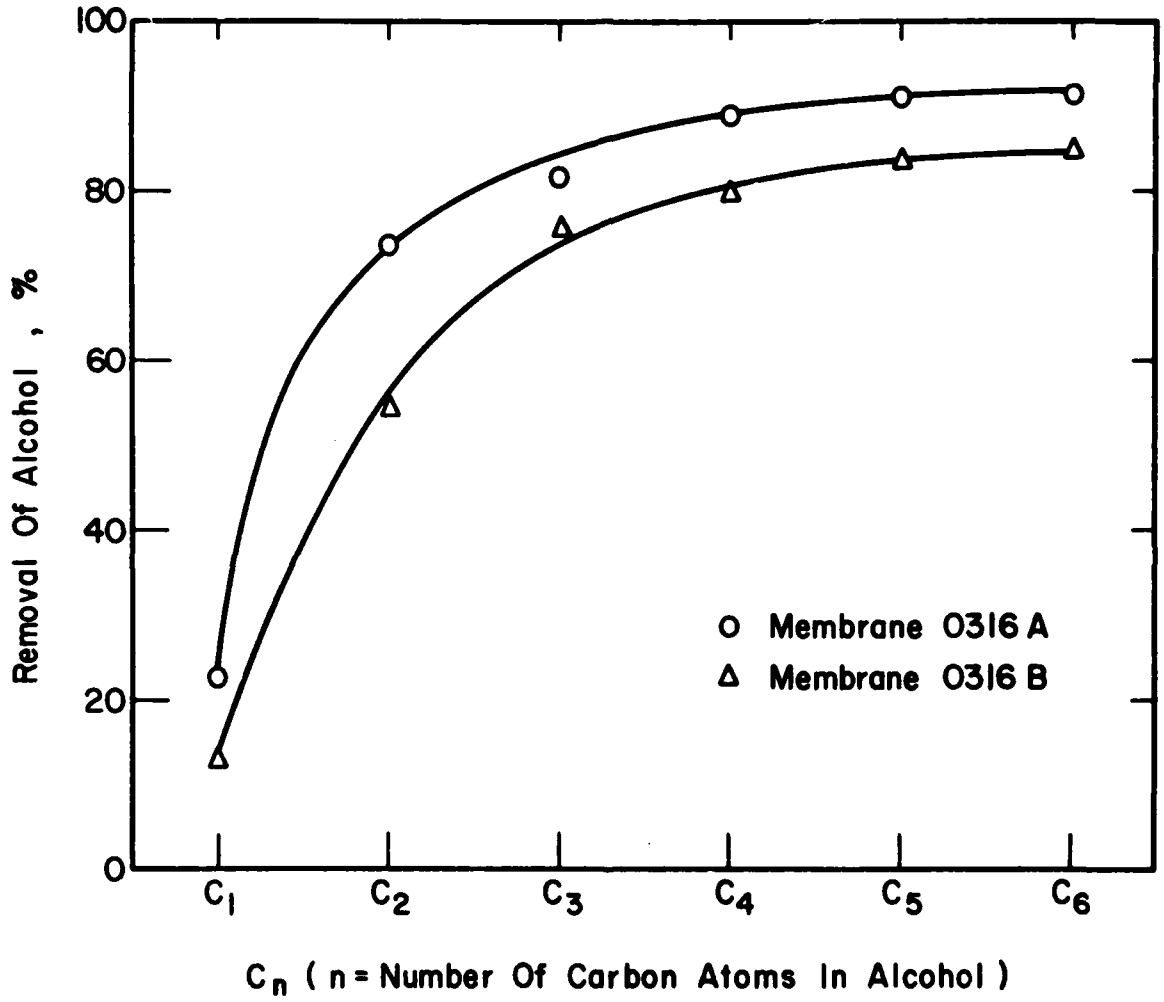


Figure 26 Removal of n-Alkyl Alcohols

have also been observed in the study of pesticide removal. Chian, Bruce and Fang (1975c) have reported that nonpolar pesticides, such as most chlorinated pesticides, were strongly adsorbed on the skin layer of NS-100 membranes. The adsorption resulted from the London- van der Waals interaction between the membrane and the solute molecule.

Figure 27 illustrates the removal of isomeric alcohols by membranes 0316A and 0316B. With no exception, a tert-alcohol was removed better than its iso-isomer, which was removed better than its normal isomer. In other words, the removal increases with increased isomer branching. This agrees with the results observed in the alcohol removal by cellulose acetate membranes (Duval, 1972).

An alcohol molecule enters the NS-100 membrane by passing into a gap between polymer segments which is large enough to accommodate the molecule. Once in the membrane, the molecule then diffuses through the membrane under the influence of concentration gradient. The diffusivity of the molecule in the membrane decreases with the increase in molecular size (molecular weight) and cross-sectional area (molecular branching). Consequently, alcohols with high molecular weight and/or large branching are removed effectively by NS-100 membranes.

Amines are weak bases; their basicity can be expressed by the pK_a values, which are defined as follows:

$$K_a = \frac{[NR_3][H^+]}{[R_3NH^+]} \tag{14}$$

$$pK_a = -\log K_a \tag{15}$$

where R can be a hydrogen atom, alkyl or aryl group attached to the N atom. According to Weast and Selby (1974) the pK_a of aliphatic amines ranges from 10 to 11. As a result, aliphatic amines exist as ions in ordinary solutions (pH 10). On the other hand, the skin layer of NS-100 membranes consists of primary, secondary and tertiary amines as shown in Figure 13. Therefore, it also possesses the characteristics of a weak anion exchanger. An anion exchanger with amines and imines as ionogenic groups has an apparent pK_a value of 7-9 (Helfferich, 1962). In other words, the skin layer of NS-100 membranes carries positive charges in solutions at pH < 7. Since both the skin layer and the solute amines carry positive charges at pH < 7, the electrostatic repulsion force acts between them and becomes a predominant factor in solute removal.

A series of experiments were conducted to study the removal of methylamine at various degrees of ionization with membranes 0906A and 0906B. The concentration of methylamine was 0.01 M for each test. The pH value of the test

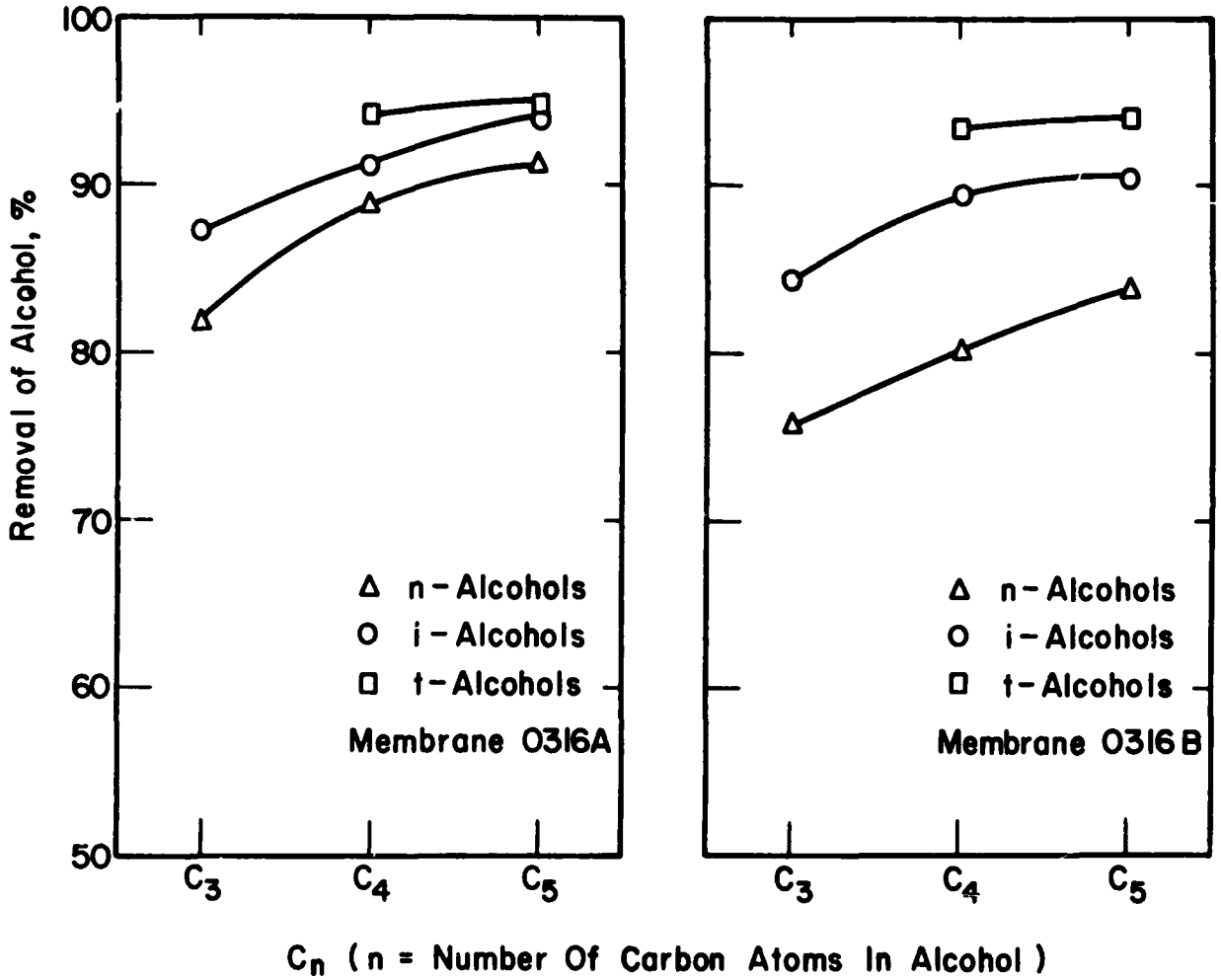


Figure 27 Steric Effect on the Removal of Isomers of Propanol, Butanol and Pentanol

solutions was adjusted from 2.5 to 12.0 by adding hydrochloric acid. The degree of ionization of methylamine was calculated from the pK_a (10.66) and pH of the solution.

$$\alpha\% = \frac{[CH_3NH_3^+]}{[CH_3NH_2] + [CH_3NH_3^+]} \times 100\% \qquad (16)$$

From the definition of K_a as shown in Equation 14

$$\alpha\% = \frac{[H^+]}{K_a + [H^+]} \times 100\% \qquad (17)$$

$$= \frac{10^{-pH}}{10^{-pK_a} + 10^{-pH}} \times 100\% \qquad (18)$$

Figure 28 illustrates the correlation between the removal of methylamine and its degree of ionization. In acidic solution, methylamine existed as an ion and hence was removed effectively, i.e. 98 percent by both membranes. On the other hand, in basic solution at pH 12, 96 percent of methylamine existed as molecules; hence it was removed less effectively, i.e. 50 percent, because of the drastic decrease in electrostatic repulsion between the solute and the skin layer of the membrane. When the solute was partially ionized, the removal of the solute was proportional to its degree of ionization as shown in Figure 28.

Figure 29 illustrates the removal of primary and secondary amines by membranes 0710A and 0710B. Since the pK_a values of the test amines were within a narrow range, i.e. 10.50-11.00, there was no significant difference in the degree of ionization among the test amines. Figure 29 illustrates that the removal of an amine depends upon its molecular weight and classification. Similar to the alcohols, the removal increases with increase in molecular size (molecular weight). On the other hand, secondary amines were removed better than the primary amines. This is attributed to the spatial configuration of the amines; primary amines consist of a straight-chain while secondary amines have a branch on the chain. A test of a tertiary amine, such as tripropylamine, indicated 98.3 percent and 99.2 percent removal by membranes 0710A and 0710B, respectively. Such a high degree of removal is obviously due to its high molecular weight and its degree of branching.

Table 21 shows the removal of four isomers of primary butylamine. The spatial configuration was the sole factor for the differences among the removal of these amines. Table 21 indicates that the removal of butylamine follows the order: tert- > iso- > sec- > normal. Again, it shows that the amine with more branching was better removed. This agrees with the conclusions drawn from the study of alcohol removal.

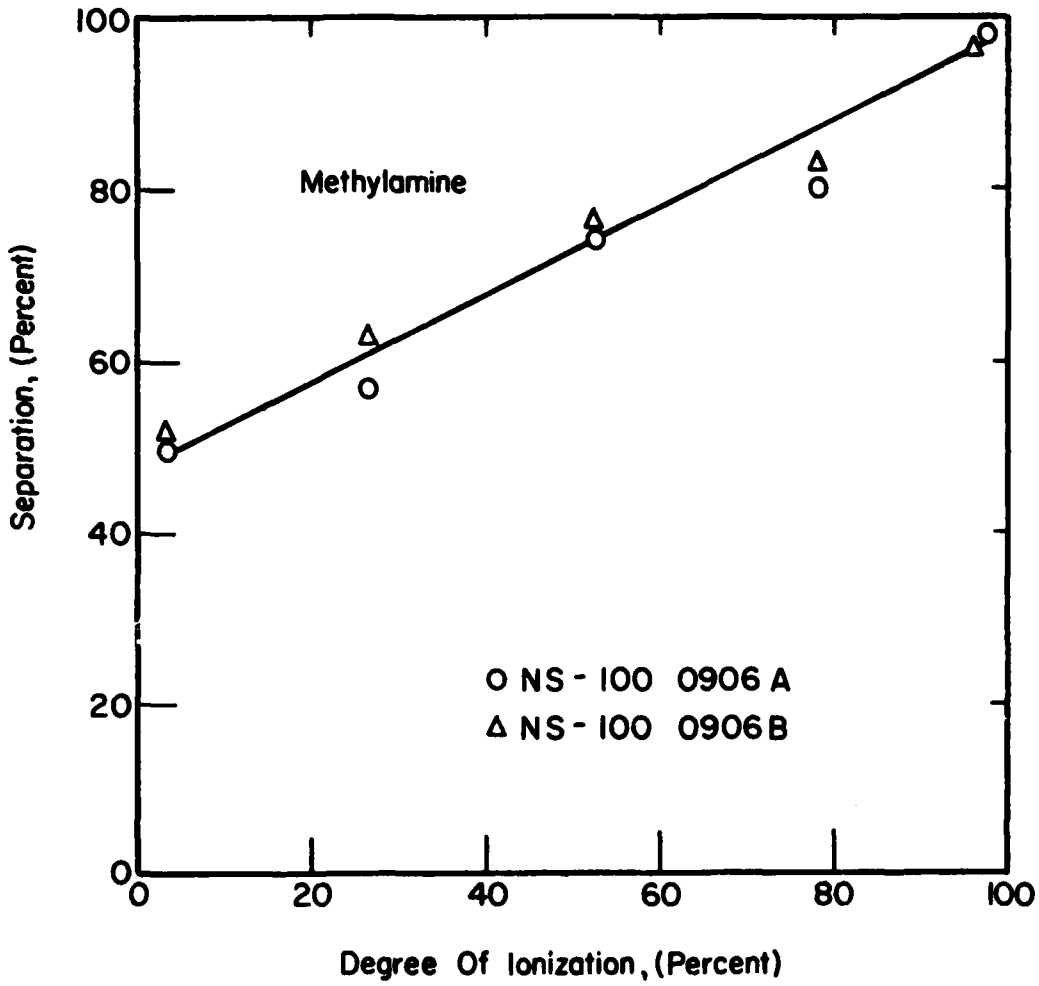


Figure 28. Removal of Methylamine at Various Degrees of Ionization

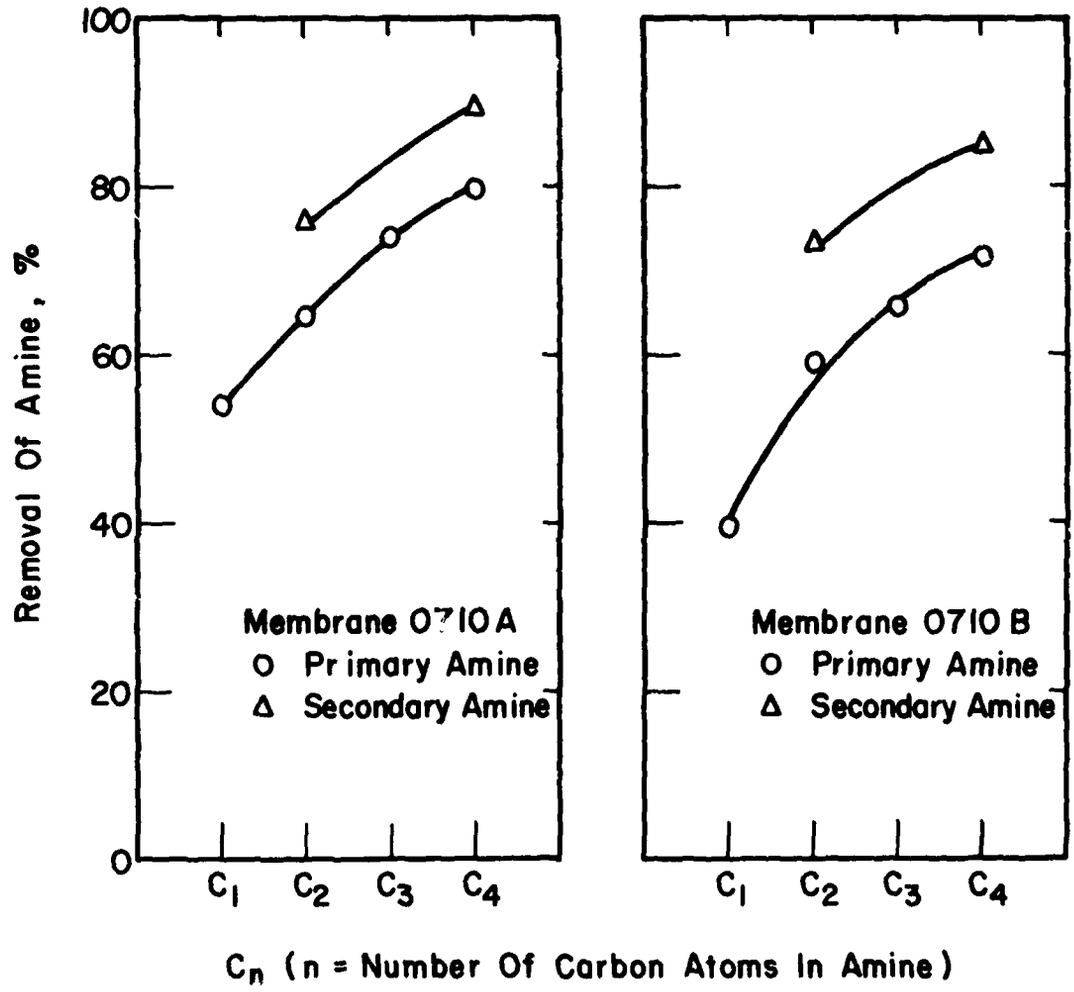


Figure 29 Comparison of the Removal of Primary and Secondary Amines

TABLE 21

Removal of Isomers of Butylamine
by NS-100 Membranes

Butylamine	0710A Removal (%)	0710B Removal (%)
normal	80.1	71.8
sec-	85.3	78.8
iso-	91.6	87.0
tert-	93.9	88.3

Aliphatic acids are weak acids with pK_a ranging from 3.75 to 4.90. They carry negative charges in aqueous solution at pH > 5. Hence the electrostatic interaction between the anion and the skin layer of the NS-100 membrane is the predominant factor in the removal of aliphatic acids. Aqueous solutions containing 0.01 M of acetic and formic acids, respectively, were tested at various degrees of dissociation by NS-100 membranes. The degree of dissociation of an acid was determined by its pKa and the pH of the test solution. The pK_a is defined in Equation 15 where the dissociation constant, K_a, of an acid, say acetic acid, is defined as

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \tag{19}$$

The degree of dissociation, α', is defined as

$$\alpha'\% = \frac{[CH_3COO^-]}{[CH_3COOH] + [CH_3COO^-]} \times 100\% \tag{20}$$

Hence, by combining Equations 19 and 20

$$\alpha'(\%) = \frac{K_a}{K_a + [H^+]} \times 100\% \tag{21}$$

$$= \frac{10^{-pK_a}}{10^{-pK_a} + 10^{-pH}} \times 100\% \tag{22}$$

Figures 30 and 31 illustrate that the removal of both acetic and formic acids is proportional to their degree of dissociation. This is consistent with the observation of methylamine as shown in Figure 28, although the acids and methylamine carry opposite charges.

Single-solute aqueous solutions containing alkyl acids at a concentration of 200 ppm were tested by membranes 0517A, 0517B and 0517C. In order to ensure that the acids existed as molecules, the pH of each test solution was adjusted to pH 2 by adding hydrochloric acid. Figure 32 illustrates that the removal of undissociated n-alkyl acids increases with an increase in molecular weight. On the other hand, Figure 33 illustrates the comparison between the removal of isomers of butyric and valeric acids. The iso-isomers were removed consistently better than normal-isomers. Both of these observations are congruent with those observations from the study of alcohol and amine removal.

Figures 26, 29 and 32 show a general trend, i.e. the membrane exhibiting better salt removal also removed a higher percentage of organic solute. For instance, membrane 0316A removed n-alkyl alcohols 10 percent better than membrane 0316B as shown in Figure 26; the former exhibited 98.20 percent salt removal as compared to 97.62 percent by the latter. The existence of this trend is further illustrated in the following series of experiments.

By adjusting the polyethylenimine concentration in aqueous solution, five membranes, 1008A, 1008B, 1008C, 0508A, and 0508B, were fabricated at various degrees of crosslinkage. Their removal of salt varied from 96.28 percent with 1008A to 99.29 percent with 0508B. Thirteen model organic compounds were tested individually by these membranes. They were methanol, ethanol, i-propanol, acetic acid, formaldehyde, acetone, ethyl ether, glycerol, hydroquinone, phenol, urea, aniline and methyl acetate. The removal of each model compound is illustrated in Figure 34.

With few exceptions, a general trend also suggests that for a given membrane material a membrane with a higher salt removal also removes a greater percentage of organic compounds. This trend is independent of the characteristics of solutes, e.g. salt or molecule, organic or inorganic, basic or acidic, and polar or nonpolar solute. For NS-100 membranes, the salt removal is a measure of the degree of crosslinkage of the skin layer. As a consequence, it is reasonable to characterize the membrane performance for a given membrane material with a simple test using sodium chloride solution. This has indeed been conducted in the following study on the optimization of membrane performance.

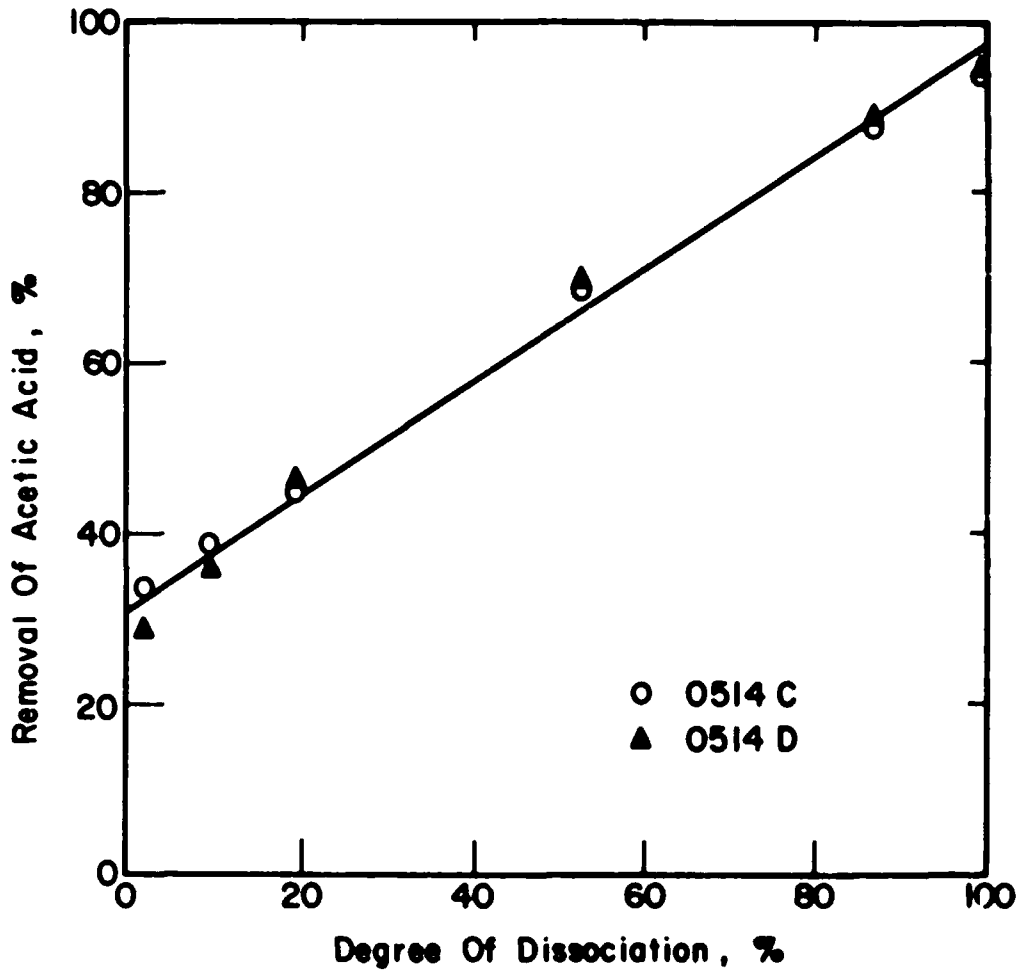


Figure 30 Removal of Acetic Acid at Various Degrees of Dissociation

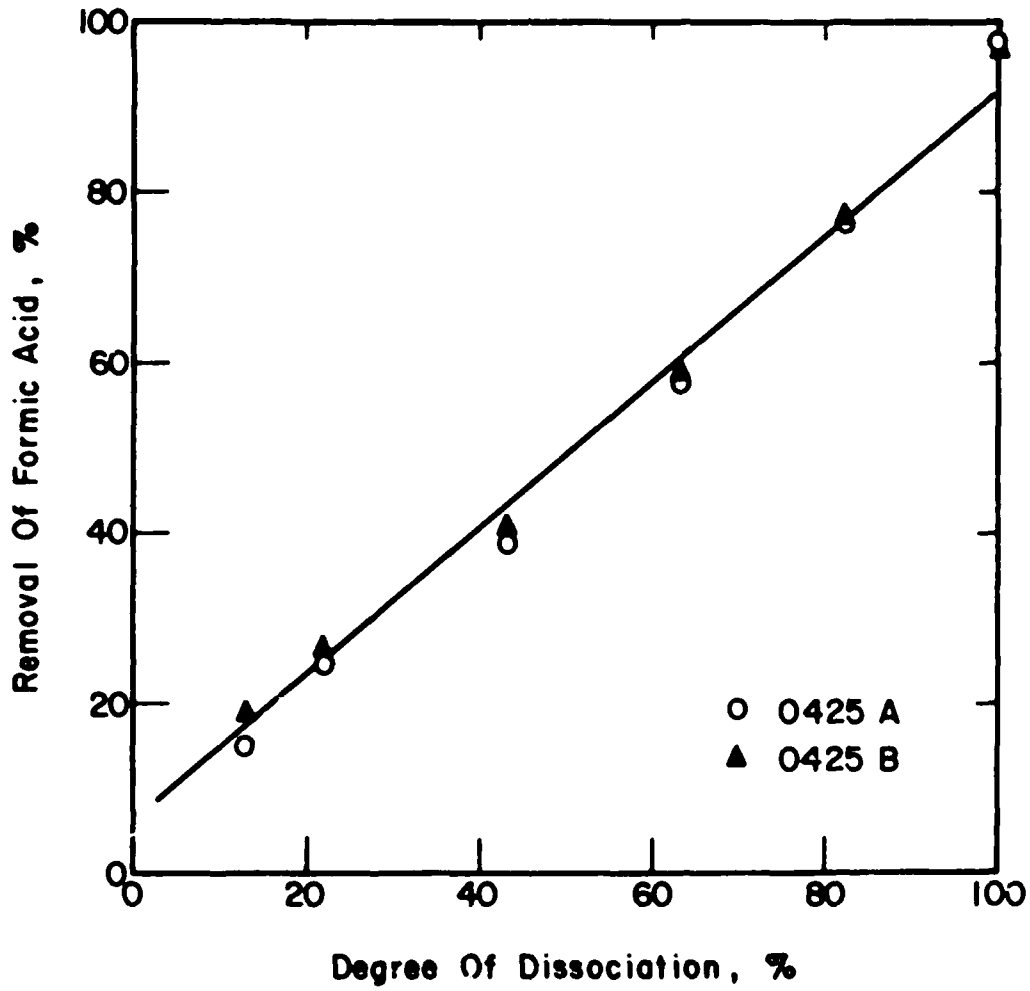


Figure 31 Removal of Formic Acid at Various Degrees of Dissociation

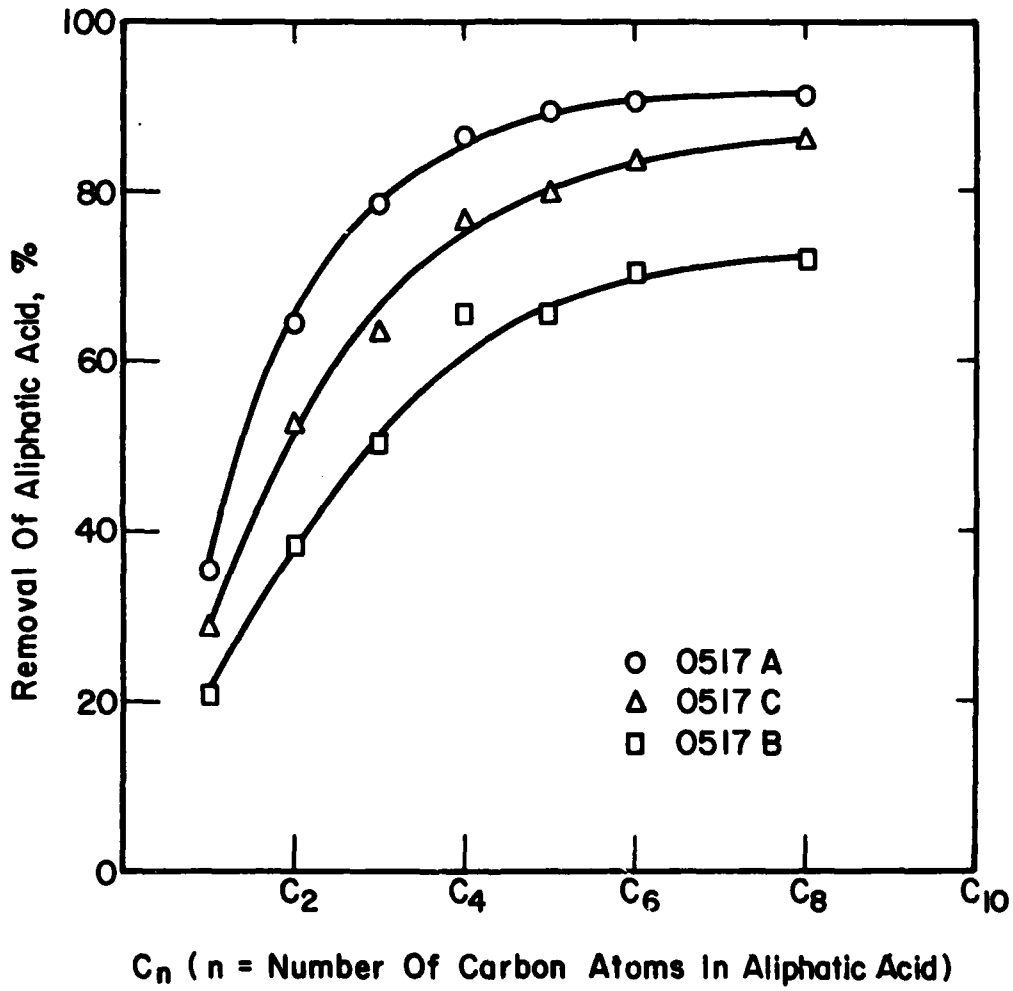


Figure 32 Removal of n-Alkyl Acids

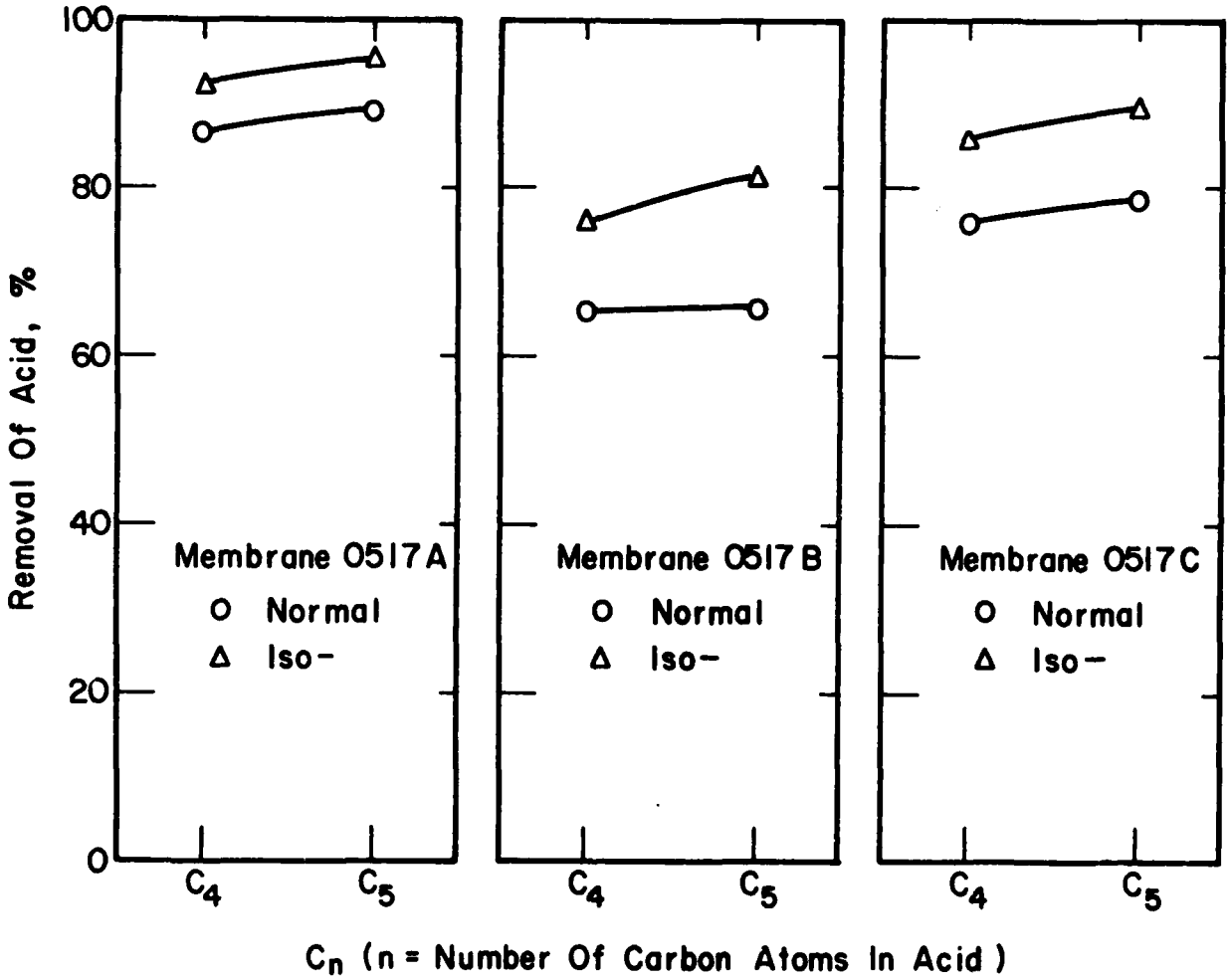


Figure 33 Steric Effect on the Removal of Isomers of Butyric and Valeric Acids

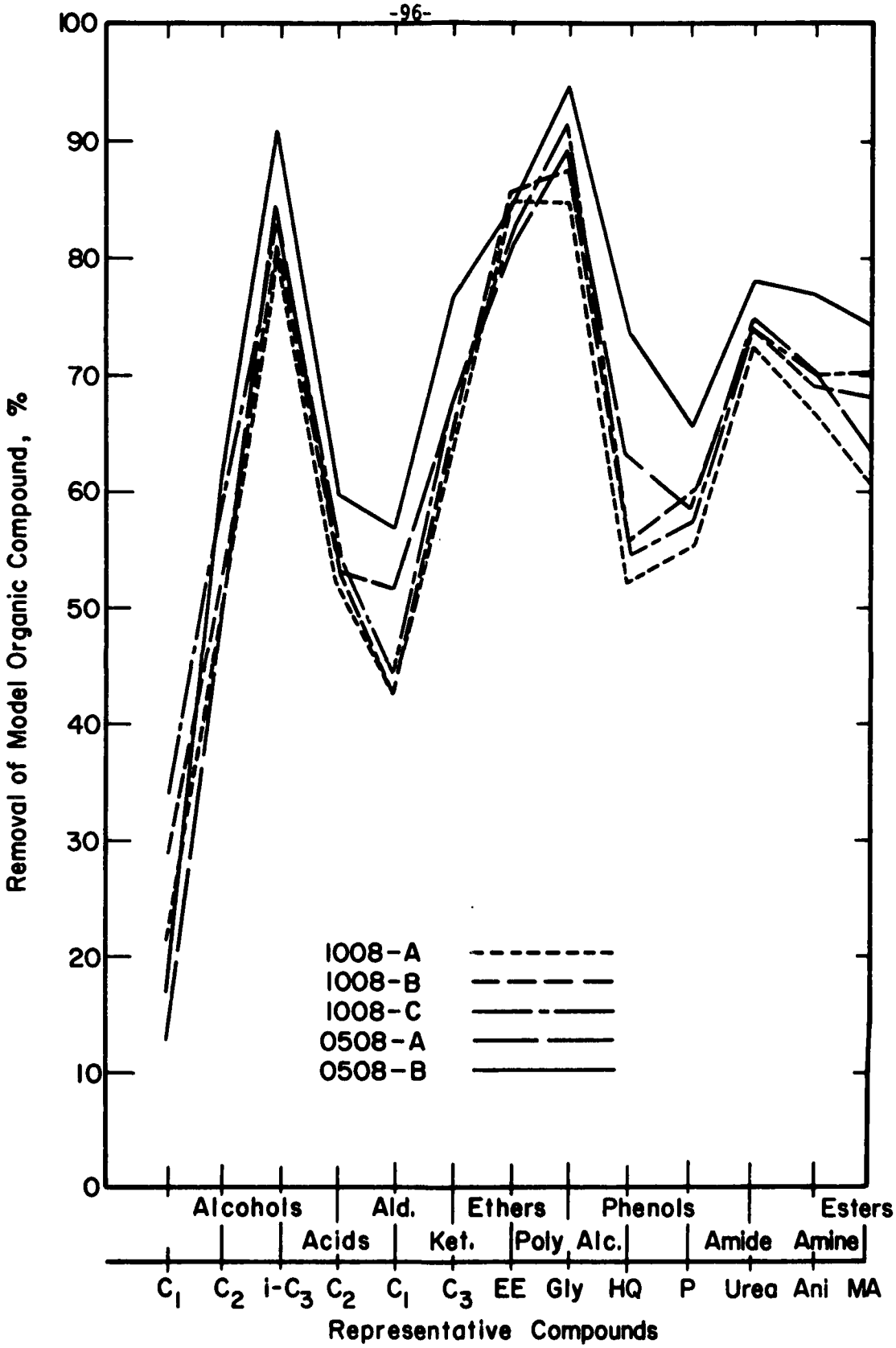


Figure 34 Removal of Model Compounds by NS-100 Membranes at 600 psi and 24° C

7. OPTIMIZATION OF MEMBRANE PERFORMANCE

During the process of fabricating the NS-100 membrane, numerous variables are involved as described in the previous sections. For example, the concentration of PS-DMF solution may affect the pore size of the PS support which in turn may affect the formation of PEI coating. The concentrations of PEI in aqueous solution and TDI in hexane solution also determine the extent of crosslinking PEI and the thickness of the active layer, etc. In the optimization study conducted by North Star, statistically designed experiments were not employed. Their study was conducted by first selecting one variable, say, the concentration of TDI-hexane solution, then performing a series of experiments varying the value of this variable over a suitable range while maintaining other variables constant. Having found the optimum value of the first variable, a second variable, say, PEI concentration in aqueous solution, was selected. A second series of experiments were conducted again while maintaining the first variable at its optimum value and keeping the other constant. Upon repeated experimentation using this procedure the optimum values of all of the variables were found.

Not only is this so called one-variable-at-a-time method time consuming, but also it often misses the overall optimum. Because of the simultaneous interactions of two or more variables, the optimum value for one variable commonly depends upon the values of others. In order to consider the potential interactions among these variables, the use of experimental protocols based upon statistical design is essential. Recently, Grethlein (1973) and Fahey and Grethlein have reported a statistically designed method for the optimization of casting the CA membrane using Manjikian's formula. In their studies, membranes cast under a given set of experimental conditions were annealed at various temperatures, and their permeate fluxes and salt rejections measured. The flux at a certain level of salt rejection, say 75 percent, was interpolated plotting the flux vs the rejection. The optimization of permeate flux at this level of salt rejection was then determined from 2^n series (where n is the number of variables in addition to annealing temperature) of experiments. This method becomes tedious and sometimes impractical to the optimization of membrane which involves as many as 8 variables, such as the case with the optimization of NS-100. In order to simplify the complexity of this membrane optimization study, a concept combining the two-level fractional factorial design and a SUMT (Sequential Unconstrained Minimization Technique) algorithm have been developed.

7.1 Two-Level Factorial Design

A full 2^k factorial design requires all combinations of two versions of each of the k variables. If a variable is continuous, the two versions become the high and low level of that variable. If a variable is qualitative, the two versions correspond to the presence or absence of that variable.

The runs comprising the experimental design are set out in either of two notations as illustrated in Table 22. In the first notation the variables are identified by capital letters and the two versions by the presence or absence of the corresponding lower case letter. When all variables are at their lower level or version, a "1" is used. In the second notation the variables are identified by numbers and the two versions of each variable by either a plus or minus sign, or by plus or minus one. The experimental design can then be viewed geometrically. A run or trial is represented by a point whose coordinates are the plus or minus version for that run. For example, the 2^3 factorial will provide the eight vertices of a cube in a three-dimensional coordinate system. The notation using plus and minus signs is used in this paper. For a 2^k factorial, the treatment combination contains k columns and N is equal to 2^k rows. In Table 22, the runs are listed in what is known as standard order. The elements of the first column are alternate minus and plus signs; the elements of the second column are alternate pairs of minus and plus signs. The last column consists of 2^{k-1} minus signs followed by 2^{k-1} plus signs.

On the assumption that the responses are uncorrelated and have equal variance, the 2^k factorial design provides independent minimum variance estimates of the grand average and of the 2^{k-1} effects:

TABLE 22

Alternative Notations for the 2^3 Factorial Design

Run Number	Notation 1 Variables	Notation 2 Variables		
	A B C	1	2	3
1	1	-	-	-
2	a	+	-	-
3	b	-	+	-
4	ab	+	+	-
5	c	-	-	+
6	ac	+	-	+
7	bc	-	+	+
8	abc	+	+	+

k	main effects
$k(k-1)/2$	two-factor interaction effects
$k(k-1)(k-2)/2\cdot 3$	three-factor interaction effects
$k(k-1)(k-2)\ldots(k-h-1)/h!$	h-factor interaction effects

and finally a single k-factor interaction effect.

The grand average is obtained by taking sum of the responses and dividing the result by the number of responses. If Y represents the responses,

$$\text{Average} = Y = \Sigma\, Y/N$$

where N = number of responses.

In general, the individual elements for an ij interaction are obtained by multiplying the corresponding elements of the i and j columns. Similarly, the elements of the i,j, and k columns are given by the product of the elements labelled i, j, and so on. The estimate then of the effect ij...k is obtained by taking the sum of products between the elements of the column ij..k and dividing this product by N where $N = 2^k$.

$$ij..k \text{ effect} = 1/N\ \Sigma\ Y(i\ j\ldots k)$$

where (i j...k) stands for the product of the k, j,..k column and the summation is taken over all N products.

By this process, 2^k estimates can be obtained from 2^k runs. When k becomes large, the quantity of such estimates becomes cumbersome. However, in many practical cases, the higher order interaction effects can often be assumed negligible in size. For example, with continuous variables, it is reasonable to expect the responses to vary smoothly. When factorial designs are used correctly to study qualitative variables, it is because certain aspects of similarity are expected in the responses.

In the conditions of smoothness and similarity encountered, the three-factor and multifactor interaction effects are often negligible (Box and Hunter, 1961). When this is the case, fractional factorial designs using a smaller number of runs may be employed. In some situations, the total number of variables k is large, but only a few (say k - p = 2 or 3) are expected to have any effect. In this situation, designs which are fractional in the k variables may be chosen which have the property of being complete factorials in any sub-group of p variables.

7.2 Fractional Factorial Design

A $(1/2)^p$ fraction of a 2^k factorial design is called a 2^{k-p} fractional,

or more exactly, a 2^{k-p} fractional factorial design (Box and Hunter, 1961). For example, say we are interested in testing four variables in a factorial design. However, we expect the three-factor interaction effect can be negligible while compared to the two factor intereaction effect. We then decide to run a 2^{4-1} (p = 1) fractional factorial design. We therefore have only eight runs instead of the original 16 for the full design.

The fractional design is constructed in the following manner: A full 2^3 factorial design is formed using the standard order. The minus and plus elements associated with the 123 interaction column are then used to identify the minus and plus versions of variable four. This is illustrated in Table 23.

With a full 2^4 design, 16 effects can be estimated: the grand average, four main effects, six two-factor effects, four three-factor effects, and a single four-factor effect. Yet with only eight observations it is clearly impossible to obtain these 16 independent estimates. We note that the combination of observations used to estimate the main effect "4" is identical to that used to estimate the three-factor interaction effect 123. The estimates of 4 and 123 are then said to be confounded. The "4" effect really estimates the sum of the effects of 4 and 123.

It is desirable to have a general method which enables one to determine which effects are confounded. This is accomplished in this design by introducing the equality 4 = 123 where the multiplication product 123 refers to the multiplication of the individual elements in the corresponding columns 1, 2, and 3. Now it is obvious that by multiplying the elements in any column by a column of identical elements we obtain a column of plus signs. A column of plus signs is denoted by I. Therefore, $1 \times 1 = 1^2 = I$, $2^2 = I$, $3^2 = I$ and $4^4 = I$. This identity supplies the key to the remaining relationships. Upon multiplying both sides of the equation 4 = 123 by 4, we get

$$4^2 = 1234 \text{ or } I = 1234$$

This interaction 1234 associated with I is said to be a generator of the design (Box and Hunter, 1961). The generator provides the defining relation I = 1234 which is the key to all relationships which exist between the effects. For example, if we wish to know which effect is confounded with the main effect 3, we simply multiply both sides of the defining relation by 3 which gives

$$3 = 123^2 4 = 1214 = 124.$$

Thus the main effect 3 is confounded with the three factor interaction effect 124. The quantities so associated are called aliases (Box and Hunter, 1961).

The half fractions of all the 2^k factorial designs are best obtained by first writing down the design matrix for a full 2^{k-1} factorial and then adding the kth variable by identifying its plus or minus versions with the

TABLE 23

The Construction of the 2^{4-1} Fractional Factorial Design

Design Matrix Variable			
1	2	3	4 = 1·2·3
-	-	-	-
-	+	-	+
+	-	-	+
+	+	-	-
-	-	+	+
+	-	+	-
-	+	+	-
+	+	+	+

plus or minus signs of the highest order interaction 123.....(k-1). However, as k increases, say to greater than five, the estimations of aliases again become large, many of which are again higher order interaction effects. We are therefore interested in still a smaller fraction of the 2^k designs, that is in the 2^{k-p} fractional factorials for p greater than one. For such designs there is not one, but p generators which combine to provide the defining relation.

For convenience, fractional factorial designs can be divided into two types. The type of design is usually signified by its resolution. In general, the resolution of a design is equal to the smallest number of characters in any word appearing in the defining relation. A word refers to a combination of elements such as 123, 1234, and so on. A design of resolution R is one in which no p factor effect is confounded with any other effect containing less than R-p factors. To identify the resolution of a fractional factorial design, the appropriate Roman numeral is used. Thus the defining relation for the 2^{4-1} design discussed becomes:

Design	Defining Relation
2^{4-1}_{IV}	I = 1234

In those cases in which m responses $(Y_1, Y_2, \ldots . Y_m)$ are observed, the regression equations for a two-level factorial design involving n variables $(x_1, x_2, \ldots . x_n)$ are:

$$Y_1 = C_1^o + \sum_{i=1}^{n} C_1^i x_i + \sum_{j=i+1}^{n} \sum_{i=1}^{n} C_1^{ij} x_i x_j + \ldots . + C_1^{1\ldots n} \prod_{i=1}^{n} x_i$$

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$$Y_m = C_m^o + \sum_{i=1}^{n} C_m^i x_i + \sum_{j=i+1}^{n} \sum_{i=1}^{n} C_m^{ij} x_i x_j + \ldots . + C_m^{1\ldots n} \prod_{i=1}^{n} x_i$$

where

C_ℓ^o = the grand average of Y_ℓ;

C_ℓ^i = the main effect of x_i to Y_ℓ;

C_ℓ^{ij} = the two-variable (x_i, x_j) interaction effect to Y_ℓ;

$C_\ell^{1\ldots n}$ = n-variable interaction effect to Y_ℓ;

ℓ = 1,2,.....,m.

With the aid of a digital computer, the regression equation for each response can easily be determined.

7.3 Constrained Optimization

In the optimization of a reverse osmosis membrane, performance is usually measured by two responses (m = 2): permeate flux and salt rejection. Therefore, after a series of factorial design experiments have been run on a group of membranes, two regression equations can be determined, one for salt rejection and one for permeate flux. In the case where only one regression equation would exist for a set of experiments, the optimized condition for each variable can be found using either the method of "Steepest Ascent" or "Canonical Transformation." However, in the case of membrane optimization, two responses should be simultaneously considered (Chian and Fang, 1974). Thus optimum performance of the membrane can be found only by optimizing one of the two responses and by using the other as a constraint. In other words, we can optimize the flux by setting a certain constrained value of solute separation or we can optimize the solute separation subject to a fixed flux. The technique used to solve this problem is called the "Lagrange Multiplier." The application and the procedure of such a method has recently been discussed by Luus and Jaakola (1973), and Chian and Fang (1974).

Fiacco and McCormick (1968) have developed a nonlinear sequential unconstrained minimization technique, known as the SUMT algorithm, for solving such a program. The computer code developed by Mylander *et al.* (1973) has been used with slight modifications in this study.

The concept of combining two-level factorial design and SUMT algorithm has first been tested for the optimization of CA membrane. By selecting three variables, i.e., composition of formannide, time of solvent evaporation and annealing temperature, the optimum CA performance was found after two series of designed experiments. At 97 percent rejection of salt, the maximum flux was found to be 14.52 gfd. The detail of this study has been included in an article entitled "Constrained Optimization of Cellulose Acetate Membrane Using Two-Level Factorial Design," (Chian and Fang, 1975).

7.4 The First Series of Designed Experiments

During this initial work, 8 variables were selected for the design experiments to follow. These 8 original variables and the reasons for their selection are as follows:

1) Concentration of the m-tolylene, 2,4-diisocyanate in hexane solution. This variable was immediately recognized as an important factor in the overall performance of the membrane. The TDI reacts with the PEI during curing to form the salt selective barrier of the membrane. Membranes coated with PEI alone were reported to have little or no capacity to effectively remove sufficient amounts of salt (North Star, 1972).

2) Concentration of polyethylenimene in aqueous solution. This variable was also immediately recognized as important in that it too is necessary for the effective formation of the salt selective barrier of the membrane.

3) Curing temperature. This variable is quite important since heat is

necessary to effect a good reaction between the PEI and TDI in forming the salt selective barrier. Without sufficient heat the reaction does not effectively occur.

4) Surfactant treatment. This variable was selected in order to determine if the polysulfone support film could be treated dry with the PEI and TDI solutions. North Star (1971) pointed out that indeed it could if the film had been previously treated with a 0.1 percent solution of dodecyl sodium sulfate. This procedure was included in the tests.

5) Concentration of diamino-6-pheny-s-triazine in the casting solution. This variable was included in polysulfone casting solution because North Star reported that this additive could be used to effectively increase the flux of the membrane without effectively lowering the salt rejection (North Star, 1972).

6) Concentration of the polysulfone in the casting solution. This variable was included to see if any effect in performance would take place from different concentrations of polysulfone and whether it had any noticeable effect on the formation and consistency of the resultant support film.

7) Curing time. Curing time was varied to again see if any effect on performance would occur. It was thought a very important variable as the time of curing would directly affect the overall effectiveness of the reaction of TDI and PEI in forming the all important salt barrier.

8) Time of drainage of the TDI solution. This variable was included to examine if any effect was observed from changing the time of drainage. In some of the original experiments it was thought that the time of drainage had an important effect on the reaction of PEI and TDI during curing. For this reason it was included.

With the variables of concern known and selected, the first series of design experiments was prepared. The levels of each variable or factor are given in Table 24. The levels were set on the basis of prior experiments and their results. The TDI concentration was varied from a lower level of 0.2 percent to an uppoer level of 2.0 percent with the prior knowledge that a concentration of 1.0 percent had given a membrane with a rejection of salt of over or around 99 percent. The PEI concentration was varied from 1.0 percent at the lower level to 5.0 percent for the higher level, again with the idea in mind that a concentration of 3.0 percent, the midpoint of this range, had given a membrane of greater than or around 99 percent rejection. The oven temperature was varied from 95° C to 125° C as these levels were felt the extremes possible for a good curing. The qualitative factor of using the surfactant had a lower level of not using the surfactant and a higher level of using it. The polysulfone was varied from 12.0 percent to 15.0 percent since North Star had reported that this range was capable of producing good support films. The curing time was varied from 2 minutes at the lower level to 12 minutes at the higher levels. Ten minutes had been used in earlier experiments and had been recommended by North Star (1972). However, it was thought that with an increased curing time, the resultant salt barrier would more easily form but the flux would be lowered. The effect of lower curing times was thus a factor of some interest. The time

TABLE 24

Lower and Upper Levels of Variables Studied in First Series of Design Experiments

Variable	Lower Level (-)	Upper Level (+)
X_1 TDI concentration in hexane solution	0.2%	2.0%
X_2 PEI concentration in aqueous solution	1.0%	5.0%
X_3 Oven temperature	95° C	125° C
X_4 Soaked in 1% DSS surfactant solution	No	Yes
X_5 DPT concentration in casting solution	0.2%	2.0%
X_6 Polysulfone concentration in casting solution	12.0%	15.0%
X_7 Curing time	2 minutes	12 minutes
X_8 Time of drainage of TDI solution	1 minute	7 minutes

of drainage of the TDI was varied from one to seven minutes. One minute had been used in the past, but again the effect of longer drainage times was of concern and therefore desirable to examine.

The factorial design used in this first series was a fractional factorial design with two generators. It is shown in Table 25 along with the recorded responses of salt rejection and permeate flux. The design is of resolution V or a 2_V^{8-2} fractional factorial design. A full 2^6 factorial design is first written down. The full design will then include 2^6 or 64 runs which comprise the treatment combination. The two generators of the design are respectively 7 = 1234 and 8 = 1256. The first generator gives the level of variable or factor 7 for each trial and the second generator gives the level of variable 8 for each trial. Two membranes of each trial combination were made and tested. The average salt rejection and permeate flux was obtained from the two membranes for each trial and is shown in Table 25. The corresponding regression equations were then computed using the computer program listed in Appendix IV with slight modifications. The coefficients for these regression equations for salt rejection and permeate flux are given in Table 26. The average is the value for all trials. 1 represents the main effect of factor 1, in this case the TDI concentration. 12 represents the two-factor interaction effect of factors 1 and 2, in this case the TDI concentration and the PEI concentration, and so on. The coefficient 345/678 represents an alias or the confounding of three-factor interaction effect of variables 3, 4, and 5 and variables 6, 7, and 8. The resultant coefficient is actually the sum of these two three-factor interaction effects.

Table 27 lists the observed responses for this first design series for salt rejection, the calculated response using the coefficients in the regression equation, the difference between the two, and the resultant ratio of the difference divided by the observed response. All the ratios are in the magnitude of 10^{-4} to 10^{-5} and represent a very good fit of the responses to the regression equations. Table 28 lists the same order for the responses for permeate flux. Again the ratios show a very good fit of the permeate responses to the resultant regression equation.

In Table 29, the main effects and two-factor effects for the 8 variables studied in the first series of experiments are presented. From this table, certain conclusions about the variables and how they are interacting to effect both salt rejection and permeate flux can be made.

First, upon studying the effects for salt rejection, it is seen that the magnitude of the main effect for variable 2, the PEI concentration, is by far the largest. Its sign is positive which means that the higher level of the variable is favored for greater salt rejection. Next in magnitude is the use of the surfactant in the treatment of the membrane. Its sign is negative which means that the lower level of the variable is favored for higher salt rejection, or in this case that the use of the surfactant decreases salt rejection. Next in magnitude is the concentration of DPT in the casting solution. Its sign is also negative which again means that the lower level of the variable is favoring the highest salt rejection. Overall then, the following levels of the variables are being favored for higher

TABLE 25

Experimental Conditions and Average Performance of NS-100 Membranes in First Series of Design Experiments

Run No.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	Salt Rejection (%)	Permeate Flux (gfd)
1	-	-	-	-	-	-	+	+	83.57	83.82
2	+	-	-	-	-	-	-	-	94.08	10.62
3	-	+	-	-	-	-	-	-	82.45	54.29
4	+	+	-	-	-	-	+	+	99.09	5.28
5	-	-	+	-	-	-	-	+	60.65	98.80
6	+	-	+	-	-	-	+	-	99.70	8.37
7	-	+	+	-	-	-	+	-	92.27	11.92
8	+	+	+	-	-	-	-	+	98.78	8.15
9	-	-	-	+	-	-	-	+	91.25	34.32
10	+	-	-	+	-	-	+	-	34.43	43.66
11	-	+	-	+	-	-	+	-	96.95	22.40
12	+	+	-	+	-	-	-	+	80.02	2.48
13	-	-	+	+	-	-	+	+	49.56	84.50
14	+	-	+	+	-	-	-	-	85.62	19.48
15	-	+	+	+	-	-	-	-	91.69	19.45
16	+	+	+	+	-	-	+	+	98.53	1.56
17	-	-	-	-	+	-	+	-	87.78	65.34
18	+	-	-	-	+	-	-	+	88.15	32.05
19	-	+	-	-	+	-	-	+	70.60	83.16
20	+	+	-	-	+	-	+	-	99.22	8.61
21	-	-	+	-	+	-	-	-	76.16	102.06
22	+	-	+	-	+	-	+	+	88.66	10.08
23	-	+	+	-	+	-	+	+	78.81	26.69
24	+	+	+	-	+	-	-	-	96.32	8.01
25	-	-	-	+	+	-	-	-	23.24	166.32
26	+	-	-	+	+	-	+	+	87.32	24.45
27	-	+	-	+	+	-	+	+	92.05	29.13
28	+	+	-	+	+	-	-	-	87.65	3.69
29	-	-	+	+	+	-	+	-	45.85	42.94
30	+	-	+	+	+	-	-	+	20.55	91.11
31	-	+	+	+	+	-	-	+	88.63	18.84
32	+	+	+	+	+	-	+	-	94.96	2.91
33	-	-	-	-	-	+	+	-	86.90	59.27
34	+	-	-	-	-	+	-	+	73.79	7.15
35	-	+	-	-	-	+	-	+	89.20	33.80

TABLE 25 (Continued)

Run No.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	Salt Rejection (%)	Permeate Flux (gfd)
36	+	+	-	-	-	+	+	-	98.39	4.47
37	-	-	+	-	-	+	-	-	89.41	55.30
38	+	-	+	-	-	+	+	+	94.96	5.21
39	-	+	+	-	-	+	+	+	91.07	12.10
40	+	+	+	-	-	+	-	-	98.21	4.86
41	-	-	-	+	-	+	-	-	37.46	75.66
42	+	-	-	+	-	+	+	+	33.08	40.61
43	-	+	-	+	-	+	+	+	94.65	20.95
44	+	+	-	+	-	+	-	-	94.12	7.28
45	-	-	+	+	-	+	+	-	87.67	12.04
46	+	-	+	+	-	+	-	+	10.01	124.74
47	-	+	+	+	-	+	-	+	97.01	14.45
48	+	+	+	+	-	+	+	-	91.43	13.10
49	-	-	-	-	+	+	+	+	92.62	50.01
50	+	-	-	-	+	+	-	-	96.41	8.46
51	-	+	-	-	+	+	-	-	63.03	74.31
52	+	+	-	-	+	+	+	+	99.15	6.36
53	-	-	+	-	+	+	-	+	63.18	113.36
54	+	-	+	-	+	+	+	-	67.38	5.29
55	-	+	+	-	+	+	+	-	95.74	13.90
56	+	+	+	-	+	+	-	+	96.35	4.28
57	-	-	-	+	+	+	-	+	47.30	69.85
58	+	-	-	+	+	+	+	-	21.56	90.33
59	-	+	-	+	+	+	+	-	96.27	20.96
60	+	+	-	+	+	+	-	+	60.92	2.05
61	-	-	+	+	+	+	+	+	40.57	60.57
62	+	-	+	+	+	+	-	-	64.09	38.81
63	-	+	+	+	+	+	-	-	97.05	12.71
64	+	+	+	+	+	+	+	+	86.96	1.15

TABLE 26

Coefficents of the Regression Equations of Salt Rejection and Permeate Flux for First Series of Design Experiments

Coefficient	Salt Rejection (%)	Permeate Flux (gfd)
AVERAGE	0.78571E 02	0.35748E 02
1	0.10503E 01	-0.15602E 02
2	0.12228E 02	-0.18457E 02
3	0.73596E 00	-0.30375E 01
4	0.86821E 01	0.21425E 01
5	-0.31171E 01	0.44953E 01
6	-0.18221E 01	-0.25171E 01
12	0.11569E 01	0.35768E 01
13	0.42438E 00	0.45862E 01
14	-0.47362E 01	0.94249E 01
15	0.19737E 01	-0.35384E 01
16	-0.36237E 01	0.51308E 01
23	0.18281E 01	-0.33731E 01
24	0.89387E 01	-0.73637E 01
25	0.50010E-01	-0.19884E 01
26	0.16200E 01	0.64711E 00
34	0.12612E 01	0.44373E-01
35	-0.11112E 01	-0.26616E 01
36	0.19581E 01	0.54843E 00
45	0.83626E 00	-0.14718E 00
46	-0.18075E 01	0.24553E 01
56	0.65436E 00	-0.19512E 01
47	-0.80219E 00	0.20619E 01
37	-0.70281E 00	-0.51912E 01
68	-0.17216E 01	0.39906E 00
58	0.15109E 01	-0.30822E 01
27	0.39406E 00	0.33012E 01
135	-0.16184E 01	0.21531E 00
136	-0.11203E 01	0.17656E 00
145	0.12778E 01	-0.71031E 00
146	0.11784E 01	0.29766E 01
28	0.41594E 00	-0.21737E 01
17	0.15984E 01	0.48181E 01
235	0.26678E 01	0.33594E 00
236	-0.89155E 00	0.10310E-01
245	0.90906E 00	-0.29991E 01
246	0.75533E 00	-0.10734E 01
18	-0.12503E 01	0.98873E 00
345/678	0.51095E 00	-0.29541E 01
346/578	0.16341E 01	-0.68781E 00
356/478	0.54593E 00	0.63437E 00

TABLE 26 (Continued)

Coefficient	Salt Rejection (%)	Permeate Flux (gfd)
456/378	0.13797E 01	0.31719E 01
7	0.29031E 01	-0.79987E 01
457/368	0.13319E 01	0.13278E 01
467/358	0.41375E 00	-0.21593E 00
357/468	-0.37369E 01	0.26615E 01
367/458	0.79375E-01	-0.29197E 01
8	-0.18512E 01	0.17850E 01
275	0.54188E 00	0.21884E 01
276	0.63750E-01	0.11281E 00
238	0.47781E 01	-0.73174E 01
248	-0.11369E 01	0.52375E 00
157	-0.45563E 00	0.43003E 01
167	-0.16162E 01	0.44844E 00
23562478	0.13581E 01	-0.14119E 01
148	-0.22906E 01	0.24100E 01
78	0.22925E 01	-0.63000E 00
57	0.13241E 01	-0.35746E 01
67	0.24969E 00	0.78779E 00
38	-0.46884E 01	0.77287E 01
48	-0.13719E 00	-0.87812E 00
178	0.58515E 01	-0.72712E 01
278	-0.24147E 01	0.13281E 01
567/348	-0.37319E 01	0.60818E 01

TABLE 27

Observed and Calculated Salt Rejection for First Series

NO	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.83570E 02	0.83569E 02	0.12970E-02	0.15520E 04
2	0.94080E 02	0.94079E 02	0.12665E-02	0.13462E-04
3	0.82450E 02	0.82449E 02	0.12665E-02	0.15361E 04
4	0.99090E 02	0.99089E 02	0.13580E-02	0.13705E-04
5	0.60650E 02	0.60649E 02	0.10529E-02	0.17360E-04
6	0.99700E 02	0.99699E 02	0.12054E-02	0.12091E-04
7	0.92270E 02	0.92269E 02	0.12054E-02	0.13064E-04
8	0.98780E 02	0.98779E 02	0.12817E-02	0.12976E-04
9	0.91250E 02	0.91249E 02	0.99182E-03	0.10869E-04
10	0.34430E 02	0.34429E 02	0.73242E-03	0.21273E 04
11	0.96950E 02	0.96949E 02	0.11597E-02	0.11962E 04
12	0.88020E 02	0.88019E 02	0.10071E-02	0.11441E-04
13	0.49560E 02	0.49559E 02	0.79346E-03	0.16010E-04
14	0.85620E 02	0.85619E 02	0.99182E-03	0.11584E 04
15	0.91690E 02	0.91689E 02	0.11444E-02	0.12481E-04
16	0.98530E 02	0.98529E 02	0.12054E-02	0.12234E-04
17	0.87780E 02	0.87779E 02	0.10376E 02	0.11820E-04
18	0.88150E 02	0.88149E 02	0.10529E-02	0.11944E-04
19	0.70600E 02	0.70599E 02	0.10223E-02	0.14481E-04
20	0.99220E 02	0.99219E 02	0.10376E-02	0.10458E-04
21	0.76160E 02	0.76159E 02	0.91553E-03	0.12021E 04
22	0.88660E 02	0.88659E 02	0.96130E-03	0.10843E-04
23	0.78810E 02	0.78809E 02	0.96130E-03	0.12198E-04
24	0.96320E 02	0.96319E 02	0.11139E-02	0.11564E-04
25	0.23240E 02	0.23239E 02	0.62561E-03	0.26920E-04
26	0.87320E 02	0.87319E 02	0.86975E-03	0.99605E-05
27	0.92050E 02	0.92049E 02	0.10223E-02	0.11106E-04
28	0.87650E 02	0.87649E 02	0.10071E-02	0.11490E-04
29	0.45850E 02	0.45849E 02	0.68665E-03	0.14976E-04
30	0.20550E 02	0.20550E 02	0.35095E-03	0.17078E-04
31	0.88630E 02	0.88629E 02	0.93079E-03	0.10502E-04
32	0.94960E 02	0.94959E 02	0.83923E-03	0.88378E-05
33	0.86930E 02	0.86929E 02	0.94604E-03	0.10883E-04
34	0.73790E 02	0.73789E 02	0.97656E-03	0.13234E-04
35	0.89200E 02	0.89199E 02	0.10529E-02	0.11803E-04
36	0.98390E 02	0.98389E 02	0.10071E-02	0.10236E-04
37	0.89410E 02	0.89409E 02	0.97656E-03	0.10922E-04
38	0.94960E 02	0.94959E 02	0.97656E-03	0.10284E-04
39	0.91070E 02	0.91069E 02	0.94604E-03	0.10388E-04
40	0.98210E 02	0.98209E 02	0.97656E-03	0.99436E-05

TABLE 27 (Continued)

41	0.37460E 02	0.37459E 02	0.65613E-03	0.17515E-04
42	0.33080E 02	0.33079E 02	0.70190E-03	0.21218E-04
43	0.94650E 02	0.94649E 02	0.86975E-03	0.91891E-05
44	0.94120E 02	0.94119E 02	0.85449E-03	0.90788E-05
45	0.87670E 02	0.87669E 02	0.86975E-03	0.99207E-05
46	0.10010E 02	0.10009E 02	0.50354E-03	0.50304E-04
47	0.97010E 02	0.97009E 02	0.86975E-03	0.89656E-05
48	0.91430E 02	0.91429E 02	0.80872E-03	0.88452E 05
49	0.92620E 02	0.92619E 02	0.88501E-03	0.95553E-05
50	0.96410E 02	0.96409E 02	0.82397E-03	0.85466E-05
51	0.63030E 02	0.63029E 02	0.76294E-03	0.12104E-04
52	0.99150E 02	0.99149E 02	0.86975E-03	0.87721E-05
53	0.63180E 02	0.63179E 02	0.65613E-03	0.10385E-04
54	0.67380E 02	0.67379E 02	0.65613E-03	0.97377E-05
55	0.95740E 02	0.95739E 02	0.68665E-03	0.71720E-05
56	0.96350E 02	0.96349E 02	0.65613E-03	0.68098E-05
57	0.47300E 02	0.47299E 02	0.74768E-03	0.15807E-04
58	0.21560E 02	0.21559E 02	0.54932E 03	0.25478E 04
59	0.96270E 02	0.96269E 02	0.71716E-03	0.74495E-05
60	0.60920E 02	0.60919E 02	0.62561E-03	0.10269E-04
61	0.40570E 02	0.40569E 02	0.59509E-03	0.14668E-04
62	0.64090E 02	0.64089E 02	0.71716E-03	0.11190E-04
63	0.97050E 02	0.97049E 02	0.54932E-03	0.56601E-05
64	0.86960E 02	0.86959E 02	0.65613E-03	0.75452E-05

TABLE 28

Observed and Calculated Permeate Flux for First Series

NO.	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.83820E 02	0.83819E 02	0.12360E-02	0.14745E-04
2	0.10620E 02	0.10620E 02	0.35286E-04	0.33226E-05
3	0.54290E 02	0.54289E 02	0.90027E-03	0.16583E 04
4	0.52800E 01	0.52802E 01	-0.17929E-03	-0.33957E 04
5	0.98800E 02	0.98799E 02	0.12054E-02	0.12201E-04
6	0.83700E 01	0.83698E 01	0.23365E-03	0.27915E-04
7	0.11920E 02	0.11920E 02	0.45300E-03	0.38003E-04
8	0.81500E 01	0.81500E 01	-0.22888E-04	0.28084E-05
9	0.34320E 02	0.34319E 02	0.74768E-03	0.21786E-04
10	0.43660E 02	0.43659E 02	0.79346E-03	0.18174E-04
11	0.22400E 02	0.22400E 02	0.30518E-03	0.13624E-04
12	0.24800E 01	0.24801E 01	-0.98228E-04	-0.39608E-04
13	0.84500E 02	0.84499E 02	0.11444E-02	0.13543E-04
14	0.19480E 02	0.19480E 02	0.48828E-03	0.25066E-04
15	0.19450E 02	0.19450E 02	0.33569E-03	0.17259E-04
16	0.15600E 01	0.15602E 01	-0.15545E-03	-0.99647E-04
17	0.65340E 02	0.65339E 02	0.86975E-03	0.13311E-04
18	0.32050E 02	0.32049E 02	0.53406E-03	0.16663E-04
19	0.83160E 02	0.83159E 02	0.94604E-03	0.11376E-04
20	0.86100E 01	0.86101E 01	-0.61989E-04	-0.71996E-05
21	0.10206E 03	0.10206E 03	0.13428E-02	0.13157E-04
22	0.10080E 02	0.10080E 02	0.19646E-03	0.19490E-04
23	0.26690E 02	0.26690E 02	0.47302E-03	0.17723E-04
24	0.80100E 01	0.80100E 01	-0.31471E-04	-0.39290E-05
25	0.16632E 03	0.16632E 03	0.15869E-02	0.95413E-05
26	0.24450E 02	0.24450E 02	0.42725E-03	0.17474E-04
27	0.29130E 02	0.29130E 02	0.39673E-03	0.13619E-04
28	0.36900E 01	0.36901E 01	-0.61035E-04	-0.16541E-04
29	0.42940E 02	0.42939E 02	0.50354E-03	0.11727E-04
30	0.91110E 02	0.91109E 02	0.10986E-02	0.12058E-04
31	0.18840E 02	0.18840E 02	0.13733E-03	0.72892E-05
32	0.29100E 01	0.29101E 01	-0.13733E-03	-0.47192E-04
33	0.59270E 02	0.59269E 02	0.64087E-03	0.10813E-04
34	0.71500E 01	0.71500E 01	-0.76294E-05	0.10670E-05
35	0.33800E 02	0.33799E 02	0.64087E-03	0.18961E-04
36	0.44700E 01	0.44701E 01	-0.58174E-04	-0.13014E-04
37	0.55300E 02	0.55299E 02	0.56458E-03	0.10209E-04
38	0.52100E 01	0.52099E 01	0.14496E-03	0.27823E-04
39	0.12100E 02	0.12100E 02	0.69618E-04	0.57536E-05
40	0.48600E 01	0.48599E 01	0.76294E-04	0.15698E 04

TABLE 28 (Continued)

41	0.75660E 02	0.75659E 02	0.77820E-03	0.10285E-04
42	0.40610E 02	0.40610E 02	0.45776E-03	0.11272E-04
43	0.20950E 02	0.20950E 02	0.21362E-03	0.10197E-04
44	0.72800E 01	0.72799E 01	0.67711E-04	0.93009E-05
45	0.12040E 02	0.12040E 02	0.31185E-03	0.25901E-04
46	0.12474E 03	0.12474E 03	0.93079E 03	0.74618E-05
47	0.14450E 02	0.14450E 02	0.33379E 04	0.23099E-05
48	0.13100E 02	0.13100E 02	0.35954E-03	0.27445E-04
49	0.50010E 02	0.50010E 02	0.48828E 03	0.97637E-05
50	0.84600E 01	0.84599E 01	0.83923E-04	0.99200E-05
51	0.74310E 02	0.74309E 02	0.56458E-03	0.75976E-05
52	0.63600E 01	0.63600E 01	0.12398E-04	0.19493E 05
53	0.11336E 03	0.11336E 03	0.57983E-03	0.51150E 05
54	0.52900E 01	0.52899E 01	0.55313E-04	0.10456E-04
55	0.13900E 02	0.13900E 02	0.34142E-03	0.24562E-04
56	0.42800E 01	0.42800E 01	-0.16212E-04	0.37880E-05
57	0.69850E 02	0.69850E 02	0.33569E-03	0.48059E-05
58	0.90330E 02	0.90329E 02	0.56458E-03	0.62501E-05
59	0.20960E 02	0.20960E 02	0.25940E-03	0.12376E-04
60	0.20500E 01	0.20499E 01	0.67711E-04	0.33030E-04
61	0.60570E 02	0.60570E 02	0.32043E 03	0.52903E-05
62	0.38810E 02	0.38810E 02	0.33569E-03	0.86497E-05
63	0.12710E 02	0.12710E 02	-0.38147E-04	-0.30013E-05
64	0.11500E 01	0.11499E 01	0.65804E-04	0.57220E-04

TABLE 29

Main Effects and Two-Factor Interaction Effects of Variables in the First Series to Salt Rejection and Permeate Flux

Salt Rejection

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
Main Effect	1.0503	12.228	0.73596	-8.6821	-3.1171	-1.8221	2.9031	-1.8512
Two-Factor Interaction Effect	X_1	1.1569	0.42438	-4.7362	1.9737	-3.6237	-1.5984	-1.2503
	1.1569	X_2	1.8281	8.9387	0.0500	1.6200	0.39406	0.41594
	0.42438	1.8281	X_3	1.2612	-1.1112	1.9581	-0.70281	-4.6884
	-4.7362	8.9387	1.2612	X_4	-0.83626	-1.8075	-0.80219	-0.13719
	1.9737	0.0500	-1.1112	-0.83626	X_5	0.65436	1.3241	1.5109
	-3.6237	1.6200	1.9581	-1.8075	0.65436	X_6	0.24969	-1.7216
	-1.5984	0.39406	-0.7028	-0.80219	1.3241	0.24969	X_7	2.2925
	-1.2503	0.41594	-4.6884	0.13719	1.5109	-1.7216	2.2925	X_8

Permeate Flux

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
Main Effect	-15.602	-18.457	-3.0375	2.1425	4.4953	-2.5171	-7.9987	1.7850
Two-Factor Interaction Effect	X_1	3.5768	4.5862	9.4249	-3.5384	5.1308	4.8181	0.98873
	3.5768	X_2	-3.3731	-7.3637	-1.9884	0.64711	3.3012	-2.1737
	4.5862	-3.3731	X_3	0.04373	-2.6616	0.54843	-5.1912	7.7287
	9.4249	-7.3637	0.04373	X_4	-0.14718	2.4553	2.0619	-0.87812
	-3.5384	-1.9884	-2.6016	-0.1472	X_5	-1.9512	-3.5746	-3.0822
	5.1308	0.64711	0.5484	2.4553	-1.9512	X_6	0.78779	0.39906
	4.8181	3.3012	-5.1912	2.0619	-3.5746	0.7878	X_7	-0.63000
	0.9887	-2.1737	7.7287	-0.8781	-3.0822	0.39906	-0.5300	X_8

salt rejection: the higher concentration of TDI, the higher concentration of PEI, the higher oven temperature, the lower concentration of DPT in the casting solution, not using the surfactant treatment, the lower concentration of the polysulfone in the casting solution, the higher cure time, and the lower time of drainage of the TDI after treatment.

Turning to the effects upon permeate flux, the first fact observed is that in 7 out of 8 variables the signs of the main effects are reversed. This fact seems to lead to the familiar analogy that to increase salt rejection, permeate flux must be sacrificed. The only variable whose signs are the same is that of the concentration of polysulfone in the casting solution.

Upon examining magnitudes, the effect of the PEI concentration is again seen to be the largest, but as noted, here the lower level of the variable is favoring the higher permeate flux. Next in magnitude is the TDI concentration. Here again the lower level of the variable is favored for greatest permeate flux. Next in order is the curing time where the lower level is again favored for greatest flux. Next in order of magnitude is the concentration of DPT, where the higher level is favored. This makes sense becasue DPT is considered an additive which should indeed improve flux. The other two factors that are positive are the use of the surfactant and the time of drainage of the TDI.

The following conclusions were drawn from this first series of design experiments:

1) The concentration of TDI enhances salt rejection by effectively forming the salt selective barrier. However, this barrier is formed at the expense of greatly reducing the permeate flux of the membrane. The upper level of this variable used in this series of 2.0 percent is considered too large.

2) The concentration of PEI also has the effect of greatly enhancing salt rejection but again at the expense of greatly reduced permeate flux. Whereas both levels of the variable, when used with different combinations of the other variables, have given good responses to both rejection and flux, no change in the level of the variable should occur until more conclusive results have been obtained.

3) The oven temperature has shown little effect in enhancing rejection, and the lower temperature is somewhat favored for higher permeate flux. The higher level of the variable should then be lowered. Because some discoloring of the membrane was observed using the higher temperature, an upper level of 115° C is recommended for use in the next series of design experiments.

4) From the results of the first series, it can be seen that the use of the surfactant treatment seriously affects salt rejection while at the same time has little effect on increasing the flux of the membrane. For this reason, it is suggested that the use of the surfactant be dropped from further optimization work.

5) The DPT concentration in the casting solution acts to increase flux; however, it is doing this at the expense of lowered salt rejection. For this reason, it is suggested that this variable be kept for further study and examination at the levels used in this first series.

6) The polysulfone concentration acts to increase both flux and rejection at the lower level of the variable. However, because North Star reported 15 percent as optimum and membranes of 99 percent rejection were made using 15 percent polysulfone in earlier experiments, it is suggested that this variable be included for further study at the levels used in this series.

7) The curing time was found to enhance rejection slightly but again at the expense of lowering the flux. Because the flux greatly favors the lower level of the variable, it is recommended that the upper level of this variable be lowered somewhat for the next series, say to 10 minutes as had been used successfully for earlier experiments.

8) The drainage time of the TDI during treatment had very little effect on both rejection and permeate flux. The higher level is favored for greater flux and the lower for salt rejection. However, its magnitude for flux compared to all of the other variables is the lowest. For this reason, it is recommended that the variable be dropped from further studies.

The results of this experimental design were then used to find the optimum conditions of each variable using the constrained optimization program and to find the predicted optimum flux at the 99 percent level of rejection. Using the two regression equations, and the coefficients listed in Table 26, the optimum flux was predicted mathematically to be 42.29 gfd at 99 percent rejection of salt. The corresponding casting conditions are 1.75 percent TDI, 1 percent PEI, 125° C curing temperature, no surfactant treatment, 0.2 percent DPT in the casting solution, 12 percent polysulfone in the casting solution, 12 minutes for the cure time, and 7 minutes for the time of drainage of the TDI during treatment. However, membranes cast under these conditions failed to reproduce the predicted optimum. The reasons for this seem to be the wealth of variables studied and possible experimental errors in the results obtained. Because of the wealth of experiments run in this design, the casting was split up into 4 sections and cast over a series of 3 weeks. The problem of precipitation in the 2.0 percent TDI solution was first observed here, also adding to the possible experimental errors. However, the effects obtained were of great help in analyzing the interactions of the variables and their effects on salt rejection and permeate flux. With this knowledge in hand, the next series of factorially designed experiments was undertaken.

7.5 The Second Series of Designed Experiments

With the results from the first series in mind, a second experimental design was constructed. Part of the shortcomings of the first series was undoubtedly due to the extremely large number of variables under study and the fact that very little, if any, prior knowledge about the effects of the variables is statistically available. Therefore, with the new wealth of

statistical information, the second series was developed using two fewer variables. The advantage is immediately seen with respect to the actual number of experiments run. In the first series, 64 out of a possible 256 treatment combinations were actually run, using the 2^{8-2} fractional factorial. Now, using a 2^{6-1} fractional factorial, the design selected for the second series, we need only run 32 out of 64 possible treatment combinations. Also, from the first series, it was found that curing time of the membrane was interacting only slightly with the other factors in affecting the rejection of salt, while having a somewhat higher effect on the flux. Because at this stage of design work primary concern was still with the goal of reaching 99 percent salt rejection, this variable was selected to be fractionally designed (p = 1). Therefore, the generator of the second series of experiments became

$$6 = 12345$$

and the resolution again V. The variables and their selected levels are given in Table 30. The TDI concentration was varied from 0.2 percent as in the first series, to 1.0 percent instead of the original 2.0 percent. The PEI concentration was kept as before, from 1.0 percent to 5.0 percent. The oven temperature was varied from 95° C as before to 115° C instead of the original 125° C. The DPT concentration was varied from 0.2 to 2.0 percent as before. The polysulfone concentration was varied from 12 to 15 percent as before and the curing time varied from 2 minutes to 10 minutes instead of the original 12 minutes. The variables of drainage time of the TDI solution and the use of the surfactant treatment were dropped. The constant of 1.7 mils for the polysulfone film thickness was maintained. The 32 experiments were then run and the results obtained.

The fractional factorial design used and the resultant responses for the design are listed in Table 31. The resultants are again the average of two membranes with that particular treatment combination. The design is obtained by first writing down the full factorial design for the first 5 variables using the standard order. The level of variable 6 is found by multiplying the first 5 levels of each combination and noting the resultant sign. The corresponding coefficients for the regression equations of salt rejection and permeate flux are given in Table 32. They were again obtained using the program in Appendix IV . The observed values for salt rejection, the calculated value using the resultant salt rejection regression equation, the difference, and the ratio of difference by the observed value is given in Table 33. The same is presented for permeate flux in Table 34. The differences are again quite low, varying from 10^{-4} to 10^{-6}. This again represents a good fit of the data to the regression equations. The main and two-factor effects for both salt rejection and permeate flux are given in Table 35. The effects of variable 6 are not listed as they are confounded with other interaction effects. These interactions are found by using the generator of the design and are shown in Table 32 for both salt rejection and permeate flux.

The main effects of the variables to salt rejection are as follows:

TABLE 30

Lower and Upper Levels of Variables Studied in Second Series of Design Experiments

Variable	Lower Level (-)	Upper Level (+)
X_1 TDI concentration in hexane solution	0.2%	1.0%
X_2 PEI concentration in aqueous solution	1.0%	5.0%
X_3 Oven temperature	95° C	115° C
X_4 DPT concentration in casting solution	0.2%	2.0%
X_5 Polysulfone concentration	12.0%	15.0%
X_6 Curing time	2 minutes	10 minutes

Fixed Variables:

1.7 mils thickness

No surfactant

1 minute drainage

TABLE 31

Experimental Conditions and Average Performance of NS-100 Membranes in Second Series of Design Experiments

Run No.	X_1	X_2	X_3	X_4	X_5	X_6	Salt Rejection (%)	Permeate Flux (gfd)
1	-	-	-	-	-	-	57.22	129.62
2	+	-	-	-	-	+	98.45	14.58
3	-	+	-	-	-	+	98.58	17.13
4	+	+	-	-	-	-	97.16	7.94
5	-	-	+	-	-	+	96.09	38.56
6	+	-	+	-	-	-	96.22	33.43
7	-	+	+	-	-	-	90.01	33.13
8	+	+	+	-	-	+	99.55	6.70
9	-	-	-	+	-	+	89.07	82.56
10	+	-	-	+	-	-	95.15	47.27
11	-	+	-	+	-	-	85.61	43.41
12	+	+	-	+	-	+	98.78	11.13
13	-	-	+	+	-	-	50.82	224.90
14	+	-	+	+	-	+	95.91	33.00
15	-	+	+	+	-	+	97.76	27.53
16	+	+	+	+	-	-	92.95	11.65
17	-	-	-	-	+	+	90.42	77.51
18	+	-	-	-	+	-	94.74	23.72
19	-	+	-	-	+	-	79.07	47.66
20	+	+	-	-	+	+	96.76	11.07
21	-	-	+	-	+	-	85.57	84.84
22	+	-	+	-	+	+	93.18	11.87
23	-	+	+	-	+	+	96.81	25.08
24	+	+	+	-	+	-	77.85	9.12
25	-	-	-	+	+	-	62.19	110.04
26	+	-	-	+	+	+	93.24	29.47
27	-	+	-	+	+	+	95.66	39.29
28	+	+	-	+	+	-	70.78	11.80
29	-	-	+	+	+	+	86.29	68.58
30	+	-	+	+	+	-	98.11	18.31
31	-	+	+	+	+	-	85.20	40.81
32	+	+	+	+	+	+	99.34	7.75

TABLE 32

Coefficients of the Regression Equations of Salt Rejection and Permeate Flux for Second Series

Coefficient	Salt Rejection (%)	Permeate Flux (gfd)
Average	0.88892E 02	0.43108E 02
1	0.47437E 01	-0.25057E 02
2	0.24750E 01	-0.21158E 02
3	0.12119E 01	-0.90437E 00
4	-0.15880E 01	0.73606E 01
5	-0.10662E 01	-0.45506E 01
12	-0.44644E 01	0.12752E 02
13	-0.70375E 00	0.66750E 00
14	0.98500E 00	-0.41138E 01
15	-0.20694E 01	0.18887E 01
23	-0.14500E 00	-0.82437E 00
24	0.98125E 00	-0.51394E 01
25	-0.26169E 01	0.66731E 01
34	-0.21810E 00	0.45019E 01
35	0.12563E 01	-0.43581E 01
45	0.11375E 00	-0.51618E 01
123-456	0.41812E 00	0.15562E 01
124-356	-0.15619E 01	0.28300E 01
125-346	0.28875E 00	-0.37212E 01
134-256	0.32600E 01	-0.65500E 01
135-246	-0.13937E 00	0.23038E 01
145-236	0.35687E 00	0.33587E 01
234-156	0.22037E 01	-0.50094E 01
235-146	-0.20638E 00	0.27044E 01
245-136	0.55438E 00	0.37806E 01
345-126	0.36337E 01	-0.61331E 01
1234-56	-0.33938E 00	0.70149E 01
1235-46	0.72625E 00	-0.13100E 01
1245-36	-0.96375E 00	-0.30750E 01
1345-26	0.61874E-01	0.80050E 01
2345-16	-0.32106E 01	0.93906E 01
12345-6	0.64762E 01	-0.11745E 02

TABLE 33

Observed and Calculated Salt Rejection for Second Series

NO	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.57220E 02	0.57220E 02	0.45776E-03	0.80001E-05
2	0.98450E 02	0.98450E 02	0.42725E-03	0.43397E-05
3	0.98580E 02	0.98580E 02	0.47302E-03	0.47984E-05
4	0.97160E 02	0.97160E 02	0.45776E-03	0.47114E-05
5	0.96090E 02	0.96089E 02	0.57983E-03	0.60343E-05
6	0.96220E 02	0.96219E 02	0.53406E-03	0.55504E-05
7	0.90010E 02	0.90009E 02	0.53406E-03	0.59333E-05
8	0.99550E 02	0.99549E 02	0.57983E-03	0.58246E-05
9	0.89070E 02	0.89070E 02	0.41199E-03	0.46254E-05
10	0.95150E 02	0.95150E 02	0.42725E-03	0.44902E-05
11	0.85610E 02	0.85610E 02	0.36621E-03	0.42777E-05
12	0.98780E 02	0.98780E 02	0.42725E-03	0.43252E-05
13	0.50820E 02	0.50820E 02	0.27466E-03	0.54045E-05
14	0.95910E 02	0.95910E 02	0.30518E-03	0.31819E-05
15	0.97760E 02	0.97760E 02	0.33569E-03	0.34339E-05
16	0.92950E 02	0.92950E 02	0.27466E-03	0.29549E-05
17	0.90420E 02	0.90420E 02	0.38147E-03	0.42189E-05
18	0.94740E 02	0.94740E 02	0.33569E-03	0.35433E-05
19	0.79070E 02	0.79070E 02	0.35095E-03	0.44385E-05
20	0.96760E 02	0.96760E 02	0.44250E-03	0.45732E-05
21	0.85570E 02	0.85570E 02	0.24414E-03	0.28531E-05
22	0.93180E 02	0.93180E 02	0.25940E-03	0.27839E-05
23	0.9681[illegible]E 02	0.96810E 02	0.25940E-03	0.26795[illegible]-05
24	0.77850E 02	0.77850E 02	0.21362E-03	0.27440E-05
25	0.62190E 02	0.62190E 02	0.21362E-03	0.34350E-05
26	0.93240E 02	0.93240E 02	0.22888E-03	0.24548E-05
27	0.95660E 02	0.95660E 02	0.24414E-03	0.25522E-05
28	0.70780E 02	0.70780E 02	0.19836E-03	0.28025E-05
29	0.86290E 02	0.86290E 02	0.13733E-03	0.15915E-05
30	0.98110E 02	0.98110E 02	0.91553E-04	0.93316E-06
31	0.85200E 02	0.85200E 02	0.10681E-03	0.12537E-05
32	0.99340E 02	0.99340E 02	0.12207E-03	0.12286E-05

TABLE 34

Observed and Calculated Permeate Flux for Second Series

NO	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.12962E 03	0.12962E 03	0.88501E-03	0.68277E-05
2	0.14580E 02	0.14580E 02	0.15068E-03	0.10335E-04
3	0.17130E 02	0.17130E 02	0.18311E-03	0.10689E-04
4	0.79400E 01	0.79399E 01	0.91553E-04	0.11531E-04
5	0.38560E 02	0.38560E 02	0.41199E-03	0.10684E-04
6	0.33430E 02	0.33430E 02	0.38147E-03	0.11411E-04
7	0.33130E 02	0.33130E 02	0.30518E-03	0.92115E-05
8	0.67000E 01	0.67000E 01	-0.27657E-04	-0.41278E-05
9	0.82560E 02	0.82559E 02	0.54932E-03	0.66535E-05
10	0.47270E 02	0.47270E 02	0.38147E-03	0.80700E-05
11	0.43410E 02	0.43410E 02	0.42725E-03	0.98421E-05
12	0.11130E 02	0.11130E 02	0.95367E-05	0.85685E-06
13	0.22490E 03	0.22490E 03	0.99182E-03	0.44101E-05
14	0.33000E 02	0.33000E 02	0.18311E-03	0.55486E-05
15	0.27530E 02	0.27530E 02	0.27466E-03	0.99767E-05
16	0.11650E 02	0.11650E 02	0.12779E-03	0.10969E-04
17	0.77510E 02	0.77510E 02	0.41199E-03	0.53153E-05
18	0.23720E 02	0.23720E 02	0.16785E-03	0.70762E-05
19	0.47660E 02	0.47660E 02	0.24414E-03	0.51225E-05
20	0.11070E 02	0.11070E 02	0.83923E-04	0.75812E-05
21	0.84840E 02	0.84840E 02	0.44250E-03	0.52158E-05
22	0.11870E 02	0.11870E 02	0.20027E-04	0.16872E-05
23	0.25080E 02	0.25080E 02	0.21362E-03	0.85177E-05
24	0.91200E 01	0.91200E 01	0.14305E-04	0.15685E-05
25	0.11004E 03	0.11004E 03	0.38147E-03	0.34666E-05
26	0.29470E 02	0.29470E 02	0.91553E-04	0.31066E-05
27	0.39290E 02	0.39290E 02	0.12207E-03	0.31069E-05
28	0.11800E 02	0.11800E 02	0.57220E-04	0.48492E-05
29	0.68580E 02	0.68580E 02	0.22888E-03	0.33374E-05
30	0.18310E 02	0.18310E 02	0.15259E-04	0.83336E-06
31	0.40810E 02	0.40810E 02	0.91553E-04	0.22434E-05
32	0.77500E 01	0.77500E 01	0.0	0.0

TABLE 35

Main Effects and Two-Factor Interaction Effects of Variables in the Second Series to Salt Rejection and Permeate Flux

	Salt Rejection					
Main Effect	X_1 4.7437	X_2 2.475	X_3 1.2119	X_4 -1.588	X_5 -1.1066	X_6 6.4762
Two-Factor Interaction Effect	X_1	-4.4644	-0.70875	0.9850	-2.0694	-3.2106
	-4.4644	X_2	-0.145	0.98125	-2.6169	0.0610
	-0.70875	-0.145	X_3	-0.2181	1.2563	-0.9638
	0.9850	0.98125	-0.2181	X_4	0.11375	0.7263
	-2.0694	-2.6169	1.2563	0.11375	X_5	-0.3394
	-3.2106	0.0619	-0.9638	0.7263	-0.3394	X_6

	Permeate Flux					
Main Effect	X_1 -25.057	X_2 -21.158	X_3 -0.90437	X_4 7.3606	X_5 -4.5506	X_6 -11.7450
Two-Factor Interaction Effect	X_1	12.752	-0.6675	-4.1138	1.887	9.3906
	12.752	X_2	-0.82437	-5.1394	-6.6731	8.0050
	-0.6675	-0.82437	X_3	4.5019	-4.3581	-3.0750
	-4.1138	-5.1394	4.5019	X_4	-5.1618	-1.3100
	1.8887	-6.6731	-4.3581	-5.1618	X_5	7.0149
	9.3906	8.0050	-3.0750	-1.3100	7.0149	X_6

The highest effect was observed in the TDI concentration. The higher level of the variable is being favored for higher rejection. Next in magnitude is the second variable of the PEI concentration. Again the higher level is being favored. Next in magnitude is the DPT concentration in the casting solution which is again favoring the lower level for greatest rejection. Next is the oven temperature, favoring the higher temperature and the polysulfone concentration, and as before, favoring the lower level.

Upon examination of the main effects of the variables toward the response of permeate flux, the signs are reversed in all cases except for that of the polysulfone concentration in the casting solution. In this case, the lower level of the polysulfone is being favored for both better rejection and better flux. The variable of highest magnitude is again the TDI concentration. A very strong leaning to the lower level for better flux is shown. Next in magnitude is the PEI concentration. These two effects are by far the largest ones observed and show the tremendous effect both have on the performance of the membrane. The magnitude of the effects for rejection is smaller than those for the flux mainly due to the fact that that the range in responses for the rejection was a great deal smaller than the range of permeate responses. A tremendous reduction in flux for only a few percent increase in rejection is immediately seen. The variable of next highest magnitude is that of the DPT concentration in the casting solution. Again, the effect of the DPT is to indeed increase the flux but at the expense of decreasing rejection. The variable of polysulfone is next, and the last is the oven temperature where only a very small effect is shown.

The two-factor effects for the salt rejection regression equation show first that all the two-factor effects for DPT are small (less than 0). DPT is interacting with the other variables only slightly in effecting rejection. The two-factor interaction effect of highest magnitude is that of TDI and PEI which suggests that the reaction of the two is dependent on the amounts of both variables supplied and in what ratio. The same holds true for the two-factor interactions for permeate flux. Again the PEI-TDI reaction and the amounts applied affect the resultant flux of the membrane. However, small interactions are observed for that of PEI and TDI with the oven temperature indicating that the range employed is quite good. The interactions that are confounded with variable 6 are all in all quite small. This is hoped for since one of the basic assumptions of factorial design is that the higher order interactions are negligible. The highest magnitudes are observed in the interaction of variable 6 and the five-factor interaction 12345. A major factor in this seems to be the interaction of 1 and 2 or TDI and PEI. However, variable 6 is seen to be affected by TDI more than PEI. It seems that the curing time establishes how completely the TDI reacts with the PEI in forming the salt barrier.

The following conclusions from this second series can be made:

1) The TDI concentration continues to play the dominant role in controlling the performance of the NS-100 membrane. The lower level of 0.2 percent is considered too low to effectively form the salt selective barrier, even with the high concentration of PEI used. Its overall effect on membrane performance is greatly determined by the variable of PEI.

2) The PEI concentration also continues to play a dominant role, along with the TDI concentration, in determining the performance of the membrane. The lower level of the variable, 1 percent, is considered too low for the formation of a good salt selective barrier, even with a high concentration of TDI. In fact, it is now thought that when a large concentration of TDI is applied with a somewhat small concentration of PEI, deterioration of the polysulfone pore structure results. For this reason, it is suggested that the lower level of this variable be raised somewhat for the next series of experiments.

3) It is now apparent that the oven temperature is not as important in determining salt rejection as originally thought. The effect of varying the temperature from 95° C to 115° C was very low for both the rejection and the flux of the membrane. This factor seems to show little interactions with the other factors. For this reason the optimum level of the variable is considered 115° C, as better salt rejection favors this level of the factor and only at the loss of very little flux.

4) The concentration of DPT in the casting solution once again favors the higher level for increase in flux and the lower level for best rejection. Very small interactions are observed with other factors in affecting salt rejection of the membrane; however, the main effect for salt rejection favors the lower level less than the factors of TDI and PEI alone. It is therefore suggested that the factor be set at the lower level of 0.2 percent for the next series of experiments. Whereas the DPT concentration does in fact act to increase the flux of the membrane in both cases of experiments now run, it does so at the expense of lost salt rejection. Because 99 percent rejection is the goal for optimization, it seems reasonable to drop the variable from further concern in this study.

5) The concentration of polysulfone in the casting solution again favors the lower level of 12 percent for both rejection and flux. However, in work undertaken so far, it has been noticed that the texture and continuity of the support film is much better at the higher level of 15 percent. Because of this fact, it is recommended that this variable again be used in the next series of experiments and at the same levels used in the first and second series of experiments.

6) The curing time was confounded with higher order interaction effects in this series and optimum analysis of the results is difficult. The lower level seems favored for best permeate flux and the higher level for best rejection. It is thought that the lower level of 2 minutes is just not sufficient for an optimum cure. Therefore, it is suggested that this variable be included for further study in which it would not be confounded and the lower level of the variable be raised somewhat.

The coefficients were supplied with the regression equations for the optimization computer program. The resultant optimized permeate flux for the constraint of 99 percent - rejection was predicted as 28 gfd at the following levels of the variables: TDI equal to 1.0 percent, PEI equal to 0.5 percent, oven temperature at 115° C, DPT concentration in the casting solution at 0.2 percent, polysulfone concentration in the casting solution

at 12 percent, and curing time at 2 minutes. Again, membranes cast under these conditions failed to give the predicted flux and rejection. However, the resultant prediction was considered far better than the first series as the combination of 3.5 percent PEI and 1.0 percent TDI was thought to be able to produce membranes of 99 percent rejection, although at a much greater reduced flux than predicted by the computer. A majority of the predicted high flux probably came from the prediction of 2 minutes for the curing time. This level of the factor of curing time had produced very large values of flux during testing. Also, some of the confounding suggested interaction effects higher than three which could not be safely neglected. It was now considered necessary to run yet another series, this time a full series, where all the possible combinations could be run and no confounding would result.

7.6 The Third Series of Designed Experiments

With two series of experiments already run and studied, four of the original eight variables have been dropped. Since the use of a surfactant as part of the treatment procedure lowers salt rejection considerably but increases flux only slightly, no surfactant use is now being followed. Also, from the first series of tests, the variable of TDI drainage time has been dropped due to the fact that little effect on either rejection or flux was being observed. From the second series two more variables were set and dropped from further investigation. The oven temperature had very little effect on salt rejection and interacted very minutely with the other factors. Therefore, the upper level, as predicted from the second series regression equations, of 115° C has been set as constant. Also, the DPT concentration of 0.2 percent has been established as a constant for further studies, the level again predicted as optimum by the second series regression equations. Thus, four remaining factors are of concern for this third series of experiments.

Understandably, with only four factors left, the total number of design experiments possible is now 2^4 or 16. With the number of necessary runs so small compared to previous designs and the fact that problems had arisen using the fractional designs, a full 2^4 factorial design was constructed and run. With this full design, no factors will be confounded and no assumptions of higher order interaction effects being negligible need to be made. The level of the variables still under study were set from the knowledge that was gained from the first two series of design experiments.

The TDI concentration was varied from a low level of 0.3 percent to an upper level of 1.0 percent. The lower level was raised from the 0.2 percent level used in the second series. The PEI concentration was varied from the lower level of 1.5 percent to the upper level of 3.5 percent. This was changed from the earlier levels of 1.0 and 5.0 percent. The optimized predicted PEI concentration from the second series of experiments had given this 3.5 percent value. Also, it was thought that the lower level of 1.0 percent used before was not sufficient to produce membranes capable of 99 percent employing the range of TDI concentrations now being studied. The curing time was varied from 4 minutes to 10 minutes, whereas the lower level

of 2 minutes had been used in the past. Even though the computer program had given 2 minutes as optimum, it was thought that this time of curing was not sufficient for production of good membranes. The polysulfone concentration in the casting solution was again varied from 12 to 15 percent. The constant of 1.7 mil thickness of the polysulfone support film was again used.

A list of the variables for this third series of experiments and their respective levels is given in Table 36. The design was then constructed and the experiments run. The design used and the resultant responses to rejection and flux are given in Table 37. The design is found simply by using the standard order for factorial designs. As can be seen the responses for salt rejection are finally approaching the desired level of 99 percent in almost all trials tested. This has been the goal of all designs employed so far and these results seem to signify that prior conclusions on variables and their effects have been right. The range in responses is now all over 94 percent and as high as 99.58 percent. The fluxes range from a high of 35.78 gfd to a low of 4.50 gfd. The data were then supplied to the coefficient computer program and the results tabulated and given in Table 38. The average salt rejection for all the responses was 98.415 percent and the average flux 12.92 gfd. As can be seen, all the main effects and interaction effects are now obtained without any confounding. The observed values, the calculated values using the regression equations, the difference, and the ratio of the difference to the observed values for both salt rejection and permeate flux are given in Table 39. As in previous design series, the ratios are in the 10^{-5} to 10^{-7} range indicating an excellent fit of the data to the regression equations.

The main and two-factor interaction effects are given in Table 40 for both salt rejection and permeate flux. Upon examining the main effects for salt rejection, it is immediately seen that they are all smaller than one. This signifies that the range in observed responses for rejection is now very small and that the range of the variables now being used for the trials is having only very small effects in changing the rejection of the membrane. The effect of greatest magnitude is now found to be the curing time in which the higher level of the variable is being favored for best salt rejection. Next in magnitude is the polysulfone concentration in the casting solution. Here for the first time, the higher concentration of the variable, 15 percent, is being favored for greatest rejection. Next in magnitude is the concentration of PEI where, as before, the higher level is being favored. Last in this series is the concentration of TDI where just as before the higher level is being preferred.

Upon examining the two-factor interaction effects, all are seen to be less than 1.0 and all are negative. This seems to point out the fact that the interactions are now very small in all cases and affecting rejection only slightly. Also, it shows that the various levels of the factors are now all in a good range and all acceptable for good rejection.

The three-factor interactions for salt rejection, listed in Table 31, are less than -0.16 and less than 0.1 in all but one case. Again, this is a good sign that the levels now in use are satisfactory for good rejection.

TABLE 36

Lower and Upper Levels of Variables Studied in the Third Series of Design Experiments

Variable	Lower Level (-)	Upper Level (+)
X_1 TDI concentration in hexane solution	0.3%	1.0%
X_2 PEI concentration in aqueous solution	1.5%	3.5%
X_3 Curing time	4 minutes	10 minutes
X_4 Polysulfone concentration in casting solution	12.0%	15.0%
Fixed Variables:		
No surfactant		
1.7 mils thickness		
115° C oven temperature		
1 minute drainage		
0.2% DPT concentration in casting solution		

TABLE 37

Experimental Conditions and Average Performance of NS-100 Membranes in Third Series of Design Experiments

Run No.	Level of the Variable X_1	X_2	X_3	X_4	Salt Rejection (%)	Permeate Flux (gfd)
1	-	-	-	-	94.81	35.78
2	+	-	-	-	97.57	11.04
3	-	+	-	-	98.15	17.95
4	+	+	-	-	98.47	4.63
5	-	-	+	-	98.50	19.58
6	+	-	+	-	97.81	10.40
7	-	+	+	-	99.10	13.24
8	+	+	+	-	99.58	4.85
9	-	-	-	+	99.25	15.35
10	+	-	-	+	98.68	8.28
11	-	+	-	+	98.48	17.18
12	+	+	-	+	99.06	4.50
13	-	-	+	+	98.98	16.53
14	+	-	+	+	99.17	7.84
15	-	+	+	+	98.93	14.30
16	+	+	+	+	98.12	5.20

TABLE 38

Coefficients of the Regression Equations for Salt Rejection and Permeate Flux for the Third Series

Coefficient		Salt Rejection (%)	Permeate Flux (gfd)
1	0	0.98415E 02	0.12916E 02
2	1	0.14250E 00	-0.58251E 01
3	2	0.32125E 00	-0.26844E 01
4	3	0.35629E 00	-0.14231E 01
5	4	0.41634E 00	-0.17681E 01
6	12	-0.71250E-01	0.38687E 00
7	13	-0.24375E 00	0.14031E 01
8	14	-0.21625E 00	0.11306E 01
9	23	-0.16000E 00	0.58938E 00
10	24	-0.50500E 00	0.18319E 01
11	34	-0.39249E 00	0.12431E 01
12	123	0.89999E-01	-0.33937E 00
13	124	0.87501E-01	-0.11394E 01
14	134	0.16750E 00	-0.11581E 01
15	234	0.73750E-01	-0.95437E 00
16	1234	-0.36125E 00	0.98937E 00

TABLE 39

Observed and Calculated Salt Rejection and Permeate Flux in the Third Series

Salt Rejection

NO	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.94810E 02	0.94810E 02	0.32043E-03	0.33798E-05
2	0.97570E 02	0.97570E 02	0.30518E-03	0.31278E-05
3	0.98150E 02	0.98150E 02	0.32043E-03	0.32647E-05
4	0.98470E 02	0.98470E 02	0.30518E-03	0.30992E-05
5	0.98500E 02	0.98500E 02	0.25940E-03	0.26335E-05
6	0.97810E 02	0.97810E 02	0.25940E-03	0.26521E-05
7	0.99100E 02	0.99100E 02	0.24414E-03	0.24636E-05
8	0.99580E 02	0.99580E 02	0.25940E-03	0.26049E-05
9	0.99250E 02	0.99250E 02	0.16785E-03	0.16911E-05
10	0.98680E 02	0.98680E 02	0.16785E-03	0.17009E-05
11	0.98480E 02	0.98480E 02	0.15259E-03	0.15494E-05
12	0.99060E 02	0.99060E 02	0.19836E-03	0.20025E-05
13	0.98960E 02	0.98960E 02	0.15259E-04	0.15419E-06
14	0.99170E 02	0.99170E 02	0.61035E-04	0.61546E-06
15	0.98930E 02	0.98930E 02	0.15259E-04	0.15424E-06
16	0.98120E 02	0.98120E 02	0.15259E-04	0.15551E-06

Permeate Flux

NO	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.35780E 02	0.35780E 02	0.18311E-03	0.51175E-05
2	0.11040E 02	0.11040E 02	0.95367E-06	0.86384E-07
3	0.17950E 02	0.17950E 02	0.12207E-03	0.68006E-05
4	0.46300E 01	0.46300E 01	0.95367E-06	0.20598E-06
5	0.19580E 02	0.19580E 02	0.12207E-03	0.62344E-05
6	0.10400E 02	0.10400E 02	0.57220E-05	0.55020E-06
7	0.13240E 02	0.13240E 02	0.35286E-04	0.26651E-05
8	0.48500E 01	0.48500E 01	0.19073E-05	0.39327E-06
9	0.15350E 02	0.15350E 02	0.10872E-03	0.70827E-05
10	0.82800E 01	0.82800E 01	0.95367E-06	0.11518E-06
11	0.17180E 02	0.17180E 02	0.61035E-04	0.35527E-05
12	0.45000E 01	0.45000E 01	0.95367E-06	0.21193E-06
13	0.16530E 02	0.16530E 02	0.61035E-04	0.36924E-05
14	0.78400E 01	0.78400E 01	-0.28610E-05	-0.36493E-06
15	0.14300E 02	0.14300E 02	0.18120E-04	0.12671E-05
16	0.52000E 01	0.52000E 01	-0.57220E-05	-0.11004E-05

TABLE 40

Main Effects and Two-Factor Interaction Effects of Variables to Salt Rejection and Permeate Flux in the Third Series

	Salt Rejection			
	X_1	X_2	X_3	X_4
Main Effect	0.1425	0.32125	0.35629	0.41634
Two-Factor Interaction Effect	X_1	-0.07125	-0.24375	-0.21625
	-0.07125	X_2	-0.16	-0.505
	-0.24375	-0.16	X_3	-0.39249
	-0.21625	-0.505	-0.39249	X_4

	Permeate Flux			
	X_1	X_2	X_3	X_4
Main Effect	-5.8231	-2.6844	-1.4231	-1.7681
Two Factor Interaction Effect	X_1	0.38687	1.4031	1.1306
	0.38687	X_2	0.58938	1.8319
	1.4031	0.58938	X_3	1.2431
	1.1306	1.8319	1.2431	X_4

Also, it can be seen that the signs are reversed in all cases when the factors for flux and rejection are compared. The analogy that increased rejection is only accomplished at the expense of reduced flux is again being borne out. The magnitude of the factors for permeate flux are again seen to be higher than those of rejection. As mentioned in the past discussions of results, this is due to the greater range of responses in flux which were observed for the various combinations of the factors. However, this now seems acceptable since the range in rejections has been cut to the 94 percent and over range. The highest magnitude of the factors is observed to be that of the TDI where again the best flux is observed at the lower level of the factor. Next in order is the PEI concentration, the curing time, and finally the polysulfone concentration in the casting solution. The two-factor interactions are seen to be of smaller magnitude than the main effects except for the interaction effect of the PEI concentration and the curing time. The PEI is seen to have little effect with both the TDI and polysulfone in affecting the flux, but it is evident that the curing time is interacting with the PEI concentration. The reason for this is still not clear. However, in all the interactions of the curing time with the other factors, the magnitude of the interaction is greater than one. The curing time is indeed playing a definite role in establishing both the rejection and the flux of the membrane. The three-factor interaction effects are again seen as small when compared to both the main and two-factor effects.

With these optimistic responses, the regression equations were fed into the optimization program and the resultant optimum calculated. The result was the prediction of 21.8 gfd for a set rejection of 99 percent. The predicted levels of the variables were to use 0.3 percent TDI, 1.5 percent PEI, 15 percent polysulfone in the casting solution and a curing time of 10 minutes. This corresponded to run number 13 in the third series of experiments where the recorded response was 98.96 percent rejection at a flux of 16.53. Membranes of this configuration were made in the laboratory and tested. Of the six membranes tested, the average rejection was again 98.96 percent but the flux was 14.73 gfd. However, the range of values was quite discouraging. The rejection varied from 97.73 to 99.4 percent and the flux from 12.91 to 18.33 gfd. The membrane was not reproducible and investigation of prior tests seemed to indicate that a more realistic value of rejection was around 97.5 percent and at a higher flux. Additional tests were then run where six membranes were cast using the predicted optimum levels; only the curing time was varied so that three were run at 7 minutes and three at 10 minutes as predicted. Again, the responses were not reproducible. No noticeable difference in either flux or rejection was observed with the change in curing time. The averages were 18.89 gfd at a rejection of 98.87 percent for the membranes using 7 minutes and 18.46 gfd at a rejection of 98.79 percent using 10 minutes.

It was obvious that although not verifying the predicted optimum, membranes cast using this optimum were very close to predicted values. The greatest concern, however, was that the membranes were not reproducible. A growing fear was that the response recorded in the third series for trial 13 was incorrect due to some outside experimental error. However, before reaching this conclusion a new set of tests were run in which the TDI

concentration was varied from 0.25 to 0.35 percent, the PEI concentration varied from 1.25 to 1.75 percent, and the curing time varied from 5 to 15 minutes. The results and the levels used are given in Table 41. As can be seen from the responses, the level of 99 percent rejection was not reached although most of the responses were in the 98 percent plus range. These results indicated that the levels of 1.5 and 0.3 percent were in actuality too low to produce membranes of 99 percent rejection. Also, it now seems obvious that in order to attain the 99 percent level, a great deal of flux will have to be sacrificed. If the level of desired rejection is lowered to 97 percent, a guaranteed flux of from 20 to 30 gfd can be safely made. With these facts in mind, the following conclusions can now be made from the third series of design experiments:

1) The levels of the TDI concentration, combined with the levels of the PEI concentration have given membranes capable of producing from 95 to 99.5 percent rejection of salt.

2) The curing time has been seen to be of some importance from this third series but independent tests carried out which varied the curing time from 5 to 15 minutes have given responses indicating that the flux and salt rejection are changed only slightly. It is reasonable to assume that the time of 10 minutes is adequate with a possible range of 7 to 10 minutes being acceptable without affecting the performance of the membrane.

3) The polysulfone concentration in the casting solution still favors the lower level for greatest flux, but for the first time it favors the higher concentration for the best salt rejection. Based on the prior tests and the experience gained over the period of study, the use of the 15 percent concentration seems best. Handling is much better accomplished with this higher level of the variable; however, it seems reasonable to assume that either concentration used in the range studied will form a support film adequate to produce membranes of 99 percent rejection.

4) Reproducibility of responses of the membranes has been found to be quite difficult. Because of the large number of steps involved in producing a membrane, and with the equipment available for such fabrication in the laboratory, this problem seems to be almost unsolveable.

5) It seems evident that the final series of experiments using factorial design should now contain only two variables, that of PEI and TDI concentrations.

6) In order to improve reproducibility, new variables previously thought unimportant should be reexamined and studied.

7.7 The Fourth Series of Designed Experiments

With the wealth of information now available, the final factorial design was constructed. One factor or variable found to be of possible help in solving the overall optimization problem which had been excluded from past work was the utilization of a 2 percent dimethyl formamide solution in

TABLE 41

Levels of the Variables and Responses Observed for Verification of Third Series Predicted Optimum Performance

Variables	Lower Level (-)	Upper Level (+)
X_1 - TDI	0.25%	0.35%
X_2 - PEI	1.25%	1.75%
X_3 - Cure time	5 minutes	15 minutes

Experimental Design X_1	X_2	X_3	Rejection (%)	Flux (gfd)
-	-	-	96.55	33.29
+	-	-	97.53	27.11
-	+	-	98.49	17.24
+	+	-	98.45	19.96
-	-	+	98.00	25.45
+	-	+	98.76	24.15
-	+	+	98.24	20.68
+	+	+	98.10	13.04

Fixed Variables:

115°C Oven temperature

15% Polysulfone

0.2% DPT

No surfactant

1 minute TDI drainage

No DNF to gel polysulfone

the gelling of the polysulfone film. Because it was now felt that the levels of the variables of PEI and TDI were acceptable for possible production of 99 percent rejecting membranes, the effect of adding this variable to see its effect on performance was thought advantageous. Therefore, a 2^3 factorial design was constructed and is shown in Table 42. The levels of the variables studied are given in Table 43. The TDI concentration was again varied from 0.3 to 1.0 percent, the PEI from 1.5 to 3.5 percent and the new qualitative variable from the levels of no use to use in the casting procedure. In this series, the responses vary even less in total range than in the previous series but, unfortunately, the fluxes are somewhat decreased from the previous trials. The rejection range is now from 97.53 to 99.53 percent or a difference of 2.0 percent rejection for the entire series. Three of the responses are over 99 percent, and two others very close to that level.

The resultant coefficients and the observed versus calculated values for both rejection and flux are given in Table 44. Again, the data seem to fit the regression equations very well. The main and two-factor effects for both rejection and flux are given in Table 45. As in the previous series, all the rejection main effects are positive and all the flux main effects are negative. The effect of largest magnitude is the PEI concentration for its effects on salt rejection. Next is the use of DMF in the casting procedure and last the TDI concentration. The two-factor interaction effects are all smaller than the main effects and only the interaction of PEI and DMF is greater than 0.1. DMF is thought to change the surface characteristics of the polysulfone support film during casting. This interaction seems to bear this fact out since the PEI is interacting strongest with this variable. The TDI would be expected to show less of an effect because the PEI is applied to the support film first. This fact is borne out in the resulting effects.

Upon examining the permeate flux main effects, it is seen that the TDI main effect has the highest magnitude, again signifying that the level of TDI greatly affects the flux of the membrane. Next in order is the PEI concentration, and last the DMF variable. Again, the greatest two-factor interaction is observed in the interaction of the PEI concentration and the use of DMF. The use of DMF thus seems to increase rejection while slightly lowering the flux of the membrane.

The following conclusions thus seem reasonable to draw from this fourth series of design experiments:

1) Using a 2 percent DMF solution during the casting procedure is definitely worthwhile for obtaining the desired level of 99 percent rejection and above. The flux decreases only slightly.

2) The lower combination of PEI and TDI is not sufficient to produce a membrane of 99 percent rejection and thus the reported response in previous trials for this combination was either a special case or a definite experimental error.

3) The upper combination of TDI and PEI is very capable of producing

TABLE 42

Experimental Conditions and Observed Responses for the Fourth Series of Design Experiments

Run No.	X_1	X_2	X_3	Salt Rejection (%)	Permeate Flux (gfd)
1	-	-	-	97.53	13.37
2	+	-	-	98.32	8.65
3	-	+	-	98.81	9.44
4	+	+	-	99.13	3.40
5	-	-	+	98.66	12.40
6	+	-	+	98.92	6.12
7	-	+	+	99.02	8.82
8	+	+	+	99.53	4.45

TABLE 43

Levels of the Variables Studied in the Fourth Series of Design Experiments

Variable		Lower Level (-)	Upper Level (+)
X_1	TDI concentration in hexane solution	0.3%	1.0%
X_2	PEI concentration in aqueous solution	1.5%	3.5%
X_3	2.0% DMF solution used in casting procedure	No	Yes
	Fixed Variables:		
	15% polysulfone		
	115°C oven temperature		
	10 minute curing time		
	0.2% DPT		
	1 minute TDI drainage		
	No surfactant		
	1.7 mils thickness		

TABLE 44

Coefficients of the Regression Equations for Salt Rejection and Permeate Flux and Observed Versus Calculated Values

Coefficient	Salt Rejection	Permeate Flux
0	0.98740E 02	0.83312E 01
1	0.23500E 00	-0.26762E 01
2	0.38250E 00	-0.18037E 01
3	0.29254E 00	-0.38374E 00
12	-0.27500E-01	0.73750E-01
13	-0.42496E-01	0.13750E-01
23	-0.14000E 00	0.49125E 00
123	0.90000E-01	0.40375E 00

Salt Rejection

NO	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.97530E 02	0.97530E 02	0.18311E-03	0.18774E-05
2	0.98320E 02	0.98320E 02	0.16785E-03	0.17071E-05
3	0.98810E 02	0.98810E 02	0.16785E-03	0.16987E-05
4	0.99130E 02	0.99130E 02	0.18311E-03	0.18471E-05
5	0.98660E 02	0.98660E 02	0.76294E-04	0.77330E-06
6	0.98920E 02	0.98920E 02	0.76294E-04	0.77127E-06
7	0.99020E 02	0.99020E 02	0.76294E-04	0.77049E-06
8	0.99530E 02	0.99530E 02	0.76294E-04	0.76654E-06

Permeate Flux

NO	OBSERVED	CALCULATED	DIFFERENCE	RATIO
1	0.13370E 02	0.13370E 02	0.24796E-04	0.18546E-05
2	0.86500E 01	0.86500E 01	0.14305E-04	0.16538E-05
3	0.94400E 01	0.94400E 01	0.14305E-04	0.15154E-05
4	0.34000E 01	0.34000E 01	0.38147E-05	0.11220E-05
5	0.12400E 02	0.12400E 02	0.95367E-05	0.76909E-06
6	0.61200E 01	0.61200E 01	-0.95367E-06	-0.15583E-06
7	0.88200E 01	0.88200E 01	0.47684E-05	0.54063E-06
8	0.44500E 01	0.44500E 01	-0.57220E-05	-0.12859E-05

TABLE 45

Main Effects and Two-Factor Interaction Effects for Salt Rejection and Permeate Flux in the Fourth Series

	Salt Rejection		
	X_1	X_2	X_3
Main Effect	0.235	0.3825	0.29254
Two-Factor Interaction Effects	X_1	-0.0275	-0.042496
	-0.0275	X_2	-0.14
	-0.042496	-0.14	X_3

	Permeate Flux		
	X_1	X_2	X_3
Main Effect	-2.6762	-1.8037	-0.38374
Two-Factor Interaction Effects	X_1	0.07375	0.01375
	0.07375	X_2	0.49125
	0.01375	0.49125	X_3

a membrane of 99 percent plus rejection; however, the flux is decreased substantially.

4) A range of possible levels of PEI and TDI that will indeed produce membranes of good performance now seems reasonable. The purpose of this study has therefore been substantially obtained.

The regression equations were then supplied to the optimization program and the predicted optimum flux obtained. The predicted value was 9.02 gfd at a set rejection of 99 percent. The corresponding levels of the three variables were 0.33 percent TDI, 3.26 percent PEI, and the use of the 2 percent DMF solution during the casting procedure. The response most closely associated with this optimum point is the response of run number 7 in the fourth series, where the rejection was 99.02 percent at a flux of 8.82 gfd. This seems to indicate that the predicted point is indeed reproducible. Membranes were then cast using the predicted values of the optimization program. The average of 9 membranes was 9.64 gfd at 98.97 percent rejection. The predicted value of the computer program is finally reproducible in the laboratory.

7.8 Results and Discussion

With the experimental series of tests now complete and the final prediction of the optimization program verified, certain aspects of this study need to be further expounded on. Because few or no prior studies on the NS-100 membrane are in print and the test conditions used by North Star in their optimization studies differ from those used in this study, no numerical comparisons between the results of this study and those of North Star can be made. However, observations made throughout this study need to be further discussed.

The use of factorial design brought out certain aspects of the NS-100 fabrication that would not have been observable otherwise. Originally, 8 variables were considered. The wealth of experiments necessary to fully analyze these variables would have been so excessive that a final optimized procedure might never have been found. Factorial design allows the possibility of examining all these variables independently and with a great deal of time and expense saved. Not only is this form of analysis a timesaver, but also a statistically advantageous method of finding the true optimum response from a set of many variables. This method is indeed quite adaptable to many industrial and chemical problems. However, it should be strongly noted that for this method to work acceptably, extreme care is necessary in selecting not only the variables of concern but their levels of magnitude as well. Without prior knowledge of how these variables are acting to affect the response of a process, misleading conclusions can be easily made. The responses of the variables of concern must be continuous and smooth; the two major requirements of a successful factorial design. In this study, a variable was included late in the experiments that indeed had a major effect on both the rejection and flux of the membrane. However, it was introduced to the study after all but two of the variables had been dropped. This sort of procedure is not recommended simply because additional variables added after studies have already begun and progressed may indeed interact

substantially with variables already dropped. In this case, the introduction of the variable of using DMF in the casting procedure produced results that would have led to its inclusion in the fabrication procedure, even if it had been included from the beginning of the test series.

Concerning the membrane itself, many observations can be made. The primary point observed is that of the great loss of flux at the expense of an increase in rejection from 97 to 99 percent plus rejection. During these tests, membranes were found that could deliver more than 20 gfd permeate flux if the rejection desired was lowered from 99 to 97 percent. The optimized flux for 99 percent rejection was 9.64 gfd. In other words, more than half the flux is sacrificed for an increase of 2 percent in rejection. TDI and PEI are clearly the variables that principally dominate the performance of the NS-100 membrane. Membranes using as little as 1.5 percent PEI and 0.3 percent TDI were observed to give fluxes as high as 18 gfd at rejections of close to 99 percent. However, these membranes were unfortunately not reproducible and in some cases gave rejections as low as 97 percent. If the PEI concentration is raised to the 3.0 to 3.5 percent range, membranes giving fluxes of about 10 gfd at 99 percent rejection are obtainable and reproducible. The curing temperature seems to be in a fairly short range for production of suitable membranes. The currently used level of 115° C is considered optimum, however, a range of 110° C to 120° C seems acceptable with no serious side effects on membrane performance.

The use of DPT deserves special attention. DPT, the additive suggested for increased flux, indeed does accomplish this fact. However, the results of this study indicate that it does so at the expense of lost rejection. It was dropped as a variable for this reason and given its lower level of 0.2 percent. If this study were undertaken again, with the knowledge now available, this variable would have been omitted and included only after the membrane had been optimized. Because of the primary goal of 99 percent rejection in this study, this variable had to be dropped. In actuality, after the 99 percent level has been obtained, the use of a higher concentration of DPT could indeed succeed in raising the flux of the optimized membrane by as much as 5 percent. If the resultant loss in rejection is offset by the increase in flux, the use of this higher concentration of DPT could be warranted. For this study's purpose, the level of 0.2 percent is recommended.

The polysulfone concentration also deserves special attention. Original tests suggested that the use of 12 percent polysulfone in the casting solution both increased flux and rejection more than the use of 15 percent polysulfone. However, from laboratory experience it was seen that the 15 percent solution produced support films of better continuity and strength. If this point is neglected, a solution of between 12 and 15 percent polysulfone will produce membranes of the desired rejection with the use of the smaller concentration probably giving some additional flux. However, if 99 percent or greater is completely necessary, the level of 15 percent is recommended.

The curing time, if kept between 7 and 10 minutes, will produce acceptable membranes. It is very difficult to assign a definite level of this variable because the difference of a few minutes seems to have little effect on the total performance of the membrane. For this study's purpose, 10 minutes is assigned as optimum where in true fact the previously

mentioned range of 7 to 10 minutes will give good membranes.

The use of a 2.0 percent DMF solution to get the polysulfone during casting resulted in obtaining the 99 percent rejection goal of this study. It seems to act to effectively change the surface of the polysulfone support film and help in coating the PEI more effectively. It is strongly recommended for the fabrication procedure of the membrane.

The variables of TDI drainage time and surfactant were seen early in the experiments as having little effect in increasing the rejection of the NS-100 membrane. The surfactant used to allow the polysulfone support film to be treated with PEI and TDI seemed to lower rejection and therefore, for the purpose of this study, is not recommended for inclusion in the fabrication procedure. The TDI drainage time is considered substantial at the level of one minute and was left at this level for all the trials run except for the first series of design experiments. The procedure for treatment of application of PEI for one minute, drainage for one minute, TDI for one minute and drainage for one minute is recommended.

Thus the study has produced its goal of an optimized NS-100 membrane for rejection of a 5000 ppm solution of salt. Results have verified that at an operating pressure of 600 psig and a flow rate of 0.3 gpm, a flux of 9.64 gfd at 99 percent rejection can be obtained.

8. RESISTENCE OF NS-100 MEMBRANE TO OXIDANTS

In a preliminary study (Chian and Fang, 1974c), the salt rejection by NS-100 membrane was shown to drop drastically from 99% to 60% after soaking the membrane in an aqueous solution containing 4 ppm of residual chlorine for two days. As a result of this preliminary study, a more extensive study of the resistance of NS-100 membrane to oxidants seemed warranted. A series of tests has therefore been conducted for this purpose. Three strong oxidants, including chlorine, ozone and chromate, were selected for testing the NS-100 membrane.

8.1 Resistence to Chlorine

Chlorine has been widely used in municipal water supplies and waste treatment for disinfection. Hence, residual chlorine is expected to be found in tap water as well as in the effluent from sewage treatment plants. Testings of chlorine resistance of the NS-100 membranes were conducted as follows:

Membranes were first soaked in water containing various amounts of chlorine over a period of 10-24 hrs. Each membrane was then tested with 5,000 ppm of sodium chloride at 600 psi and 25°C. The average performance over a test period of 24 hrs for each concentration of chlorine is shown in Table 46. It is seen from Table 46 that increasing the concentration of chlorine residual causes the average flux to increase and the salt rejection to decrease. This clearly indicates a deterioration of the NS-100 membrane. The deterioration is probably attributable to the reaction of chlorine to the amine and/or imine groups of the crosslinked polyethylenimine skin layer on the surface of NS-100 membrane. A similar reaction to the amine groups also results in poor chlorine tolerance by the aromatic polyamide membrane, e.g., the membrane material used in the duPont's B-9 and B-10 permeators.

In order to protect the NS-100 and aromatic polyamide membranes from attack by chlorine, a short section of activated carbon column is recommended to precede these membranes for the removal of residual chlorine. Activated carbon has been found to be very effective in dechlorinating drinking water.

8.2 Resistance to Ozone

Ozone has a higher oxidation potential than chlorine and has gradually found its application in tertiary treatment of wastewater. The combination of ozonation and reverse osmosis for MUST wastewater treatment calls for the study on the resistance of NS-100 membrane toward ozone residual.

The same procedures for testing chlorine resistance were employed for the ozone tests. It is seen from Table 47 that the NS-100 membrane showed a slight deterioration when exposed to water containing ozone residue.

TABLE 46

Performance of NS-100 Membranes After Soaking in Aqueous Solutions Containing Chlorine Residual

concentration of chlorine (ppm)	time of soaking (hr)	No. of membranes	average performance flux (gfd)	average performance rejection (%)
0	24	3	7.76	98.45
0.1	24	2	9.78	89.78
0.5	24	3	12.15	86.62
2.0	24	2	16.82	79.83
5.0	24	2	23.85	71.10

TABLE 47

Performance of NS-100 Membranes After Soaking in Aqueous Solution Containing Ozone Residual

concentration of ozone (ppm)	time of soaking (hr)	No. of membranes	average performance flux (gfd)	average performance rejection (%)
0	24	3	7.76	98.45
0.1	24	2	11.46	93.32
0.5	14	2	9.11	97.83
2.0	10	2	11.04	94.69
5.0	10	2	8.40	96.55

However, there was no definite trend in membrane deterioration as the concentration of ozone increased. The lack of correlation is also attributed to the varying time period employed in these tests due to the experimental difficulty in maintaining high ozone concentration unattended.

8.3 Resistance to Chromate

Chromate is a very effective corrosion inhibitor; hence, it is an additive widely used in cooling water. Because of its toxicity (the maximum level in an effluent is 0.05 ppm according to EPA regulations) chromate needs to be removed from cooling tower blowdown prior to discharging into the receiving stream. Reverse osmosis has been found to be a useful method for the separation of chromate. Accordingly, sodium chromate was selected as the third oxidant for this study.

Three NS-100 membranes were tested with a 5,000 ppm sodium chloride solution at 600 psi and 25°C. After 24 hrs of initial testing, doses of sodium chromate were added to the test solution. The concentration of sodium chromate was increased from 20 ppm to 500 ppm, the latter being a concentration about ten times higher than that normally found in circulating cooling water. Membranes were tested under pressure for 24 hrs at each concentration. The performance of each membrane as shown in Table 48 indicates that NS-100 membranes showed no sign of deterioration when the concentration of sodium chromate was increased from zero to 500 ppm over a testing period of six days.

TABLE 48

Performance of NS-100 Membranes when Tested with a 5,000 ppm Sodium Chloride Solution Containing Sodium Chromate

concentration of sodium chromate (ppm)	membrane 1 flux (gfd)	membrane 1 rejection (%)	membrane 2 flux (gfd)	membrane 2 rejection (%)	membrane 3 flux (gfd)	membrane 3 rejection (%)
0.0	7.72	99.63	7.72	99.34	9.84	92.29
20.0	8.70	99.34	10.75	98.87	10.14	92.92
50.0	8.58	99.63	9.95	99.20	10.24	92.62
100.0	8.11	99.60	8.63	99.21	10.24	92.62
200.0	7.49	99.66	8.97	99.30	10.15	93.17
500.0	7.15	99.71	8.08	99.29	9.79	93.34

9. METHODS FOR MINIMIZING MEMBRANE FOULING

Membrane fouling is a common cause of poor performance in reverse osmosis systems, especially when treating wastewaters, because it reduces the product water flux to uneconomical levels. In most cases, a decrease of membrane flux results in an increase in solute separation due to the formation of a slimy gel layer which itself serves as a secondary skin layer to enhance the membrane separation process. However, it is not uncommon that fouling was sometimes associated with a decrease of solute separation because of the resulting deterioration of the membranes. A way to avoid or correct such situations is to pretreat the waste to remove potential fouling constituents in waters, to use additives to complex with such constituents contributing to membrane fouling, and to restore membrane performance with appropriate cleaning procedures on a periodic basis.

Although research and development of the reverse osmosis process has been mainly for water treatment purposes, increasing efforts have been made in applying the process to wastewater treatment. Because of the high organic loading in wastewater, such as the MUST hospital wastes, a major problem has arisen in using reverse osmosis for waste treatment. This is the plugging of the membrane and consequent decline of the product water flux.

9.1 Pretreatment of Wastewaters

Most of the membranes evaluated so far for treating sewage effluents are cellulose acetate base. These membranes have been shown to perform satisfactorily for extended periods at reasonable flux-decline rates in both spiral-wrap and tubular configurations. Little information is available on the use of the hollow-fiber configuration with other types of membranes for treating sewage effluents. For purely steric arguments, the system with the largest dimension for flow should have the least problems with a high turbidity feed, since it would be less likely to have its hydrodynamic flow obstructed or plugged in the flow channel. The use of a simple membrane or ultra filtration for the removal of turbidity would serve the purpose of pretreating wastes prior to feeding to the hollow-fiber modules. One of the obvious advantages of the hollow-fiber configuration is its capability of processing a larger volume of wastes as compared to other configurations having the same spacial volume. However, requirements of bulky pretreatment systems prior to the hollow-fiber module may offset some of the advantage of volume efficiency with the hollow-fiber configuration. Trade-off between volume requirements and cost is necessary to fully assess any membrane configuration.

In general, an extensive pretreatment of wastewater will not only increase membrane flux but also reduce the need for membrane cleaning to a minimum. Figure 35 depicts various methods available for pretreatment for the reverse osmosis process as applied to wastewater renovation. There are three approaches which have been practised in the field. The first

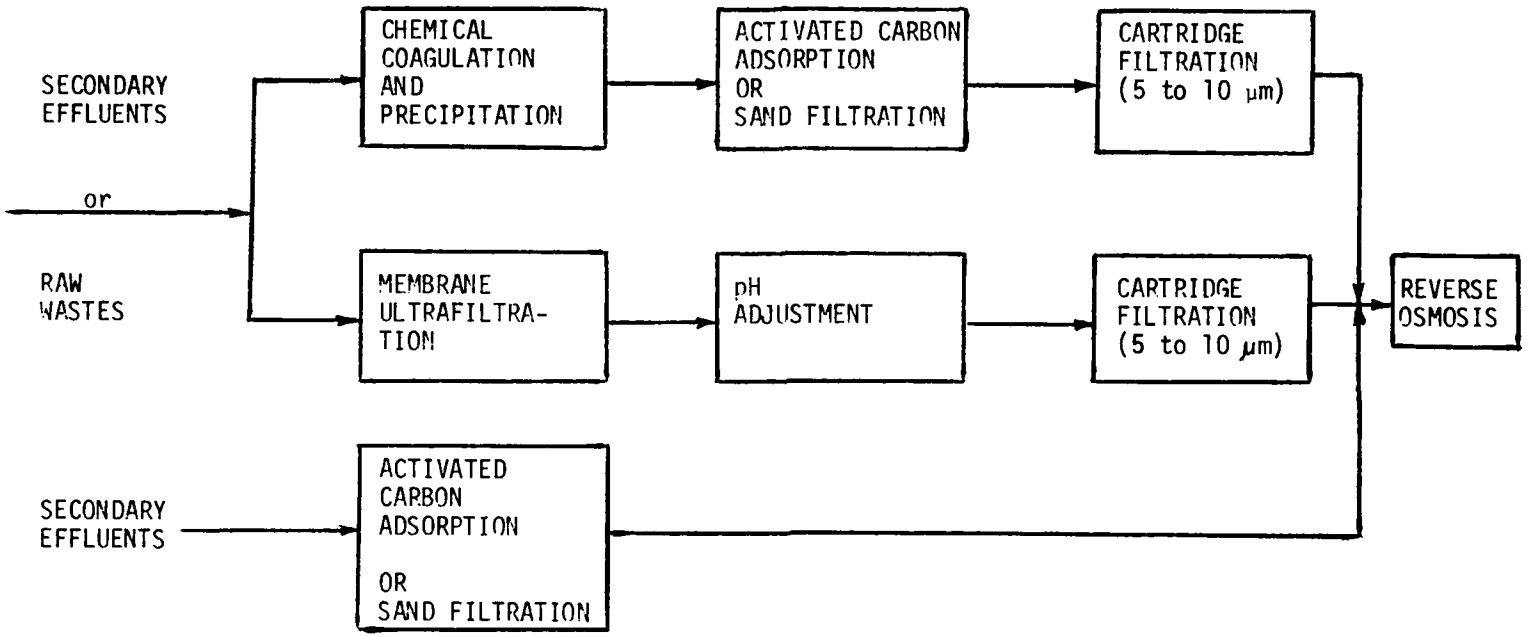

Figure 35 Pretreatment for Reverse Osmosis Process

approach involves a large amount of pretreatment with little or no membrane cleaning required. This could mean clarification with chemical coagulant and pH control followed by activated carbon adsorption and final polishing with 5 or 10 μm filter cartridges. An alternative of this could mean membrane ultrafiltration followed by pH adjustment and 5 or 10 μm filter cartridge. The former is typical for treatment of secondary effluents and the latter for raw wastes, such as cheese whey and MUST hospital wastes. The second approach is to eliminate one or more of the processes in the train described above with chemical precipitation and include periodic membrane cleaning at a somewhat higher level than required for the first approach. The last approach is to filter the feed using either activated carbon or sand columns before the reverse osmosis process and, depending on the constituents of the feed, to adjust the membrane cleaning frequency and intensity as needed.

9.2 Membrane Cleaning Techniques

Several approaches have been used in attempts to reduce the rate of flux-decline in systems treating municipal effluents and industrial wastes. Table 49 gives a summary of these techniques.

The early studies with the spiral wound and tubular modules were moderately successful in maintaining fluxes with daily air-water flushes at low pressure (Merten and Bray, 1966). Initial studies with citric acid and an anionic detergent solution proved unsuccessful in arresting flux-decline in the flat plate unit (Smith *et al.*, 1970). Periodic cleaning (approx. 1 every 10 days) with an enzyme active presoak solution (BIZ) was successful in holding the flux fairly constant for tubular modules with a carbon treated secondary effluent (Belfort *et al.*, 1973). Other studies on a similar treated feed solution, but with the spiral wound modules, used daily air and water flushes and weekly flushes with a solution of 10,000 mg/ℓ of an enzyme presoak product (Nusbaum *et al.*, 1970). They were also able to maintain a fairly low flux-decline. Later, another group at UOP (Cruver *et al.*, 1972) showed that sodium perborate, EDTA and BIZ flushes all restored the flux to 80-85% of the initial values. Each additive gave approximately equal results. One of the problems with the applications of these flushes is that their pH is usually dangerously high (> 9) for the cellulose acetate membrane. Using the UOP tubular units, raw sewage is successfully being treated by reverse osmosis in San Diego. The flux-decline rate is arrested by precoating the membrane every 8 hours under pressure with diatomaceous earth, powdered activated carbon and a surface active agent (CT, 1971). What is probably happening is that the precoat is protecting the membranes from fouling. One disadvantage may be the abrasiveness of the precoat which may reduce the life-time of the membranes. Most systems operating with tubular modules have used the foam swab flushing technique. A disadvantage is that any abrasive material adhering to the swab could appreciably damage the membrane. Two reverse osmosis tubular pilot plant studies with river water as feed have successfully maintained fluxes by using daily depressurization, washing with HCl (pH = 3) and foam

TABLE 49. Membrane Cleaning Techniques for Reverse Osmosis

Technique	Method	Description
1. Physical	(a) Mechanical	foam ball swabbing
	(b) Hydrodynamical	tangential velocity variation turbulence promoters
	(c) Reverse Flow	depressure and reverse flow (osmotic)
	(d) Air/Water Flushing	daily 15 min. depressurized flush
	(e) Sonication	Ultrasonic cleaning & wetting agent
2. Chemical	(a) Additives to feed	pH control to reduce hydrolysis and scale deposit 5 ml/gal of 5% NaClO at pH 5 friction reducing additives (polyetheleneglycol) soil dispersants (sodium silicate)
	(b) Flushing with additives at low pressure	complexing agents (EDTA, Sodium hexa-metaphosphate) oxidizing agents (citric acid) detergents (1% BIZ) percoat (diatomaceous earth, activated carbon and surface active agent high concentration of NaCl (18%)
3. Membrane	(a) Membrane Replacement	in-situ membrane replacement
	(b) Inorganic membranes	bio-growth for protection
	(c) Active insoluble enzymes attached to membrane	degradation of fouling film
	(d) Polyelectrolyte membranes	composite membranes dynamic layer technique

ball flushing (Kuiper *et al.*, 1973) and by using detergent flushing and foam swabbing (Miller, 1973). Experiments at Harwell, U.K., using glass wool filtered secondary effluent,was disappointing with respect to the effectiveness of cleaning methods in reducing flux-decline. After 2000 hours the product flux fell by more than 50% with a fairly constant rejection. Attempts to restore the flux by flushing or wiping the membrane surface were largely unsuccessful (Eden *et al.*, 1970). The sponge ball technique has also successfully been used for industrial feeds with high suspended solids (Cohen and Loeb, 1973). Thus, from Table 49 the most common membrane cleaning techniques for reverse osmosis are: 1(a) and 2(b) or foam ball swabbing and flushing with additives at low pressure.

Several new approaches are presented in Table 49 where the membrane techniques (group 3) are all somewhat untried and need development. Techniques must be sought to reduce the threshold velocity discussed by Thomas *et al.* (1973). In this regard, studies on the effectiveness of spacers or mixing promoters should be continued. Perhaps a few ppm of some additive (surfactant) to reduce the friction between liquid and membrane would effectively reduce the threshold velocity and increase the flow within the diffusion boundary layer resulting in increased axial shear at the membrane-solution interface. This approach has been very effective in increasing heat transfer rates (Sephton, 1973). Of course, the additive should not adversely affect the membrane performance and contribute toxicity.

In looking for effective cleaning additives, the fact that sodium perborate was successful (Cruver *et al.*, 1972) may lead us to believe that poorly rejecting compounds may be good candidates for cleaning. These include urea, boric acid, phenols, methanol, formaid, etc. This argument is based on the fact that if the "pores" of the membrane are plugged (by say ultra-small colloids), then cleaning compounds which traverse the "pores" may dislodge or dissolve the colloids.

For the case where colloids dominate the fouling mechanism, an interesting membrane cleaning method, developed for the transport depletion process, may be applicable to reverse osmosis (Lacey and Huffman, 1971). After it was found that the enzyme active solution was not satisfactorily cleaning the transport depletion membranes, a concentrated brine solution (18% or 3.5 N NaCl) was circulated across the fouled membrane. The brine successfully cleaned the membranes and essentially restored them to their initial performance. It is well known that increases in electrolyte concentration can, by reducing the repulsive forces between colloids, promote flocculation (O'Melia, 1972). However, if the electrolyte strength is further increased, deflocculation could occur at some critical concentration. This approach should be tried for the reverse osmosis process because of the obvious economic attractiveness of brine as a wash solution, especially where brines are readily available and cheap, such as near the Dead Sea, the Salton Sea, the Great Salt Lake or any other source.

Another possible approach, similar to the precoat method (Carrie, 1972), is to lay down on the surface of the membrane a highly porous ultrathin sacrificial film. It would protect the membrane from fouling and be periodically replaced when product fluxes decline below some critical value. Examples of a sacrificial film are large stable colloids, polyelectrolytes, and the usual slime film that grows during wastewater treatment. This latter method of membrane protection is at present successfully being used in Holland in an experimental program using reverse osmosis to treat the Rhine (Kuiper *et al.*, 1973). After the usual acid flush and foam ball swabbing, the tubular unit is filled at low pressure with the raw feed water, and allowed to remain (in the unit) for at least half an hour before the pressure is increased. During this period, a bacterial slime layer is presumed to grow on the membrane surface. This layer is then used to protect the membrane from fouling during operation. Membrane degradation due to bacterial growth may however shorten the life of the membrane and reduce its flux.

Another possible approach is to adapt a successful method used in distillation, where seeds are sometimes added to the evaporator to protect the heat transfer tubes from excessive precipitation of inorganic deposit Presumably, the seeds (say surface active colloids) would preferentially adsorb the fouling constituents and produce larger and possibly less dangerous colloids.

Although Smith (1974) was not able to successfully remove deposits from a tubular membrane using a secondary effluent feed by ultrasonication, limited success has been reported in the literature for acid mine drainage feeds (Wilmoth, 1974).

9.3 Additives

Membrane fouling is normally associated with water flux decline, and in some cases concurrent with a decrease in rejection. Several feed characterization methods have been examined by Cruver *et al.* (1972) to predict the fouling tendency of stream and to aid in the development of pretreatment techniques. The following characterization of feed have been found to be most relevant to membrane fouling:

1. Turbidity (JTU) and COD
2. Hydroxylated aromatic materials such as "humic substances".
3. Ferric compounds, mostly hydroxide of various forms in colloids.
4. Scaling forming inorganic matter, calcium sulfate etc.

In view of the possible presence of the above materials in the feed solution to the MUST hospital reverse osmosis (RO) system, turbidity, humic substances and colloids of ferric compounds are most unlikely to be found in the permeate of the ultrafiltration (UF) system employed in the first stage of the MUST treatment system. The only concern for the fouling

of RO system would be scale forming inorganic matter, especially operated at ninety (90) percent or higher product water recovery. In this case, pH adjustment of feed to RO would be the only parameter requires control.

However, in order to accelerate fouling of RO membranes, preliminary studies were conducted by exposing RO membranes to UF permeate of 10 x composite MUST hospital wastewater without pH adjustment. Flat sheets of NS-200, NS-100 and AP (aromatic polyamide from Chemstrand) membranes were evaluated using small test cells identical to those employed in studying membrane separation of organics as described previously. The operating pressure was 600 psig at a feed flow rate of 0.3 gpm and room temperature. These membranes were operated under the above conditions for one day prior to testing the effects of various additives in restoring membrane flux and rejection using 5000 ppm NaCl solution.

The test additives included EDTA, sodium hexametaphosphate (SHMP), sodium tripoly phosphate (STPP) and Duponts PT-B citric acid mixtures developed for regenerating B-10 "Permasep" permeators. The concentration of these additives used was 100 ppm for a period of one-half hour at 200 psig and 0.3 gpm. Sodium chloride (5000 ppm) rejections along with fluxes were measured before and after treatment with the above additives. A general trend showed that the rejection of sodium chloride increased consistently upon additive treatment of all the three membranes after exposing to the UF permeate of 10 x Composite wastewater under the conditions given above. An average of 1 to 1.5 percent increase in sodium chloride rejection was obtained. The average sodium chloride rejection of all these membranes after additive treatment was 99.5 percent which was similar to that prior to exposing to the wastewater.

Little effect was observed on the changes in membrane flux after additive treatment, indicating little fouling of flux was experienced after exposed to UF permeate of 10 x composite of MUST hospital wastewater. This was, however, anticipated as little of the fouling constituents in feed, such as turbidity, colloids and humic substances, was expected in the UF permeates. The decrease in salt rejection after exposing to UF permeate of 10 x composite waste might be the result of membrane-solute interaction.

Because of the relatively short duration of the above tests as well as the small number of experiments conducted, the specific effects of each additive on restoring solute separation should be evaluated extensively on pilot-scale studies using a specific RO membrane and module configuration. The tendency of decreasing solute rejection with no apparent changes in membrane flux after exposing to the UF permeate of the 10 x MUST composite wastewater was, however, an interesting observation as a result of the above preliminary studies.

10. DESIGN AND OPTIMIZATION OF A LARGE SCALE RO PLANT

Research into the optimization of reverse osmosis plant design and operation has been studied primarily as a theoretical exercise to date (Fan, *et al.*, 1968; Griffith and Draus, 1968). As the desalting of brackish and seawater becomes economically feasible, more practical engineering studies of the reverse osmosis plant layout and operation will become necessary.

10.1 Objectives and Scope

The overall goal of this study is the development of a computer program to aid in the selection of the optimum design and operation of a two-stage tubular membrane reverse osmosis plant for seawater desalination. Figure 36 is a flowchart of the major research efforts required and their relationship to each other. These major areas of research are described below:

1) To provide a theoretical model to predict the quantity and quality of purified water produced during the desalination of seawater as a function of such physically meaningful parameters as operating pressure, feed rate, feed concentration and temperature.

2) To design and fabricate suitable membrane casting apparatus, membrane support modules, and pumping and metering equipment which can be used to study membrane characteristics.

3) To conduct laboratory experiments to verify the model over the range of operating conditions usually encountered in desalination practice.

4) To develop a reverse osmosis plant layout of sufficient flexibility that all parameters of interest may be studied, yet simple enough to incorporate in an optimization routine.

5) To develop cost equations to be used as the objective function of an optimization routine yielding results accurate enough to be useful in designing a large scale desalination plant.

6) To select a suitable optimization technique and modify it as necessary to incorporate the theoretical model, plant layout, and cost equations developed in earlier research.

7) To compile sufficient data to show the usefulness of such a plant optimization study.

10.2 Mathematical Modeling

Figure 37 depicts the free communication between the two basic modeling techniques: black-box experimentation and analytical methods. The two models are quite interchangeable; the route by which analytical models can be treated as black-box methods, as well as the conversion of black-box outputs into analytical relationships, is shown.

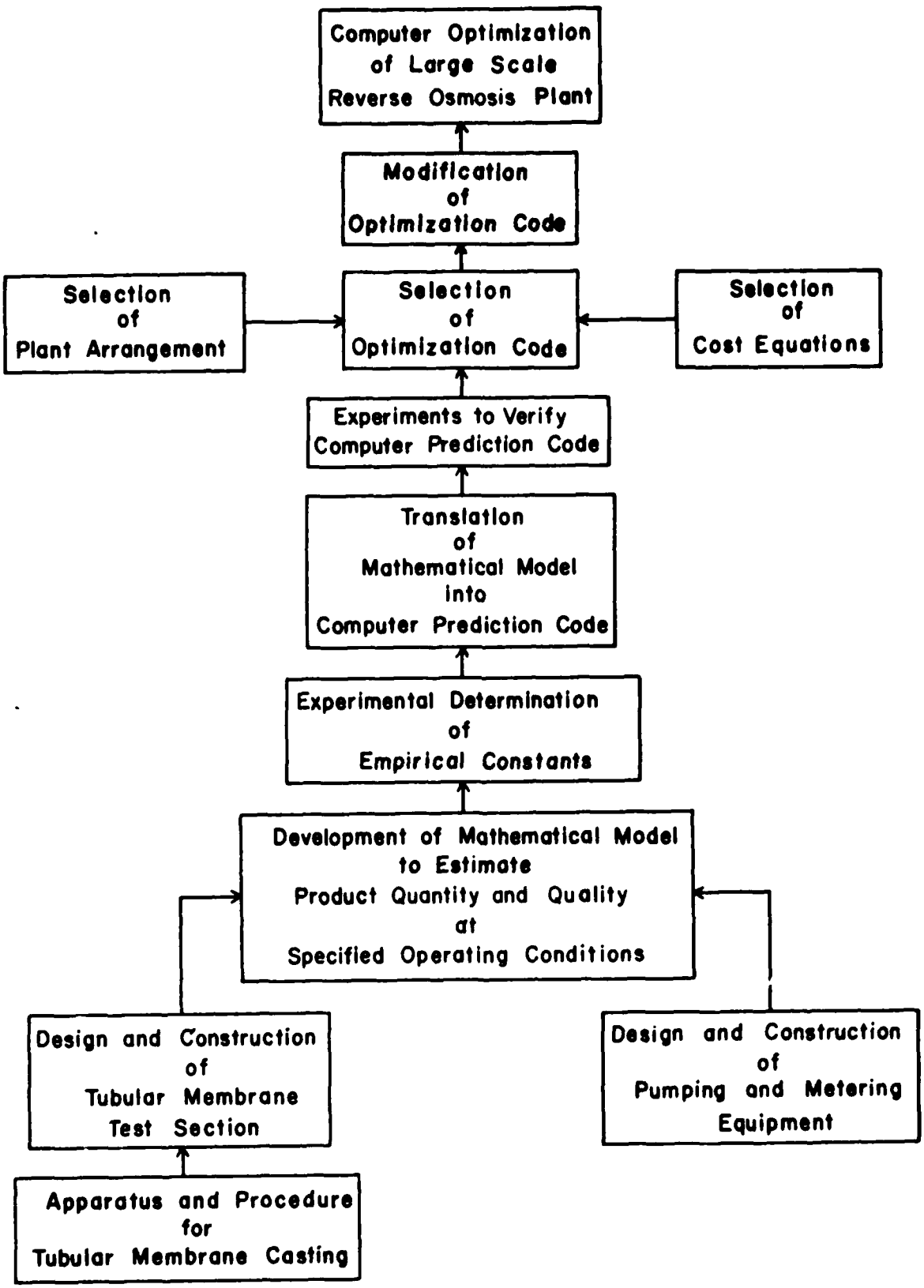

Figure 36. Flowchart of Major Research Efforts

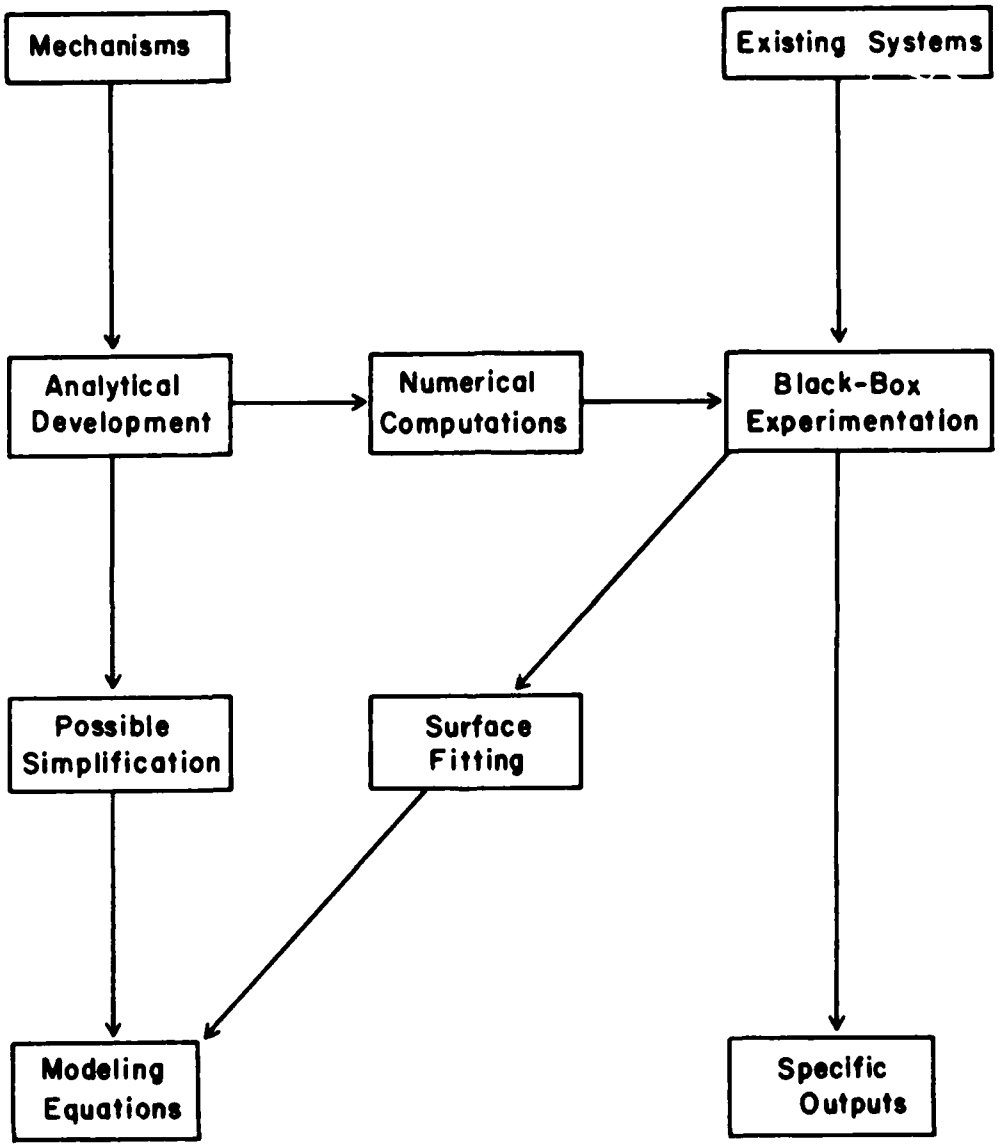

Figure 37. Basic Modeling Techniques

Using the analytical approach, certain mechanisms which are postulated as the controlling features, are used in conjunction with the accepted laws of conservation (matter, energy momentum, etc.) to derive a self-consistent set of equations defining uniquely the outputs from a system for a specific set of inputs. The resultant equations can be used in two ways.

First, it may be possible, by invoking certain physical and mathematical simplifications, to reduce these equations so that they are suitable for use in conjunction with the analytical methods of optimization. The possibility of simplification and solution by analytical means is suggested by the vertical path on the left-hand side of Figure 37.

Second, when the analytical model is complex and cannot be substantially reduced either on physical ground or by mathematical agreement to a simpler valid form, the analytical model can be used to generate black-box type outputs using appropriate numerical computer techniques. These outputs are completely determined by the particular inputs to the system. The horizontal path in Figure 37 describes this approach.

Once sufficient data has been generated, either by direct black-box experimentation or through the analytical model, surface fitting techniques can be used to produce an analytical model which is representative of the system behavior over a restricted range of inputs. The diagonal path in Figure 37 indicates such a method. This approximating function can then be manipulated in the same manner as a model developed from the mechanistic approach and is, for optimization purposes, quite indistinguishable except that its form is ordinarily much simpler than a mechanistic model derived from first principles.

10.2.1 An Analytical Model from a Mechanistic Approach

The basis of the reverse osmosis process is the employment of a semipermeable membrane barrier to permit appreciable transport rates of only certain constituents of a mixture. The observed salt rejection and solvent permeability properties of a reverse osmosis membrane are strongly affected by solution pressure, solution flow, and solution concentration at the membrane surface as well as by the intrinsic physical-chemical properties of both the solution and the membrane. It is necessary to design experimental equipment and procedures so that the immediate environment of the membrane is characterizable, and is taken into account in the interpretation of experimental data.

Whatever the geometry of a membrane, the character of fluid flow past its interface and the physical properties of this fluid determine the transport of solute to and from the membrane interface. The linear flowrate of a solution (for example through a tubular shaped membrane), the rate of permeation of product through the membrane wall, in addition to the nature of the entrance and exit flow from the tube, influence the flux of solute and solvent through the membrane by altering the velocity field from that

experienced in fully developed pipe flow. At finite rates of flow, rejected solute tends to build up a layer of solution having a higher than feed concentration at the interface. This phenomenon is called concentration polarization. Considering only turbulent flow through a tubular membrane the situation may be described qualitatively as shown in Figure 38. The upper curve is characteristic of the velocity distribution in turbulent flow where the linear velocity is approximately constant from the center of the tube to a distance near the tube wall where it decreases rapidly to zero at the membrane surface. The lower portion of the curve describes the salt concentration distribution beginning at the interface of the boundary layer and increasing to a relatively high concentration at the membrane surface. This curve represents the result of two kinetic processes, that of transport of solute to the wall by convection resulting from flux of liquid through the membrane, and the diffusion of solute back to the bulk fluid. The phenomenon of concentration polarization has many deleterious effects on the reverse osmosis process: it increases the osmotic pressure at the membrane-solution interface and thereby decreases the effective driving force for solvent flow through the membrane; it increases the driving force for the transmembrane solute flux and hence, increases the salinity of the product water; in addition it can lead to membrane fouling due to precipitation or gelation of sparingly soluble species, e.g., $CaSO_4$, $CaCO_3$, $M_g(OH)_2$ and may accelerate chemical deterioration of the membrane owing to a higher concentration of aggressive species, e.g., HOCl, OCl^-. Thus, it is necessary to develop equations describing concentration polarization in order to predict the effectiveness of membrane separation as well as to make economic appraisals of the reverse osmosis process.

Removal of inorganic or organic solutes by reverse osmosis depends upon the ability of various membranes tp permit the transport of water but not of solute. To achieve separation, the solution is placed in contact with the membrane and is subjected to a pressure difference, $\Delta P(x)$, in excess of the osmotic pressure difference $\Delta\pi(x)$. The water flux through a membrane of constant permeability has been reported (Merten, 1963) to be given by

$$N_B(x) = A[\Delta P(x) - \Delta\pi(x)] \tag{23}$$

Increases in the osmotic pressure difference, $\Delta\pi$, require a higher applied pressure to obtain a specific water flux. The coefficient, A, may be obtained experimentally using pure water as feed.

$$A = N_{BP/\Delta P(x)} \tag{24}$$

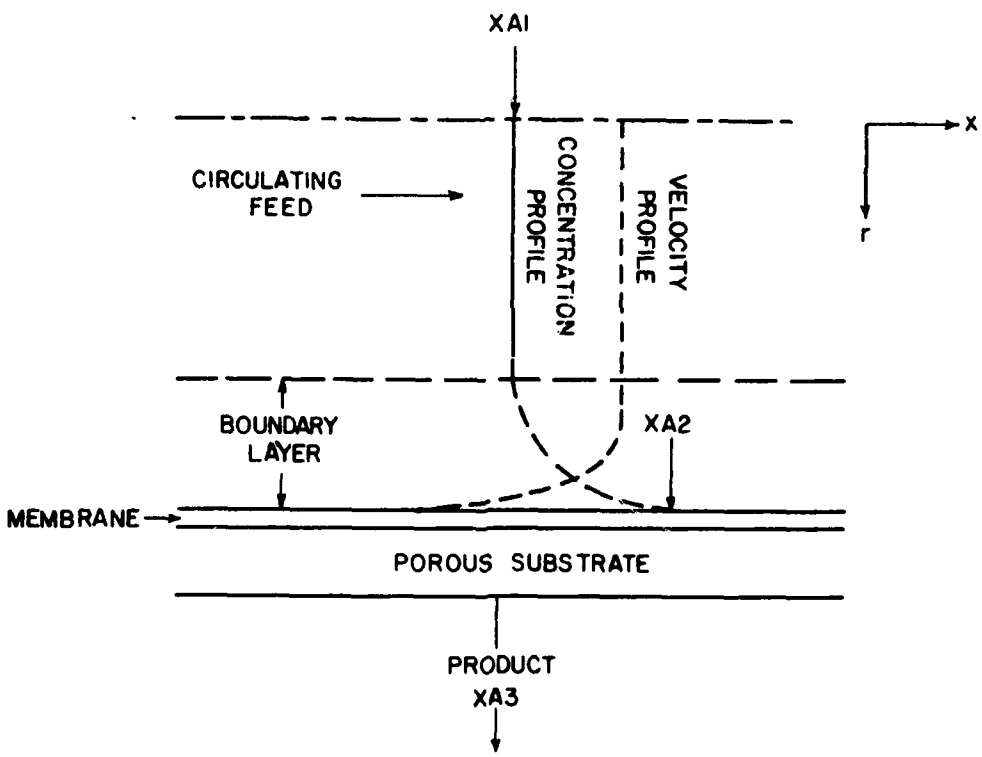

Figure 38. Velocity and Concentration Profiles During Reverse Osmosis Desalination of a Salt Solution in Turbulent Flow

Product water passing through the membrane is supplied to the phase boundary by bulk flow of solution normal to the membrane surface and solute is carried along with the water. If a steady state is to be maintained with only a portion of the solute passing through the membrane, a solute concentration gradient must be established near the phase boundary enabling the solute retained by the membrane to diffuse back into the bulk solution to an extent such that the solute collected in the product water is equal to the net solute transfer to the membrane on the high pressure side. Thus, the effective feed side osmotic pressure, which is that of the solution at the membrane surface, is greater than that of the bulk solution. As a result, $\Delta\pi$, is increased and either the water flux is reduced or the applied pressure difference, $\Delta P(x)$, must be increased to maintain a given flux.

The mechanisms of solute transfer through a semipermeable reverse osmosis membrane has been and still is a subject of much research. Furthermore, the rejection mechanism undoubtedly differs depending upon the type of membrane under consideration. Any theory of the separation mechanism must be intimately concerned with the structure and chemical properties of the membrane as well as the chemical and physical properties of the solute and solvent.

Several workers (Sherwood *et al.*, 1967; Rosenfeld and Loeb, 1967; Sourirajan, 1967) have assumed that the solute permeation rate may be described as a simple equation.

$$N_{A2}(x) = Bc\,(X_{A2} - X_{A3}) \tag{25}$$

Since

$$X_{A3} = \frac{N_{A2}(x)}{N_{A2}(x) + N_{B2}(x)} \quad \text{equation 25 may be} \tag{26}$$

rewritten as

$$N_{B2}(x) = \frac{(1-X_{A3})}{X_{A3}}\,Bc\,(X_{A2} - X_{A3}) \tag{27}$$

Sherwood *et al.* (1967) have analyzed concentration polarization occurring with membranes which completely reject salt, under conditions of both laminar and tubulent flow; only the turbulent case is of interest to this study. This theory has since been extended to membranes with less than complete rejection (Johnson and Dresner, 1966; Brian, 1967). These equations have been tested experimentally with cellulose acetate membranes supported on rotating cylinders (Sherwood *et al.*, 1967); with dynamically formed hydrous zirconium (IV) oxide membranes at high transmission rates (Shor, 1968); with tubular cellulose acetate membranes in turbulent flow (Johnson and McCutchan, 1971; Derzansky and Gill, 1974).

The use of tubular configurations as support for polymeric membranes makes them particularly amenable to hydrodynamic analysis. As Figure 38 suggests, the transfer of solute from the membrane wall where longitudinal flow approaches zero occurs by molecular diffusion. At distances from the wall, a continuous transition occurs where mass transfer results from mixing and interchange between fluid eddies.

Perhaps the simplest model for the concentration boundary layer in turbulent flow is the film theory model. The boundary layer is idealized as a thin, liquid film in which eddy motion is assumed to be negligible and therefore mass transport occurs by molecular diffusion and laminar convection. This thin film separates the membrane surface from the bulk brine solution which is assumed to be so turbulent that concentration gradients are negligible. Steady-state operation is assumed and longitudinal mass transport within the film is absent. Consequently, mass transport within the film is considered one-dimensional. If the operation is also considered isothermal with no significant free convection and the solutions are aqueous incompressible fluids containing only one solute which has a diffusion coefficient independent of concentration, then with these simplifying assumptions mass balances written over the boundary layer for cylindrical geometry become

$$2\pi L[rN_{Ar}(x)|_{r+\Delta r} - rN_{Ar}(x)|_r] = 0 \tag{28}$$

Dividing by Δr and in the limit as $\Delta r \to 0$

$$\frac{d[rN_{Ar}(x)]}{dr} = 0 \tag{29}$$

Similarly for the radial flux of solvent

$$\frac{d[rN_{Br}(x)]}{dr} = 0 \tag{30}$$

Upon integration

$$rN_{Ar}(x) = \text{constant} = RN_{A2}(x) \tag{31}$$

$$rN_{Br}(x) = \text{constant} = RN_{B2}(x) \tag{32}$$

From which

$$R[N_{A2}(x) + N_{B2}(x)] = r[N_{Ar}(x) + N_{Br}(x)] \tag{33}$$

A solute mass balance across the membrane surface provides

$$X_{A3} = \frac{N_{A2}(x)}{N_{A2}(x) + N_{B2}(x)} \tag{34}$$

$$X_{A3} = \frac{N_{Ar}(x)}{N_{Ar}(x) + N_{Br}(x)} \tag{35}$$

From Fick's first law with respect to stationary coordinates (Bird *et al.*, 1960).

$$N_{Ar}(x) = X_A[N_{Ar}(x) + N_{Br}(x)] - cD_{AB}\frac{dX_A}{dr} \tag{36}$$

Combining Equations 35 and 36 and rearranging

$$(X_{A3} - X_A) = \frac{-cD_{AB}\frac{dX_A}{dr}}{[N_{Ar}(x) + N_{Br}(x)]} \tag{37}$$

or

$$\frac{-[N_{Ar}(x) + N_{Br}(x)]}{c\ D_{AB}}\ dr = \frac{dX_A}{(X_{A3} - X_A)} \tag{38}$$

Upon integration over the film thickness

$$\int_{R-\delta_{AB}}^{R} \frac{[N_{Ar}(x) + N_{Br}(x)]}{C\ D_{AB}}\ dr = \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{(X_A - X_{A3}} \tag{39}$$

$$\frac{[N_{Ar}(x) + N_{Br}(x)]}{c\ D_{AB}} \cdot \delta_{AB} = \ln \frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}} \tag{40}$$

In the film theory the mass transfer coefficient is ordinarily defined to be

$$N_{A2}(x) = k_1\ \Delta C_A = \frac{D_{AB}}{\delta_{AB}} \tag{41}$$

with C_A being the appropriate concentration driving force. Thus Equation 40 becomes

$$\frac{[N_{Ar}(x) + N_{Br}(x)]}{k_1 \; c} = \ln \left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) \tag{42}$$

At this point it is important to realize that the movement of solute away from the membrane surface may be treated as the sum of a diffusional contribution due to concentration gradients and a bulk flow contribution due to convection. The diffusional contribution is proportional to the concentration gradient at the wall and hence should be roughly proportional to some characteristic concentration difference, X_A, between the fluid at membrane surface and that in the main stream; the bulk flow contribution, on the other hand, can occur without any concentration gradient at all. Thus, following the analysis of Bird *et al.* (1960) a mass transfer coefficient may be defined in terms of the rate of diffusion of solute normal to the interface.

$$N_{A2}(x) - X_{A2}\,[N_{A2}(x) + N_{B2}(x)] = -cD_{AB}\frac{dX_A}{dr}\Big|_{r=R} \tag{43}$$

$$N_{A2}(x) - X_{A2}\,[N_{A2}(x) + N_{B2}(x)] = -\overset{\circ}{k}_{x,loc}(X_{A2}-X_{A1}) \tag{44}$$

The mass transfer coefficient itself depends upon the transpiration rate due to the distortion of the velocity and concentration profiles by flow of solute and solvent through the interface.

In the limit of small transpiration, the distortion of the concentration and velocity profiles may be neglected. In this limiting condition it is convenient to define another mass transfer coefficient

$$k_{x,loc} = \lim_{\substack{N_{A2}\to 0 \\ N_{B2}\to 0}} \frac{N_{A2}(x) - X_{A2}[N_{A2}(x) + N_{B2}(x)]}{\Delta X_A} \tag{45}$$

That is, it is permissible at moderate mass transfer rates to replace $\overset{\circ}{k}_{x,loc}$ by $k_{x,loc}$. The difference between $\overset{\circ}{k}_{x,loc}$ and $k_{x,loc}$ becomes more evident as one compares the dimensionless Sherwood Number, Sh,

$$Sh = \frac{k_{x,loc}\,D}{c\,D_{AB}} = \text{function (Re, Sc, geometry)} \tag{46}$$

$$Sh^{\circ} = \frac{\overset{\circ}{k}_{x,loc}\,D}{c\,D_{AB}} = \text{function (Re, Sc, geometry, } \frac{N_{A2}(x) + N_{B2}(x)}{k_{x,loc}}) \tag{47}$$

Most available forced convection mass transfer correlations are of the form of Equation 46. Rewriting Equation 22 with the substitution of Equation 34 yields

$$[N_{A2}(x) + N_{B2}(x)] = \frac{\overset{\circ}{k}_{x,loc}\,(X_{A2} - X_{A1})}{(X_{A2} - X_{A3})} \tag{48}$$

From Equation 12, Equation 26 becomes

$$\frac{N_{A2}(x)}{X_{A3}} = \frac{\overset{\circ}{k}_{x,loc}\,(X_{A2} - X_{A1})}{(X_{A2} - X_{A3})} \tag{49}$$

Finally, Equations 25 and 49 may be combined to give

$$\frac{Bc(X_{A2} - X_{A3})}{X_{A3}} = \frac{\overset{\circ}{k}_{x,loc}\,(X_{A2} - X_{A1})}{(X_{A2} - X_{A3})} \tag{50}$$

Equations 23, 27 and 50 form the basis for the prediction of product water quantity and quality in the tubular reverse osmosis system being studied. It is important that for small mass transfer rates the ratio $\theta_{AB} = \overset{\circ}{k}_{x,loc}/k_{x,loc} \sim 1$ so that the concentration polarization equation becomes

$$\frac{Bc\,(X_{A2} - X_{A3})}{X_{A3}} = \frac{k_{x,loc}\,(X_{A2} - X_{A1})}{(X_{A2} - X_{A3})} \tag{51}$$

According to the film theory as presented by Bird *et al.* (1960)

$$\theta_{AB} = \frac{\phi_{AB}}{\exp\,(\phi_{AB}) - 1} = \frac{\overset{\circ}{k}_{x,loc}}{k_{x,loc}} = \frac{\overset{\circ}{Sh}}{Sh} \tag{52}$$

where

$$\phi_{AB} = \frac{(N_{A2} + N_{B2})}{k_{x,loc}} \tag{53}$$

Thus

$$\phi_{AB} = \frac{Pe_w/Sh}{\exp(Pe_w/Sh) - 1} \tag{54}$$

where

$$Pe_w = Re_w\,Sc = \frac{D\,(N_{A2} + N_{B2})\rho}{c\,\mu}\,Sc \tag{55}$$

or

$$\frac{Sh^{\circ}}{Sh} = \frac{Pe_w/Sh}{\exp\,(Pe_w/Sh) - 1} \qquad (56)$$

Typical values encountered in these reverse osmosis studies reveal $Pe_w \sim 1$, $Sh \sim 100$ to 500. Thus, the deviation of Sh° from Sh is ordinarily less than 10.0 percent and Equation 51 may be used.

10.3 Casting of NS-100 Tubular Membranes

The fabrication of NS-100 membranes involves the cross-linking of a Polyethylenimine (PEI) solution with a Tolylene 2,4-diisocyanate (TDI) solution on the surface of a fine porous polysulfone support matrix. The membrane was designated NS-100. This designation has since been changed to NS-1 by the OSW (Office of Saline Water), the funding agency. Three fundamental steps for NS-100 membrane casting have been established by North Star (1972):

1) Preparation of the porous polysulfone support matrix.

2) Coating of the polysulfone matrix with a PEI solution, draining, and subsequent coating with a TDI solution.

3) Heat curing of the membrane to form PEI-TDI cross-linkage.

In addition, preliminary casting conditions such as reactant concentration, reaction time, curing temperature and curing time, were proposed by North Star (1972) and are shown in Table 50. Fang and Chian (1976) have studied optimization of these casting variables in an attempt to maximize the water production rate of a flat sheet NS-100 membrane having a preselected level of 99.0% sodium chloride rejection. The operating conditions selected for testing the NS-100 membrane were 600 psi; 5000 ppm sodium chloride; 25°C; 0.3 gpm. Although only 99.0% rejecting membranes were considered, the technique for selection of optimum casting variables for membranes with different rejection levels could be studied using essentially the same method. During the course of their research, Fang and Chian (1976) were able to ascertain the relative importance of many of the casting variables thus giving insight into the degree of accuracy necessary in each casting step during the fabrication of NS-100 membrane. Optimum values of reactant concentrations, reaction times, curing temperature and curing time are listed in Table 51.

10.3.1 Experimental Procedure and Apparatus

Five 24 inch sections of NS-100 tubular membrane were cast in various ways to be used as a basis for modeling the reverse osmosis-desalination process. Two membrane tubes (designated NS-100-1 and NS-100-2) were cast as indicated in Table 51, with no post-treatment being used. To ascertain

TABLE 50

OPTIMIZED NS-100 MEMBRANE CASTING VARIABLES FOR FLAT SHEET MEMBRANE

(ALSO USED FOR TUBULAR MEMBRANES NS-100-1 & NS-100-2)

Polysulfone Support		
1.	Polysulfone concentration in dimethylformamide	15.19% by weight
2.	Polysulfone thickness (wet membrane)	6.0 mil
3.	Dimethylformamide concentration in gelling water	3.0% by weight
Polyethylenimine Coating		
4.	Polyethylenimine concentration in water (Tydex 12)	3.11% by weight
5.	Immersion time of Polysulfone support in PEI solution	1 minute
6.	PEI drainage time after coating	1 minute
Tolylene 2,4-Diisocynate Coating		
7.	Tolylene 2,4-diisocynate concentration in hexane	0.64% by weight
8.	Immersion time in TDI-hexane solution	1 minute
9.	Curing time	10 minutes
10.	Curing temperature	105°C

TABLE 51

NS-100 MEMBRANE CASTING VARIABLES FOR FLAT SHEET MEMBRANES

Polysulfone Support		
1.	Polysulfone concentration in dimethylformamide	15% by weight
2.	Polysulfone thickness (dry membrane)	1.7 mil
3.	Dimethylformamide concentration in gelling water	2% by weight
Polyethylenimine Coating		
4.	Polyethylenimine concentration in water	2% by weight Tydex 12
5.	Immersion time of Polysulfone support in PEI solution	1 minute
6.	PEI drainage time after coating	1 minute
Tolylene 2,4-Diisocynate Coating		
7.	Tolylene 2;4-diisocynate concentration in hexane	0.5% by weight
8.	Immersion time in TDI-Hexane solution	1 minute
9.	Curing time	15 minutes
10.	Oven temperature	110°C

the usefulness of the pressurized PEI post-treatment process and to insure that the modeling technique for the reverse osmosis process would remain essentially unchanged, three membrane tubes (designated NS-100-3, NS-100-4, NS-100-5) were cast as indicated in Table 52. The experimental procedures and apparatus used for casting these five membranes are described below.

The development of new polymer formulations for reverse osmosis membranes usually begins with laboratory casting and characterization of flat sheet membrane configurations. Frequently, many difficulties arise during the attempt to extrapolate a procedure developed for casting flat membrane to the casting of membrane in other geometries. A primary cause of these difficulties seems to involve the coupling between membrane geometry and the various phenomena occurring at the membrane interface during membrane formation. The NS-100 membrane proved to be no exception. Fang and Chian (1976) and others (North Star, 1972) have found that the fabrication of tubular shaped NS-100 membrane from procedures developed for flat sheet membrane results in membrane tubes which do not have reproducible product water permeation rates or degrees of solute separation.

Recent work conducted by Zakak *et al.* (1975) proposed a post-treatment reaction procedure involving exposure of previously cast NS-100 membrane to a PEI solution under low pressure, followed by a second heat curing step. Incorporation of the post treatment step is said to yield membranes of excellent quality with reproducible results. Conditions of post-treatment are lsited in Table 52.

Tubular polysulfone support liners were prepared by coating approximately 15 percent polysulfone in DMF solution on to the inner surface of a 1.4097 cm. I.D. 316 stainless steel tube. The thickness of the support liner was controlled by dropping a 1.3792 cm aluminum casting bob into the top of the 316 stainless steel tube and allowing the bob to fall freely. Excess polysulfone solution which did not pass through the annulus between the bob and the stainless steel tube was forced from the tube bottom by the bob and was discarded. To account for liner shrinkage during gelation and heat curing, an oversized casting tube (1.4097 cm) was used. Immediately after casting, the stainless steel casting tube was immersed slowly (approximately 10 cm /sec) into a deionized water bath at room temperature for 15 minutes to gel. The support tube was then rinsed in deionized water, removed from its stainless steel tube, and stored in another deionized water bath until further treatment.

The microporous polysulfone support thus formed has an asymmetric structure with a skin-layer on the inner surface upon which the TDI-PEI coatings are coated. For best desalting characteristics Rozelle (*et al.*, 1971) has found that pore sizes on the skin side of the polysulfone support should be on the order of 300 to 400 Å. Pore sizes of the support film increase to approximately 20,000 Å at the outer perimeter of the support tube. The flux characteristics of NS-100 are closely related to the pore diameters found in the skin layer which in turn are dependent upon:

TABLE 52

MEMBRANE CASTING VARIABLES FOR TUBULAR MEMBRANES

(NS-100-3, NS-100-4, AND NS-100-5)

Polysulfone Support		
1.	Polysulfone concentration in dimethylformamide	15% by weight
2.	Polysulfone thickness (wet membrane)	6.0 mil
3.	Dimethylformamide concentration in gelling water	none
Polyethylenimine Coating		
4.	Polyethylenimine concentration in water (Tydex 12)	2% by weight
5.	Immersion time of polysulfone support in PEI solution	1 minute
6.	PEI drainage time after coating	1 minute
Tolylene 2,4-Diisocynate Coating		
7.	Tolylene 2,4-diisocynate concentration in hexane	1% by weight
8.	Immersion time in TDI-hexane solution	1 minute
9.	Curing time	30 minutes
10.	Curing temperature	115°C
Post-Treatment		
11.	Polyethylenimine concentration in water	2.0% by weight
12.	Polyethylenimine exposure time	2 minutes at 5 psig 3 minutes at 1 ft water
13.	Curing time	30 minutes
14.	Curing temperature	115°C

a) Thickness of polysulfone liners

b) Temperature of the gelling bath

c) Concentration of the polymer in the casting solution

d) DMF concentration in the gelling bath

The formation of the PEI-TDI layer on the polysulfone support matrix prior to heat curing is a second important step in the fabrication of NS-100 membrane. To coat a pre-formed polysulfone support liner, the liner was first immersed in the PEI solution for one minute, drained for one minute, then immersed in the TDI solution for one minute, followed by final drainage for at least 30 minutes. The speed of liner entry into and removal from the solution baths was approximately 10 cm/sec. The parameters affecting the layer thickness and hence the product rate and rejection characteristics of the membrane include:

a) PEI and TDI concentrations in the immersion baths

b) Immersion time

c) PEI and TDI drainage times

d) Curing temperature

Heat curing of the coated membrane causes cross-linkage of the PEI and TDI reactants and formation of the ultrathin skin on the surface of the polysulfone support matrix. Curing is a function of both temperature and time.

Post-treatment of a pre-cast NS-100 membrane improved membrane reproducibility and consisted of a two minute in situ coating with a two percent PEI solution under 0.34 atm. pressure, followed by a three minute contact period under a pressure head of 0.029 atm. After drainage, the retreated membranes were heat cured for thirty minutes at 110°C.

10.4 Data Acquisition

The high capacity pumping system and tubular membrane test section shown in Figures 2 and 3 and described in sections 2.3 and 2.4 were used for data acquisition.

Tubular NS-100 membranes cast under laboratory conditions were used throughout these experiments. The details of the NS-100 membrane composition, casting procedure and casting apparatus have been determined through literature (North Star, 1972; Fang and Chian, 1976) and through direct experimentation as discussed previously.

Data can be taken under operating pressures in the range from one to sixty-eight atmospheres while the feed rate may be varied from four to twenty-two liters per minute. The solute concentration can be changed during operation by direct chemical addition to the feed reservoir. All experiments were carried out between 15 to 90 degrees centigrade with 25 degrees centigrade the base temperature. Temperature was controlled using a thermoregulator, electronic relay, and heat exchanger as previously described. The effective area of each reverse osmosis membrane in the tubular test cell was 233.08 cm^2, equivalent to a tube length of two feet.

At each experimental condition, that is, particular combination of feed concentration, feed rate, operating pressure and feed temperature, the degree of solute separation and throughput rate through each membrane was determined. Feed and permeate concentrations were measured conductimetrically using a standard curve relating the conductivity of the salt solution to its concentration. Any necessary dilution of feed or permeate salt solutions, whether to reduce sample conductivity or increase sample volume, was done using deionized-distilled water. In addition, the contribution of any conductivity in the dilution water was compensated by using the expression

$$\text{True Conductivity} = \frac{(\text{measured conductivity})\ (\text{total volume})}{(\text{total volume} - \text{dilution water volume})} - \frac{(\text{dilution water volume})\ (\text{Conductivity of dilution})}{(\text{total volume} - \text{dilution water volume})}$$

Separation data can be measured within an accuracy of one percent. Throughput rate was measured by determining the time required to collect 10 ml of product water. This method produced results accurate to within one percent. Feed rate was measured by a high-pressure rotameter which read to approximately three percent of the value determined by recording the time required to fill a container of known volume. Operating pressures were accurate to $\pm$ one percent according to specifications supplied by the manufacturer.

Before any actual acquisition of data, the NS-100 membranes to be studied were pre-pressurized at forty atmospheres for four hours. During this period the throughput rate was monitored until the membrane stabilized. The stabilized polymeric membranes were then ready for use. During data acquisition the operating conditions were changed frequently. To insure that the throughput rate and degree of salt separation reached their steady-state values, the system was allowed to operate for either one hour or the time necessary to produce a volume of permeate equal to ten times the collection chamber volume, whichever was longer. This procedure has been found to be quite conservative.

Data taken in the aforementioned manner were used to determine the empirical constants used in the theoretical model previously described. In addition these data were used to test the accuracy of the model by direct comparison with computer predicted results.

10.5 Empirical Correlation of Experimental Data

Before Equations 23, 24, 27 and 51 may be used as a basis to describe the reverse osmosis purification of saline water by tubular NS-100 membranes, the effect of changing operating conditions upon the pure water permeability coefficient and salt permeability coefficient must be determined. Preliminary experimentation has produced the following results.

10.5.1 Effect of Operating Pressure Upon Pure Water Permeability Coefficient

The pure water permeability coefficient, A, for NS-100 membrane remains constant with pressure to approximately forty atmospheres. Above forty atmospheres the coefficient, A, decreases slightly as the operating pressure is increased. For mathematical simplicity the pure water permeability coefficient is expressed as

$$A = A_r e^{-\alpha(\Delta P - \Delta P_r)} \tag{57}$$

Figures 39, 40 and 41 show data confirming the validity of Equation 57 for use with NS-100 membrane over the pressure range studied. A typical value of α for NS-100 membrane is 1.5×10^{-5} atm^{-1}.

10.5.2 Effect of Interfacial Concentration Upon the Salt Permeability Coefficient

Values of the salt permeability coefficient for several NS-100 tubular membranes are plotted as a function of the interfacial mole fraction, X_{A2}, in Figures 42 and 43. From these results it may be concluded that the salt permeability coefficient for the sodium chloride-water system increases with increasing interfacial salt concentration. This dependence appears to be linear at least over the concentration range studied. An equation describing the variation of the salt permeability coefficient with feed concentration may be written as

$$B = M(X_{A2} - X_{A2}^{*}) + B^{*} \tag{58}$$

The magnitude of the effect of interfacial salt concentration upon B, that is, the slope M, appears to be different for NS-100 membranes with different casting conditions. A typical value of M is 1.0×10^{-2} cm/sec.

10.5.3 Discussion of the Empirical Correlations

Figures 39, 40 and 41 suggest that the water permeability of the NS-100 membrane is unaffected until a pressure of approximately forty atmospheres is exceeded. Above forty atmospheres the porous polysulfone portion of the

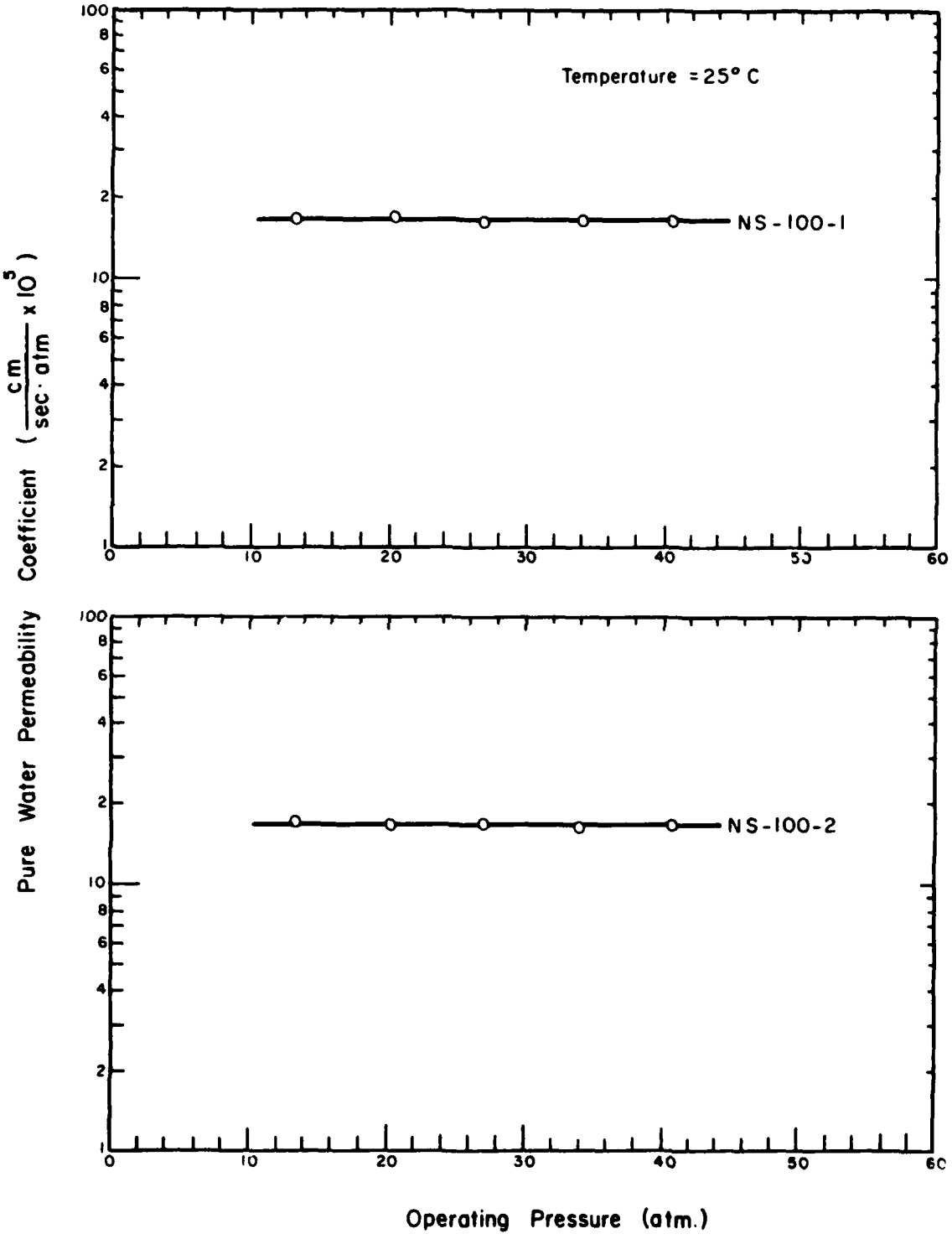

Figure 39. Effect of Operating Pressure Upon Pure Water Permeability Coefficient

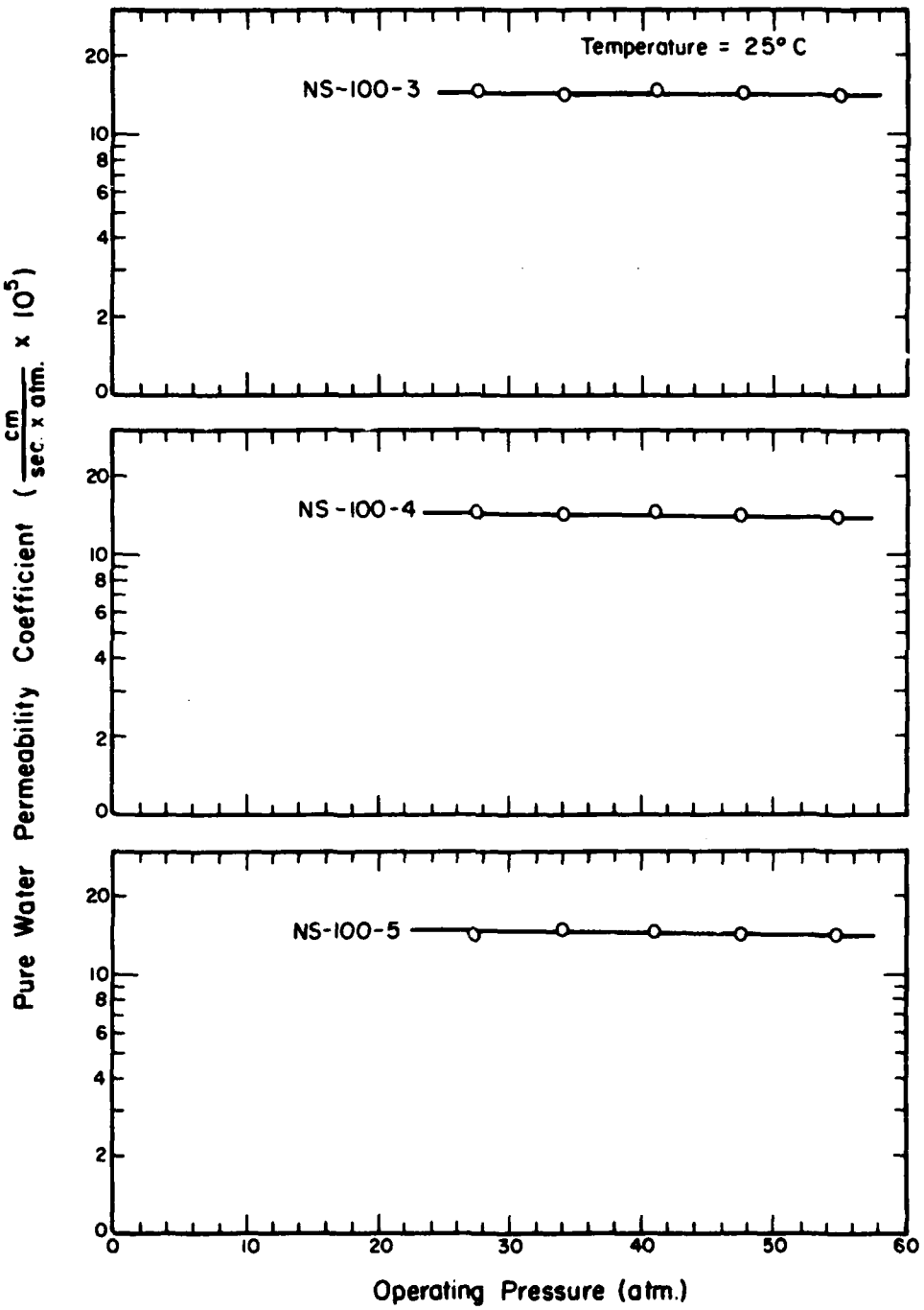

Figure 40. Effect of Operating Pressure Upon Pure Water Permeability Coefficient

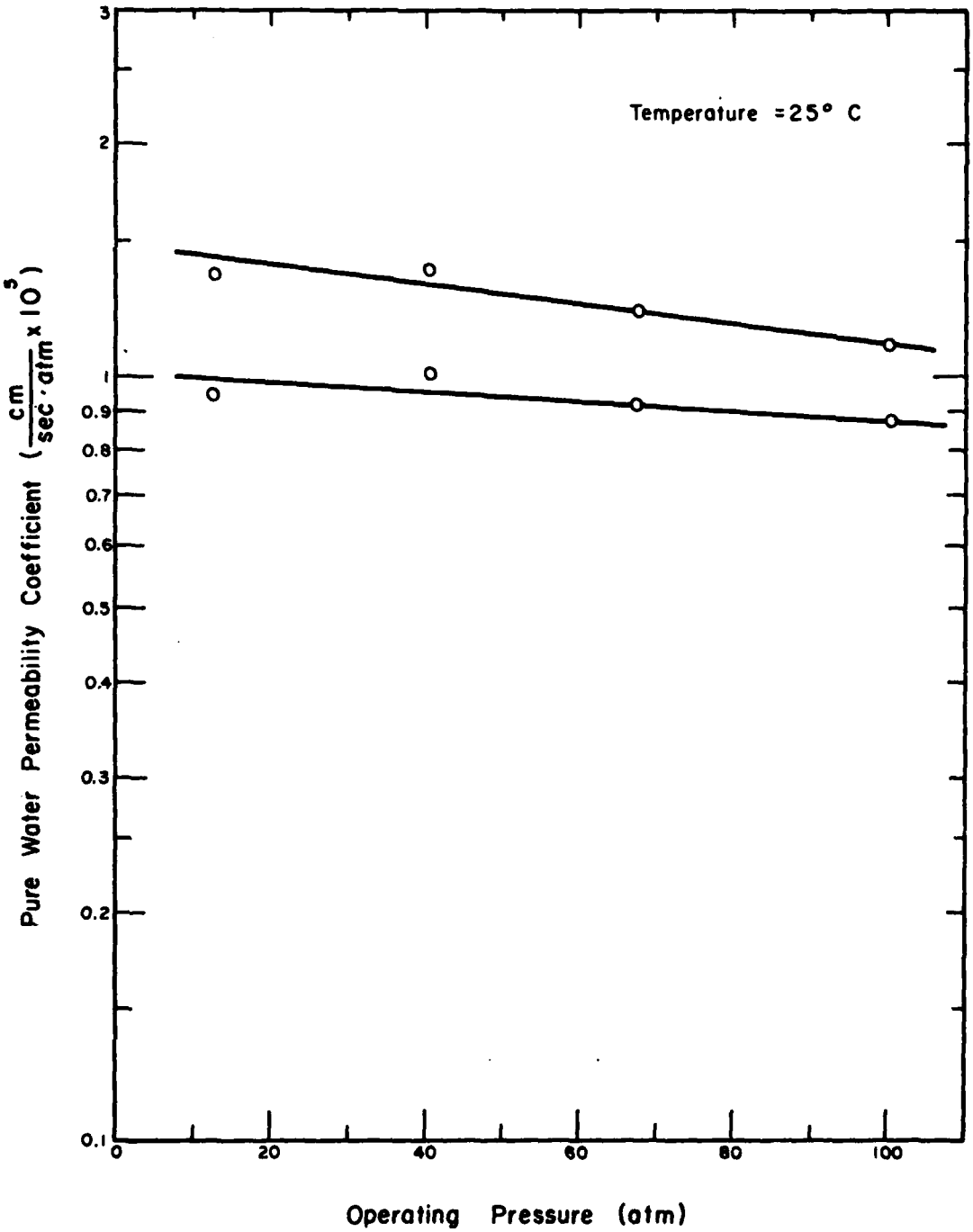

Figure 41. Effect of Operating Pressure Upon Pure Water Permeability Coefficient at Elevated Pressures

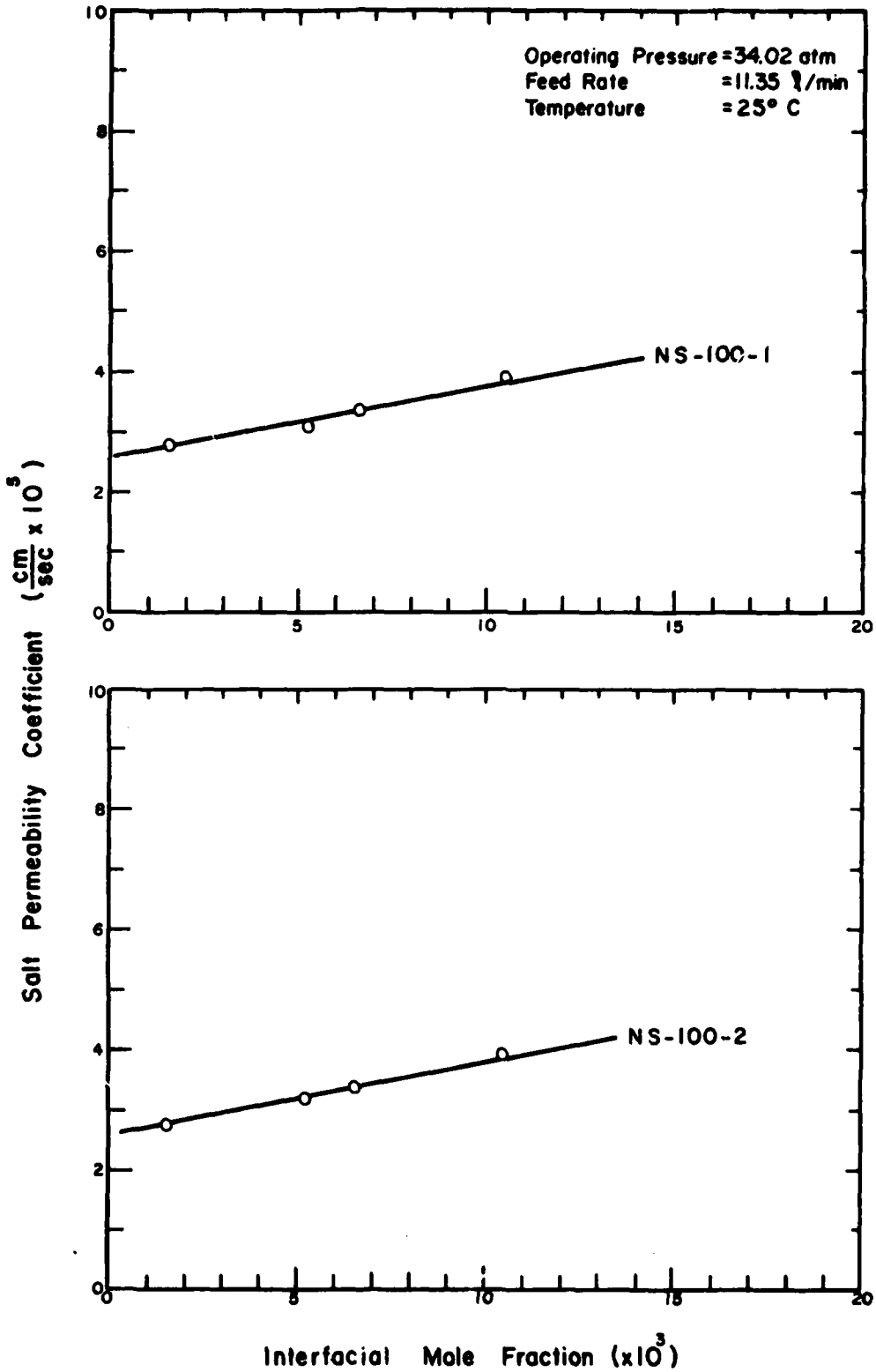

Figure 42. Effect of Interfacial Concentration Upon Salt Permeability Coefficient

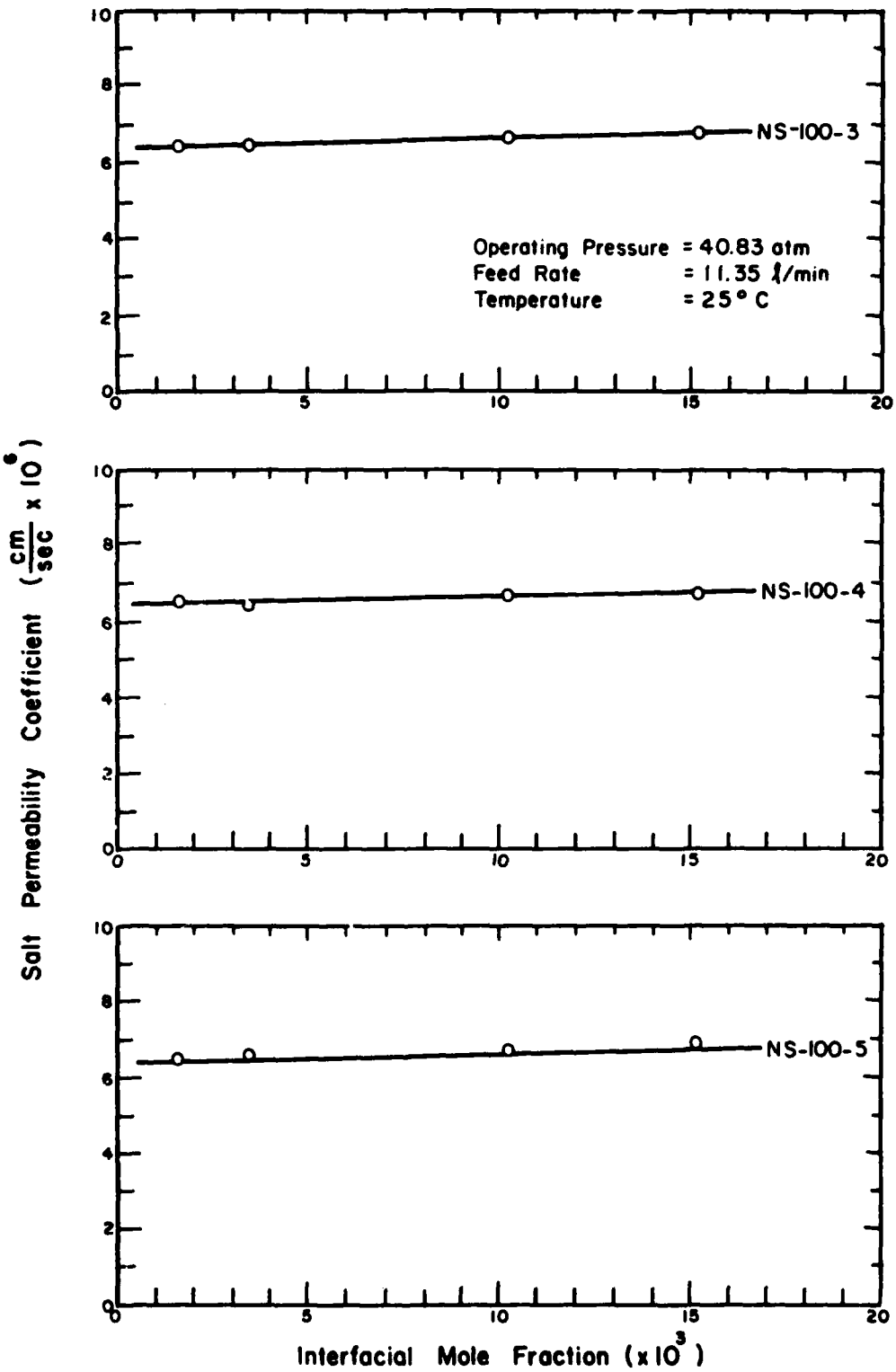

Figure 43. Effect of Interfacial Concentration Upon Salt Permeability Coefficient

membrane becomes compressed, resulting in a more compact support structure with a decreased water permeability. Figure 41 indicates that the compaction of the polysulfone portion of the asymmetric membrane continues at least to an operating pressure of 100 atmpsheres.

Figures 42 and 43 depict a linear increase in the salt permeation coefficient with increasing interfacial salt concentration for five membranes having different water production and salt rejection capabilities. These membranes were cast using the two different PEI-TDI concentrations listed in Tables 51 and 52. Kimura and Sourirajan (1968) have also conducted experiments on cellulose acetate membranes to determine the variation of solute permeability coefficient with feed concentration for many different organic and inorganic solutes in aqueous solution. According to their findings, the solute permeability coefficient, B, is not effected by changes in process fluid concentration or feed rate for sodium chloride solutions. However, for sucrose solutions these authors have found that log B decreases linearly with concentration. It is evident that solute-membrane interactions may have a marked effect upon the performance of a membrane by altering its solute permeability coefficient.

For NS-100 type membranes, the salt permeability coefficient is completely determined by the interfacial concentration, X_{A2}. A change in operating pressure or feed rate may indirectly affect the coefficient, B, only through its direct effect on the interfacial concentration X_{A2}. For example, consider the case of a highly rejecting NS-100 type membrane processing a dilute salt solution. The product water permeation rate is, for these conditions, nearly proportional to the operating pressure (see Figure 44). If the operating pressure is doubled, the product water rate is approximately doubled. Thus, the convection of salt to the membrane surface is nearly twice its initial rate and, at steady state, the diffusion of salt from the membrane surface to the bulk solution must increase to twice its initial value. Since the mass transfer coefficient remains essentially constant with a pressure change, the increase in back diffusion of salt must result from an increased concentration driving force. That is, $(X_{A2} - X_{A1})$ must approximately double. An increase in operating pressure, then, has caused the interfacial salt solution, X_{A2}, to become more concentrated with a concurrent increase with operating pressure only, because an increase in operating pressure brings about an increase in the interfacial salt concentration.

A similar conclusion results from a consideration of the effect of a change in feed rate upon the salt permeability coefficient.

10.5.4 Computer Prediction

For prediction calculations, the effect of interfacial concentration, feed rate and operating pressure on the salt permeability coefficient must be determined. In addition, the variation of the pure water permeability coefficient with pressure must be known. A minimum of four experiments

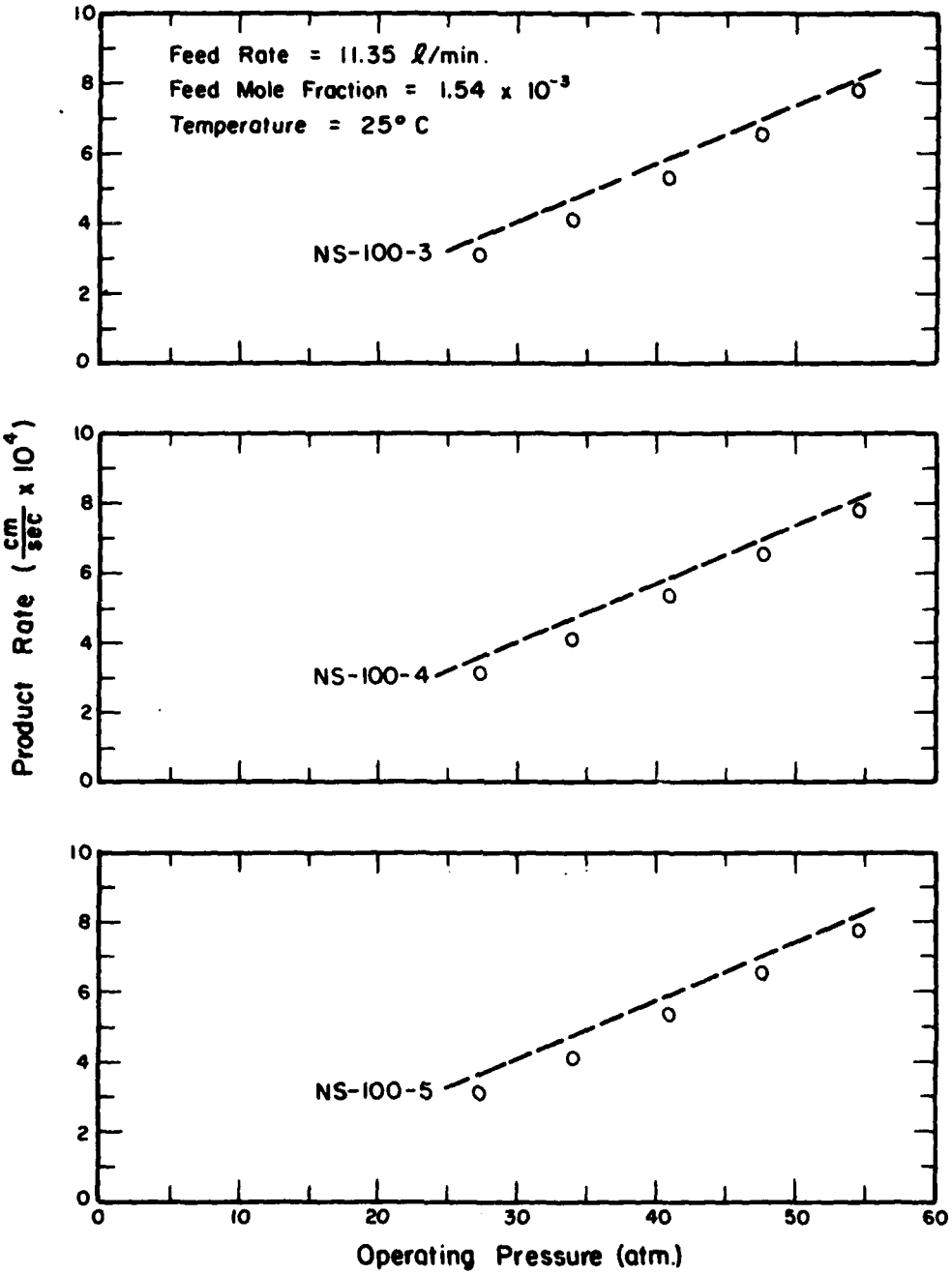

Figure 44. Comparison of Predicted and Experimental Product Rate as a Function of Operation Pressure

must be run to determine the values α, and M for each new membrane. Once the coefficients are known, Equations 57 and 58 can be used to adjust the salt permeability coefficient and pure water permeability coefficient to the conditions at which the predictions are to be made. Equations 23, 27 and 51 may be then solved simultaneously to determine the predicted values of product water rate and salt rejection.

Combination of Equations 23 and 27 yield

$$\frac{Bc(1 - X_{A3})}{X_{A3}} (X_{A2} - X_{A3}) = A[\Delta P(x) - \Delta\pi(x)] \tag{59}$$

For the dilute solutions concerned, the osmotic pressure is directly proportional to the solution concentration.

$$\pi = \theta \cdot X_A \tag{60}$$

Thus,

$$\frac{Bc(1 - X_{A3})}{X_{A3}} (X_{A2} - X_{A3}) = A\Delta P(x) - A\theta(X_{A2} - X_{A3}) \tag{61}$$

or

$$A\Delta P(x) = [\frac{Bc(1 - X_{A3})}{X_{A3}} + A\theta] (X_{A2} - X_{A3}) \tag{62}$$

As a very goo first approximation $(1 - X_{A3}) \simeq 1$ and for highly rejecting membranes $(X_{A2} - X_{A3}) \simeq X_{A2}$ so that

$$X_{A2} \simeq \frac{A\Delta P\ (x)}{[\frac{Bc}{X_{A3}} + A\theta]} \tag{63}$$

The prediction scheme is as follows:

1) From known values of ΔP, Ar, α, use Equation 57 to find A.

2) Select a first approximation to X_{A2} known to be too large (i.e. $\frac{X_{A2}}{X_{A1}} = 1.5$).

3) Use Equation 58 to determine B.

4) Calculate X_{A3} from Equation 63.

5) Compute the mass transfer coefficient from (Harriot and Hamilton, 1965):

$$Sh = 0.0096\ Re^{0.91}\ Sc^{0.35}. \tag{64}$$

6) If Equation 51 is not satisfied select a new value of $X_{A2}^{NEW} = (X_{A2} - X_{A3})$.

7) Return to Step 3 and continue until convergence.

Such calculations have been performed for the sodium chloride-water-NS-100 membrane system using the computer program listed in Figure 45. Results are shown in Figures 46 through 56 where the dashed lines indicate the computer predictions. The average deviations of the computer predicted results from the experimental results are tabulated for two sample cases in Table 53.

10.6 A General Regression Technique for Modeling

Ordinarily, the set of analytical equations which are used to relate the quality and quantity of permeate water to specific operating conditions (pressure, feed rate, feed concentration) are either unknown, complex, or inaccurate. Moreover, even if the system model is known, its usefulness is limited to membrane configuration, membrane type, solute-solvent system and hydrodynamic flow conditions for which it was developed. For example, modeling equations derived to describe the desalting of seawater by tubular NS-100 membranes could not be used successfully to model more complex hydrodynamic configurations than flow through tubes, more complex solute-solvent systems than sodium chloride in water, or polymeric membranes other than NS-100.

Since the entire concept of scale-up and optimization of a modular reverse osmosis system is based upon accurate modeling equations, most optimization modes have been written to include the membrane configuration and membrane type with which the author is most familiar, or for which sufficiently accurate modeling techniques are available. No general model has yet been developed to handle different membrane geometries, membrane types, and solute-solvent systems; thus no computer optimization code has yet been written which is general enough to permit comparisons of optimum reverse osmosis plant designs using different membrane module types.

Figure 45 Listing of Computer Code Used to Predict Water Quantity and Quality

```
$JOB
$NOWARN
C     THIS PROGRAM PREDICTS THE PRODUCT WATER RATE (CM/SEC) AND PRODUCT
C     WATER QUALITY (%) FOR NS-100 TYPE MEMBRANES PROCESSING SODIUM
C     CHLORIDE SOLUTIONS AT SPECIFIED OPERATING CONDITIONS (P,XA1,V).
C
C     THE SCHEME IS ITERATIVE IN NATURE AND TERMINATES WHEN (LHS-RHS).LT. EPS.
C
C     THE USER MUST SUPPLY VALUES OF BSTR,M,XA2STR,AREF,ALPHA,PREF,THETA
C
C     DEFINITION OF TERMS-UNITS.
C     M = SLOPE OF B V.S. XA2,CM/SEC.
C     XA2STR = REFERENCE INTERFACIAL MOLE FRACTION,DIMENSIONLESS.
C     BSTR = REFERENCE SALT PERMEABILITY COEFFICIENT,CM/SEC.
C     AREF = REFERENCE PURE WATER PERMEABILITY COEFFICIENT,CM/ATMSEC.
C     ALPHA = SLOPE OF LOG(A) V.S. P, ATM.
C     ALPHA = SLOPE OF LOG(A) V.S. P, ATM**-1.0
C     PREF = REFERENCE OPERATING PRESSURE, ATM.
C     THETA = OSMOTIC PRESSURE PROPORTIONALITY FACTOR, ATM.
C     P = OPERATING PRESSURE, ATM.
C     XA1 = FEED MOLE FRACTION, DIMENSIONLESS.
C     XA2 = INTERFACIAL MOLE FRACTION, DIMENSIONLESS.
C     XA3 = PRODUCT MOLE FRACTION, DIMENSIONLESS.
C     V = FEED RATE, CM/SEC.
C     RATIO = XA2/XA1.
C     SALT PERMEABILITY COEFFICIENT, CM/SEC.
C     A = PURE WATER PERMEABILITY COEFFICIENT, CM/SEC ATM.
C     RE = REYNOLDS NO., DIMENSIONLESS.
C     DIA = MEMBRANE TUBE DIAMETER, CM.
C     KVISC = KINEMATIC VISCOSITY, CM**2/SEC.
C     SC = SCHMIDT NO., DIMENSIONLESS.
C     K = MASS TRANSFER COEFFICIENT, CM/SEC.
C     DAB = SALT DIFFUSIVITY, CM**2/SEC.
C     LHS = AS DEFINED IN PROGRAM (LEFT HAND SIDE)
C     RHS = AS DEFINED IN PROGRAM.
C     EPS = ERROR INCREMENT
C     SCALE = ITERATION ACCELERATION FACTOR, DIMENSIONLESS.
C     PRODRT = PRODUCT WATER RATE, CM/SEC
C     REJN = SALT REJECTION, %.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 M,K,KVISC,LHS
C
      READ (5,10) M,XA2STR,BSTR,AREF,ALPHA,PREF,THETA
10    FORMAT(7D10.0)
      WRITE (6,20) M,XA2STR,BSTR,AREF,ALPHA,PREF,THETA
20    FORMAT('1','M = ',D10.4,10X,'XA2STR = ',D10.4,10X,'BSTR = ',
     1       D10.4/' AREF = ',D10.4,7X,'ALPHA = ',D10.4,11X,'PREF = ',
     2       D10.4/' THETA = ',D10.4)
C
25    READ (5,30) XA1,P,V,DIA
30    FORMAT(4D10.0)
      WRITE(6,31) P,V,DIA
31    FORMAT('0','P = ',D10.4,10X,'V = ',D10.4,15X,'DIA = ',D10.4)
C
      RATIO = 1.2
      XA2 = XA1*RATIO
      A = AREF*DEXP(-ALPHA*(P-PREF))
40    B = M*(XA2-XA2STR)+BSTR
      XA3 = B/(A*((P/XA2)-THETA))
```

```
C       SOLUTICN PROPERTIES.
        KVISC = 0.91D-2
        DAB = 1.475D-5
C       COMPUTE REYNOLDS NO.. SCHMIDT NO.
        RE = DIA*V/KVISC
        SC = KVISC/DAB
C       COMPUTE THE MASS TRANSFER COEFFICIENT.
        K = 0.0096*DAB*(RE**0.91)*(SC**0.35)/DIA
C
        LHS = K*(XA2-XA1)/(XA2-XA3)
        RHS = B*(XA2-XA3)/XA3
C       SET ERROR FACTOR.
        EPS = 1.0E-6
C
        IF((LHS-RHS) .LT. EPS) GO TO 50
        SCALE = 0.1
        XA2 = (XA2-SCALE*XA3)
        GO TO 40
50      PRODRT = A*(P-THETA*(XA2-XA3))
        REJN = (XA1-XA3)/XA1
        WRITE(6,60) PRODRT,REJN,XA1,XA2,XA3,A,B,K
60      FORMAT('0','PRODRT = ',D10.4,5X,'REJN = ',D10.4/
       1' XA1 = ',D10.4,8X,'XA2 = ',D10.4,13X,'XA3 = ',D10.4/
       2' A = ',D10.4,10X,'B = ',D10.4,15X,'K = ',D10.4)
70      STOP
        END

$ENTRY
```

```
M = 0.2175D-02          XA2STR = 0.1620D-02          BSTR = 0.2635D-04
ARSF = 0.1750D-04       ALPHA = 0.0000D 00           PREF = 0.1361D 02
THETA = 0.2535D 04

P = 0.2722D 02          V = 0.1493D 03               DIA = 0.1270D 01

PRODRT = 0.3871D-03     RE IN = 0.9289D 00
XA1 = 0.1539D-02        XA2 = 0.1592D-02             XA3 = 0.1094D-03
A = 0.1650D-04          B = 0.2629D-04               K = 0.8996D-02

CORE USAGE        OBJECT CODE=     2120 BYTES,ARRAY AREA=       0 BYTES,TOTAL A

DIAGNOSTICS        NUMBER OF ERRORS=        0, NUMBER OF WARNINGS=        0, NU

COMPILE TIME=     0.26 SEC,EXECUTION TIME=     0.06 SEC,  WATFIV - JUL 1973 \

        $STOP
```

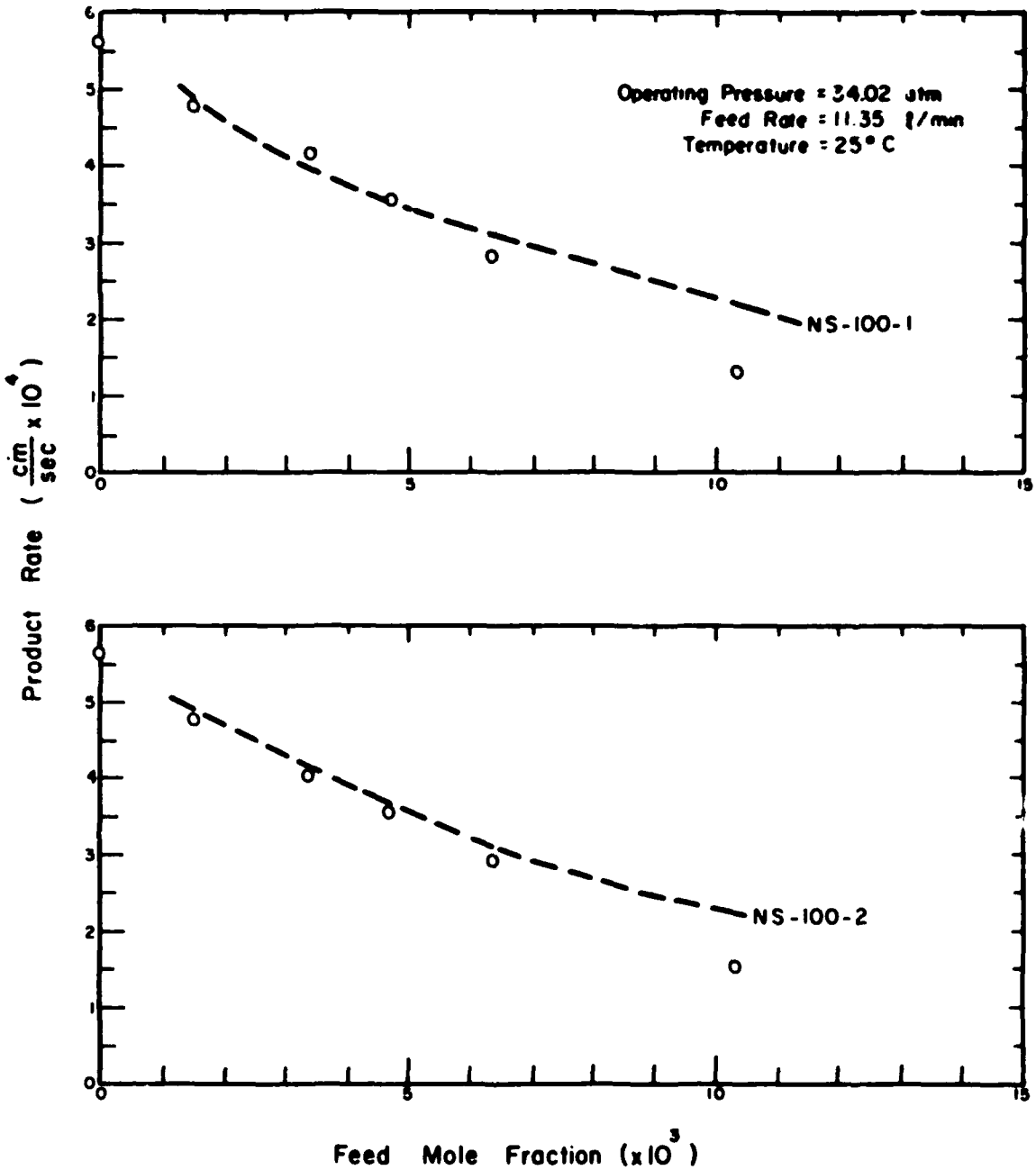

Figure 46. Comparison of Predicted and Experimental Product Rate as a Function of Feed Concentration

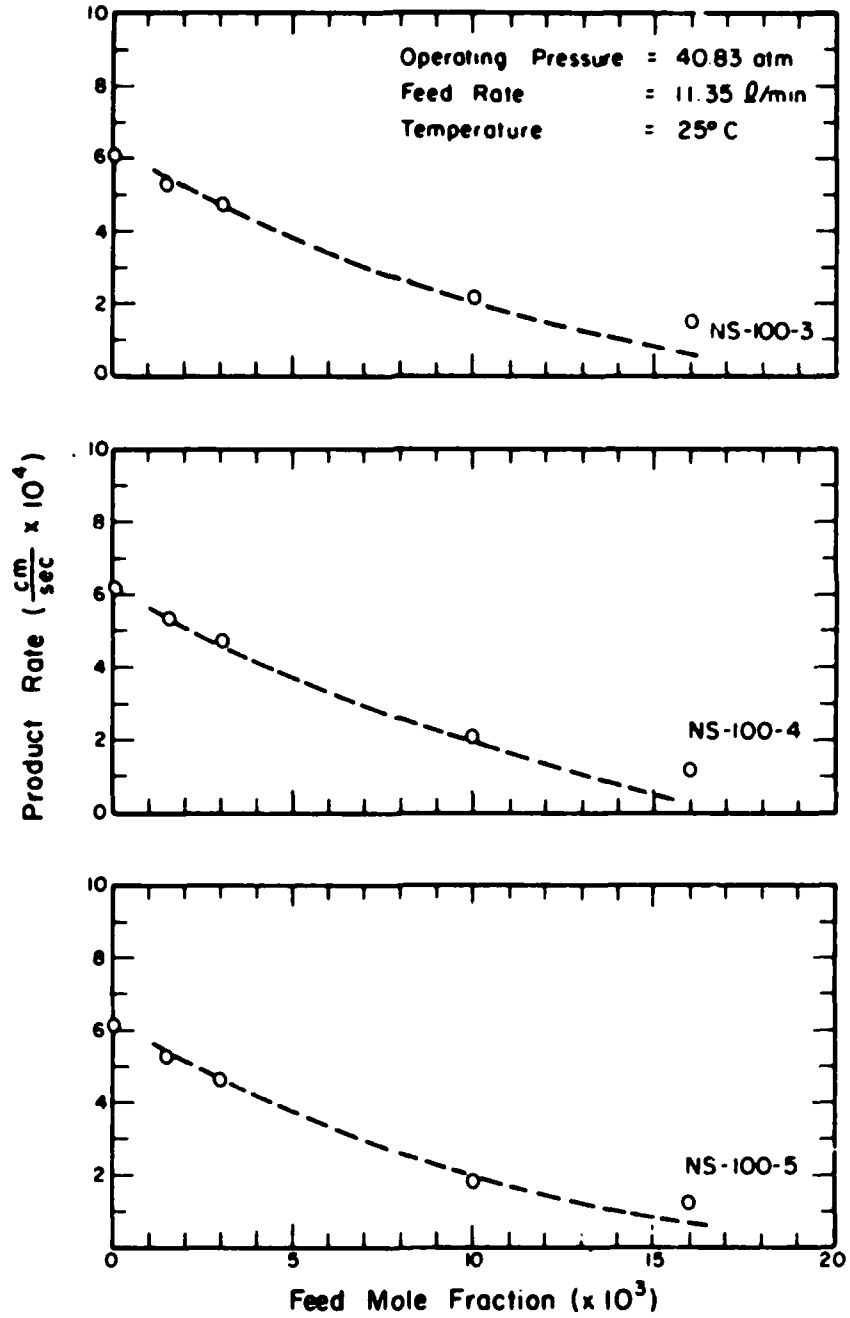

Figure 47. Comparison of Predicted and Experimental Product Rate as a Function of Feed Concentration

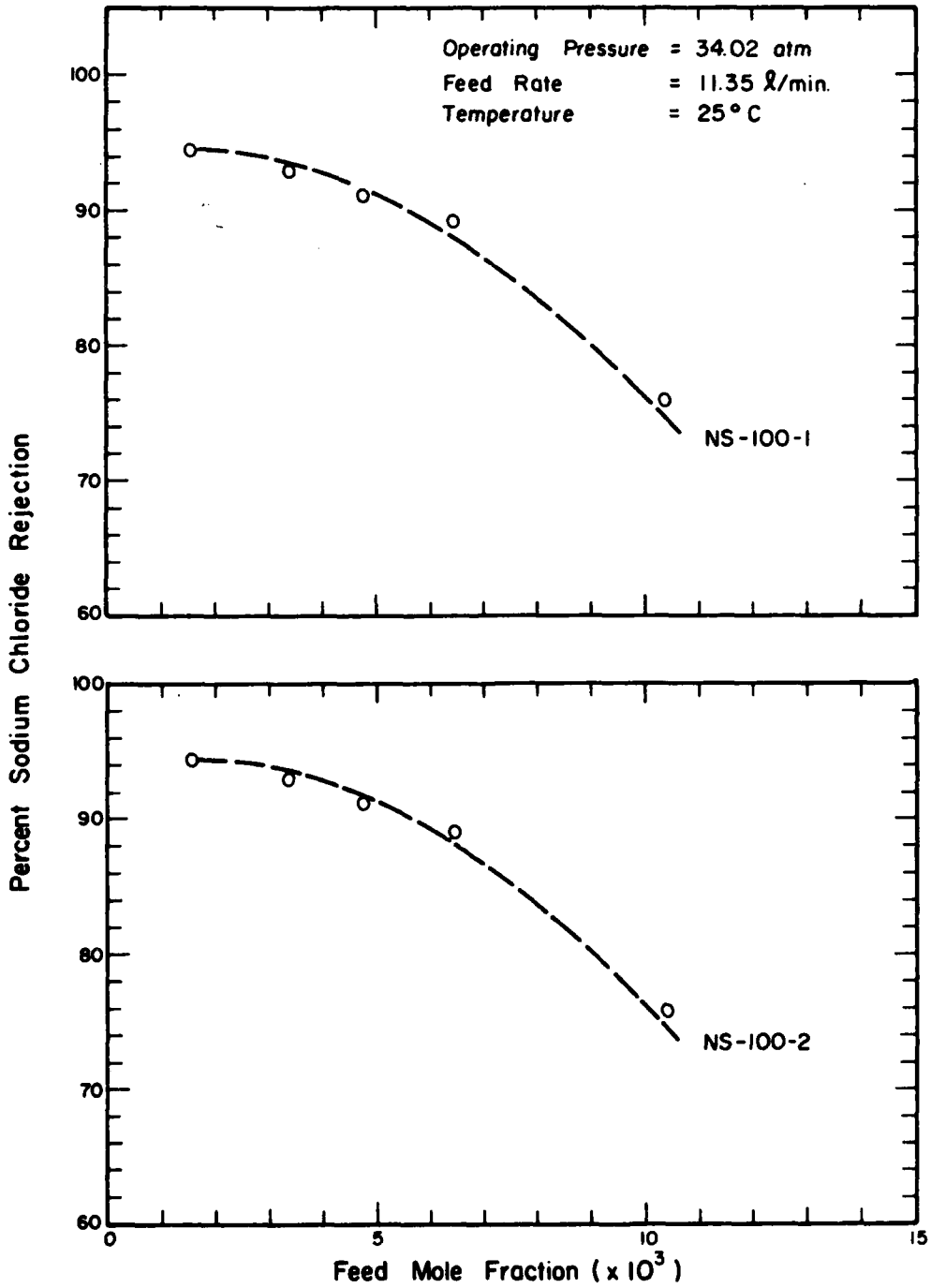

Figure 48. Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Concentration

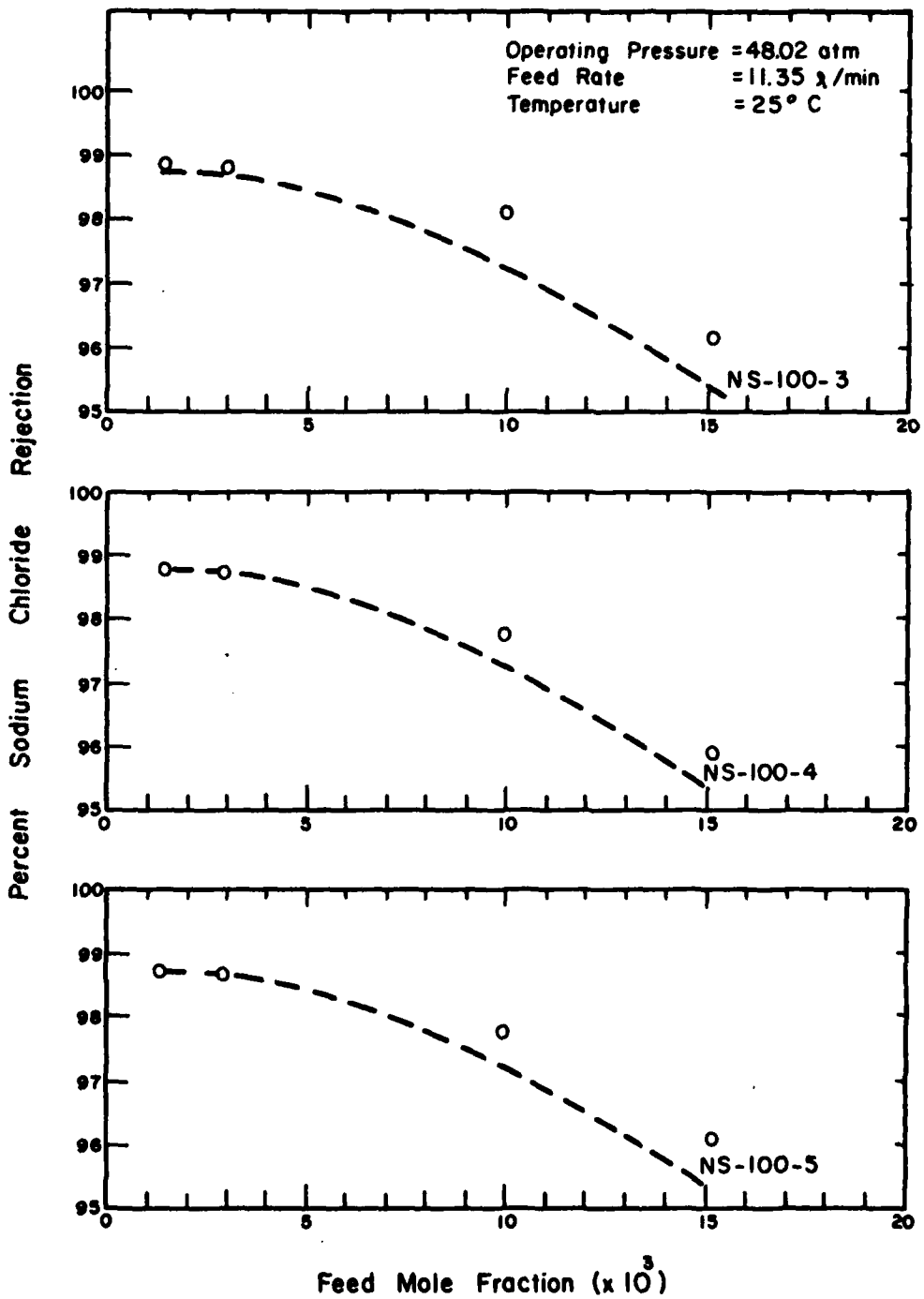

Figure 49. Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Concentration

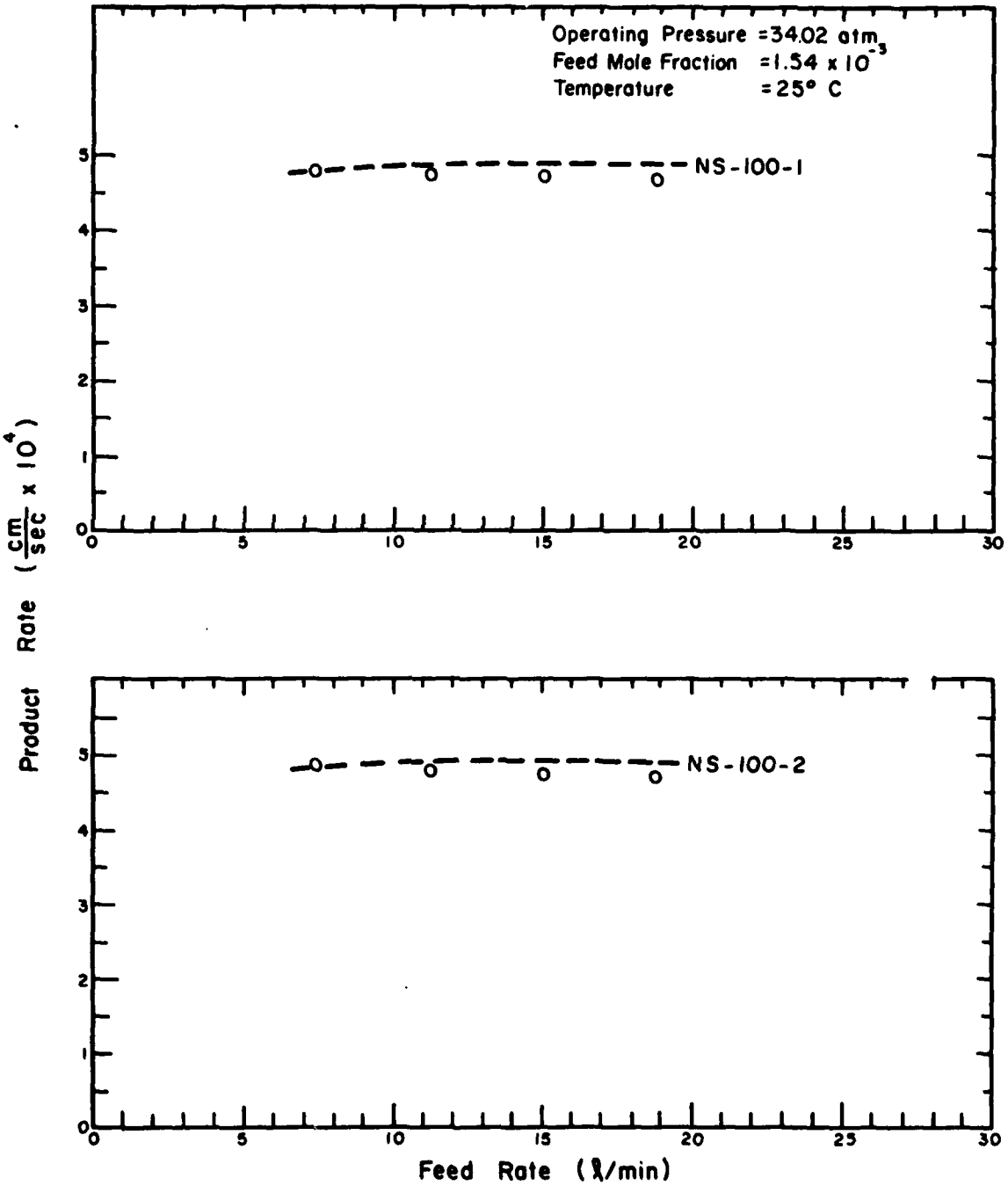

Figure 50. Comparison of Predicted and Experimental Product Rate as a Function of Feed Rate

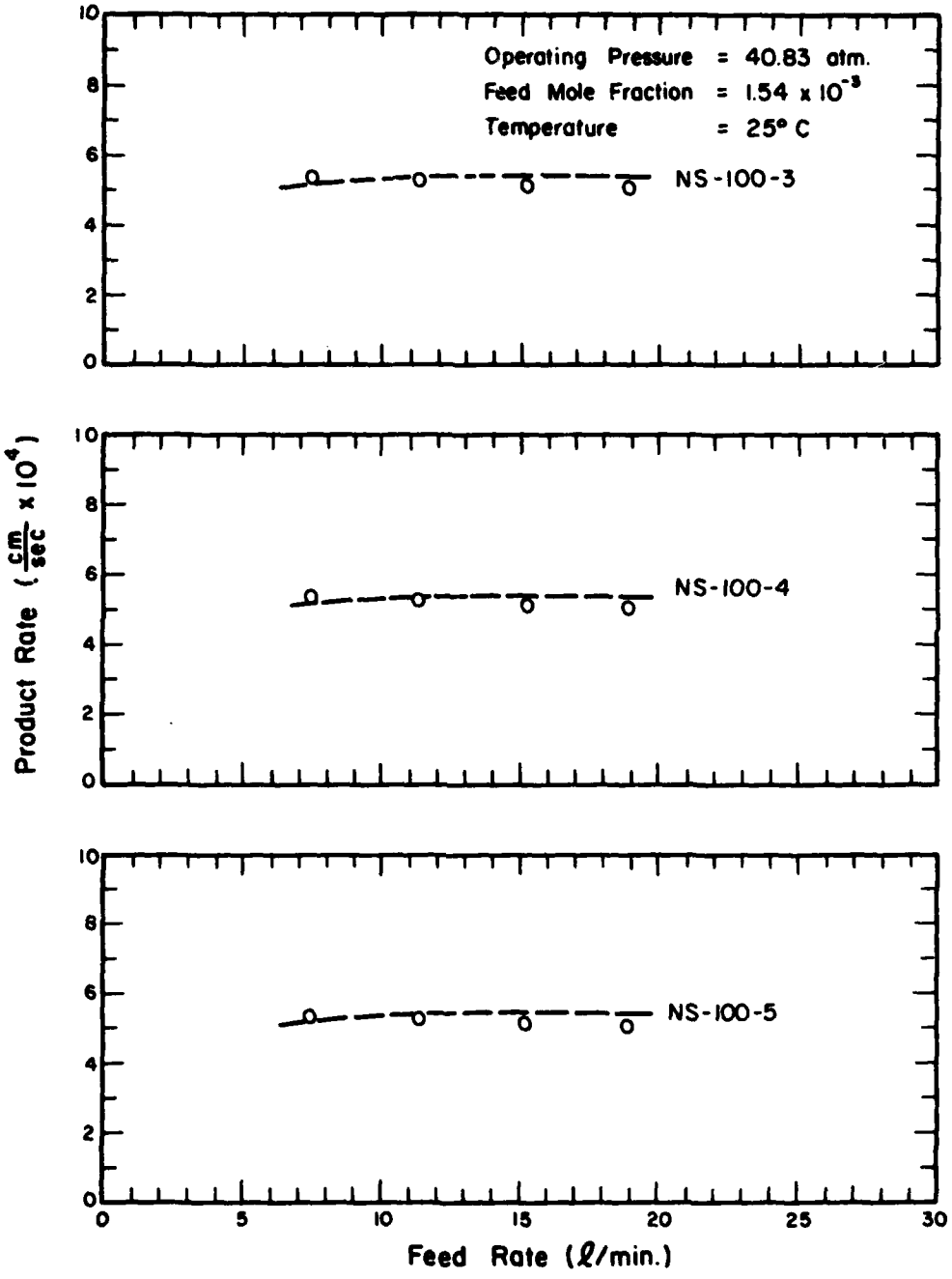

Figure 51. Comparison of Predicted and Experimental Product Rate as a Function of Feed Rate

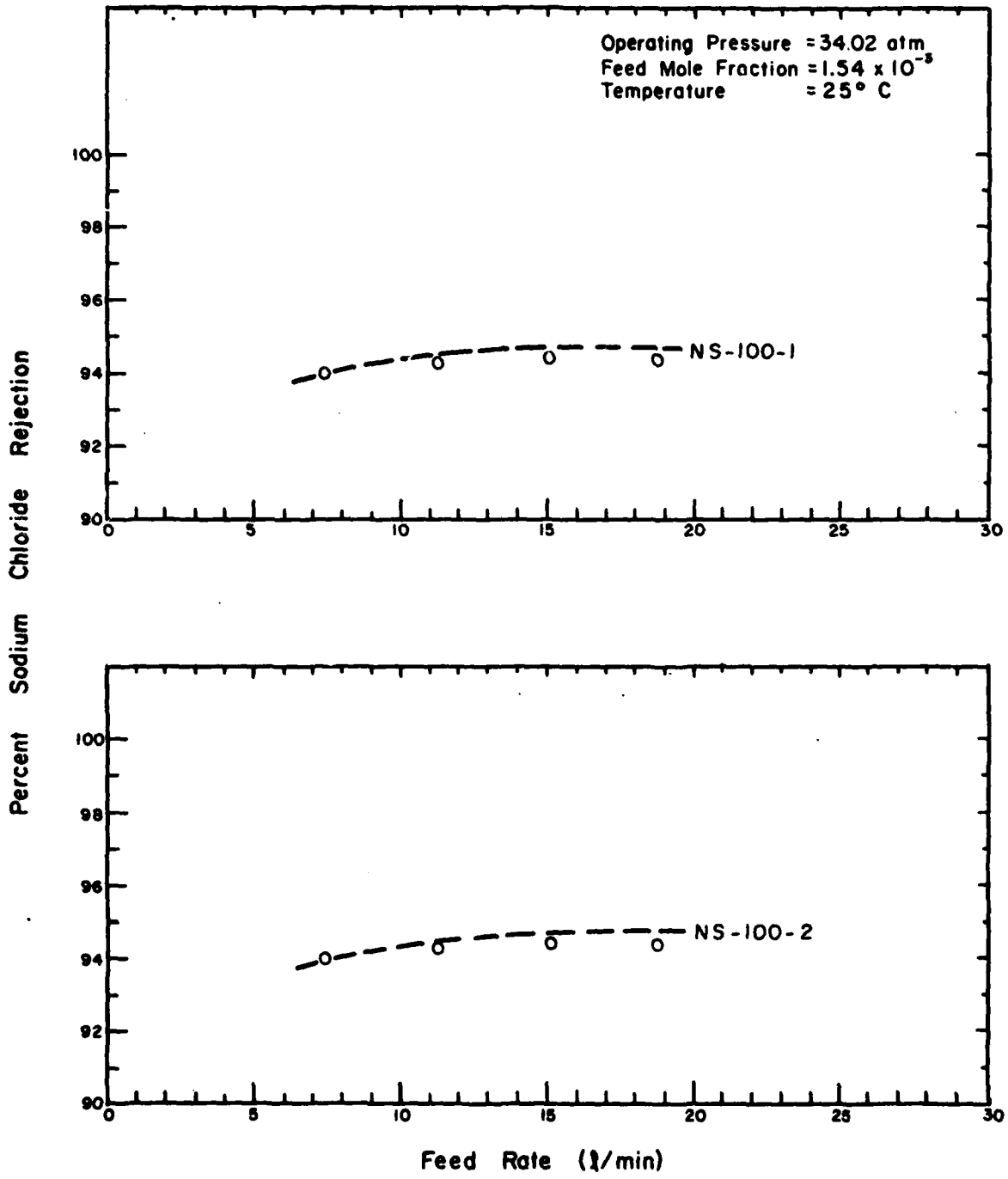

Figure 52. Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Rate

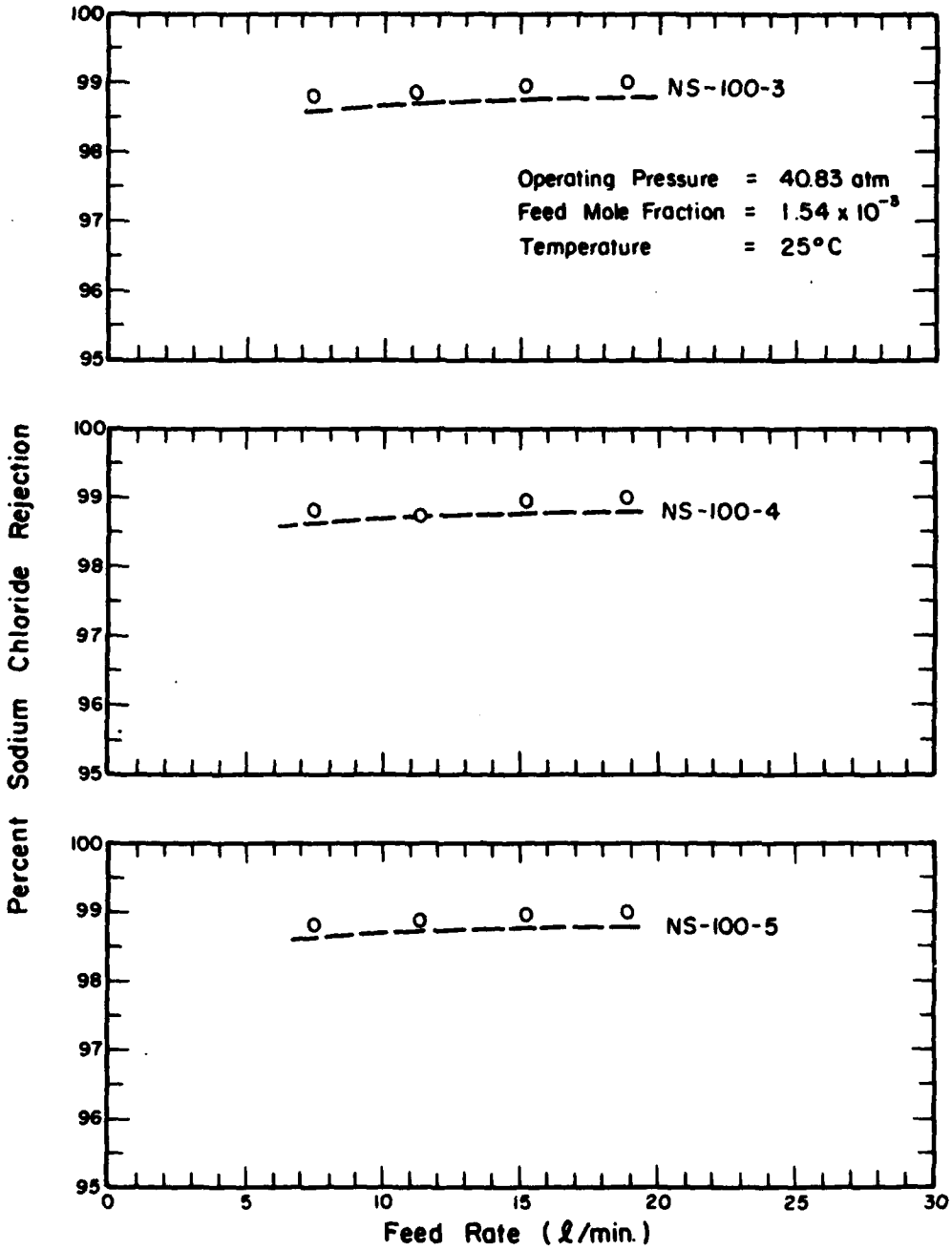

Figure 53. Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Feed Rate

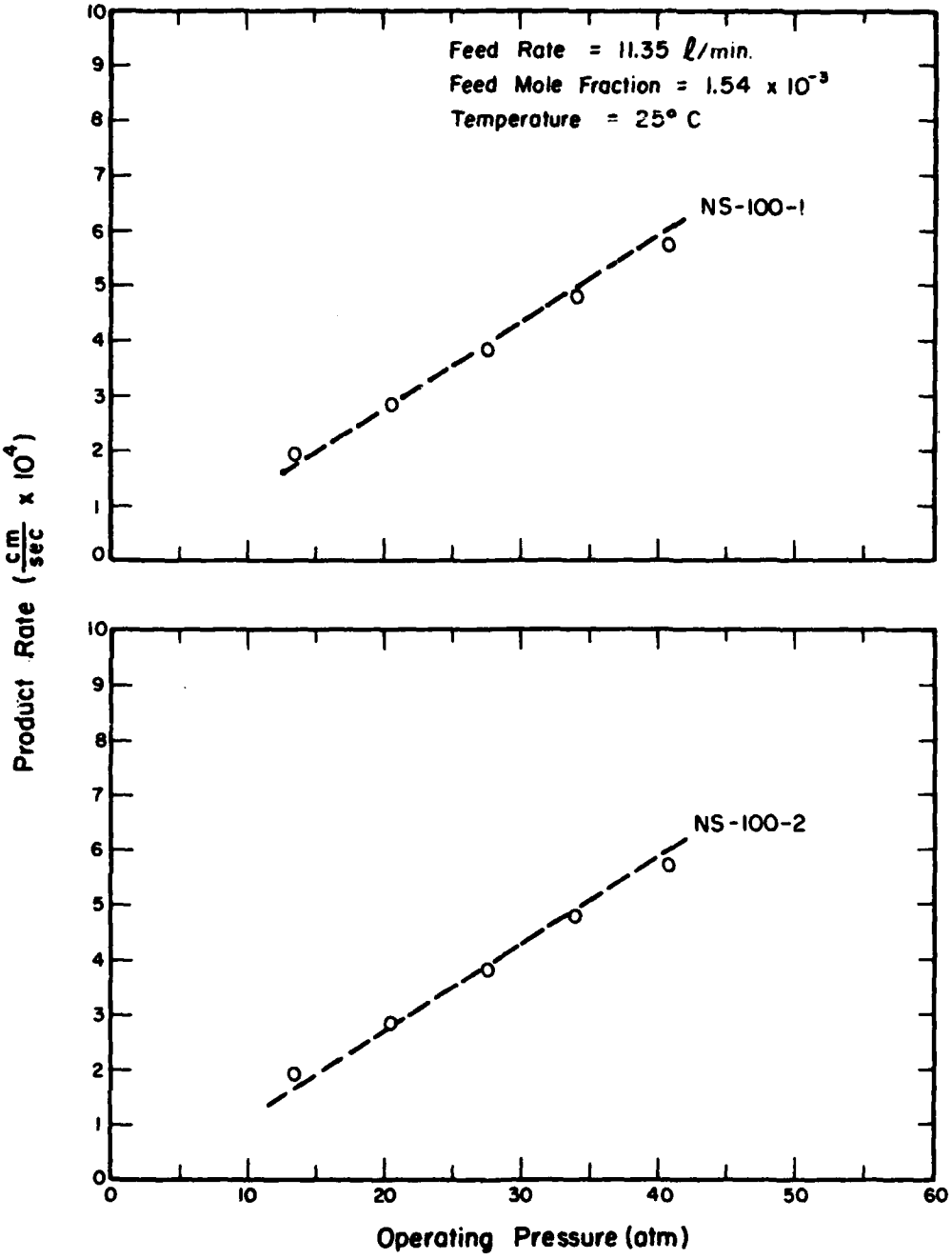

Figure 54. Comparison of Predicted and Experimental Product Rate as a Function of Operating Pressure

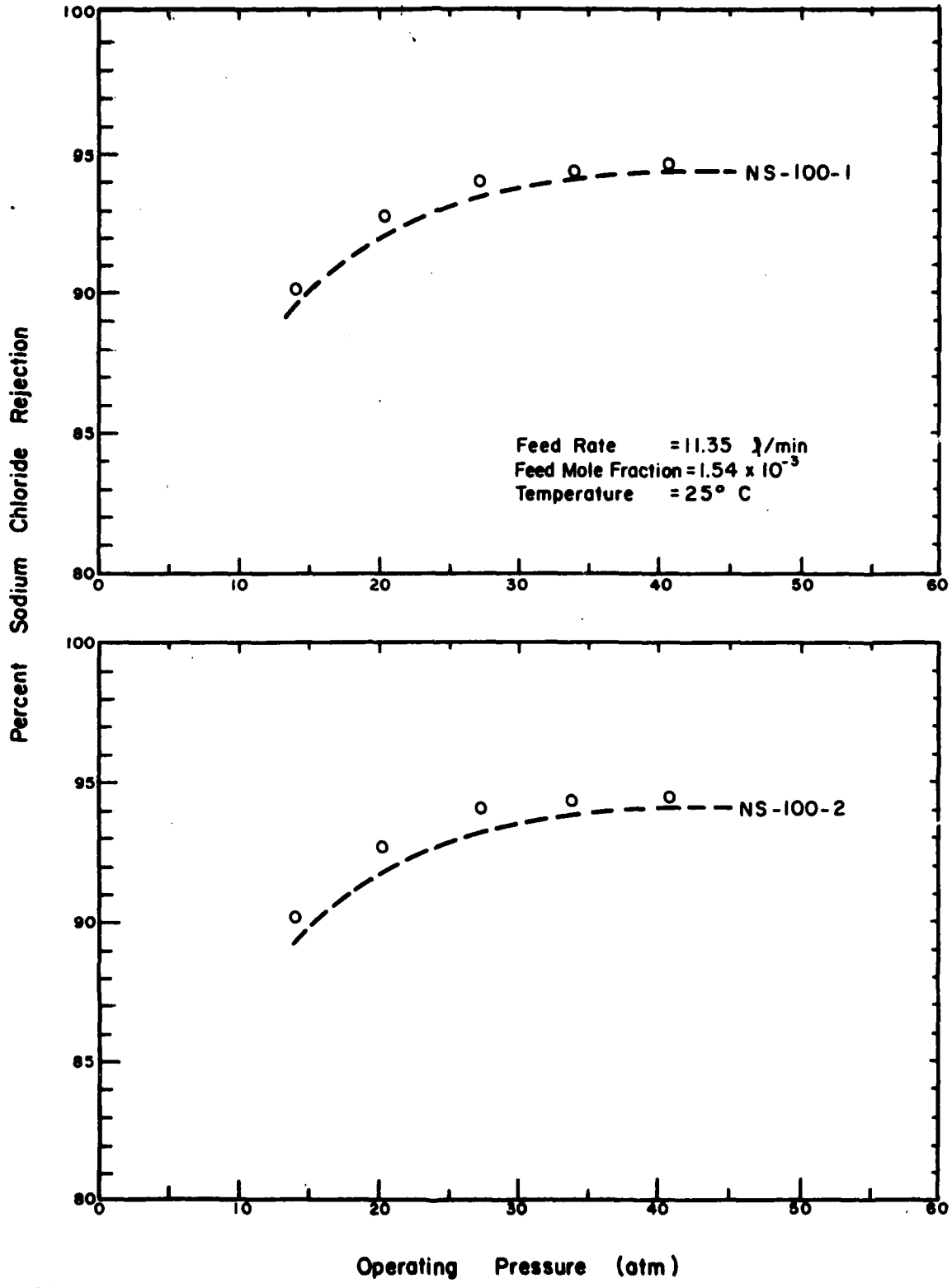

Figure 55. Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Operating Pressure

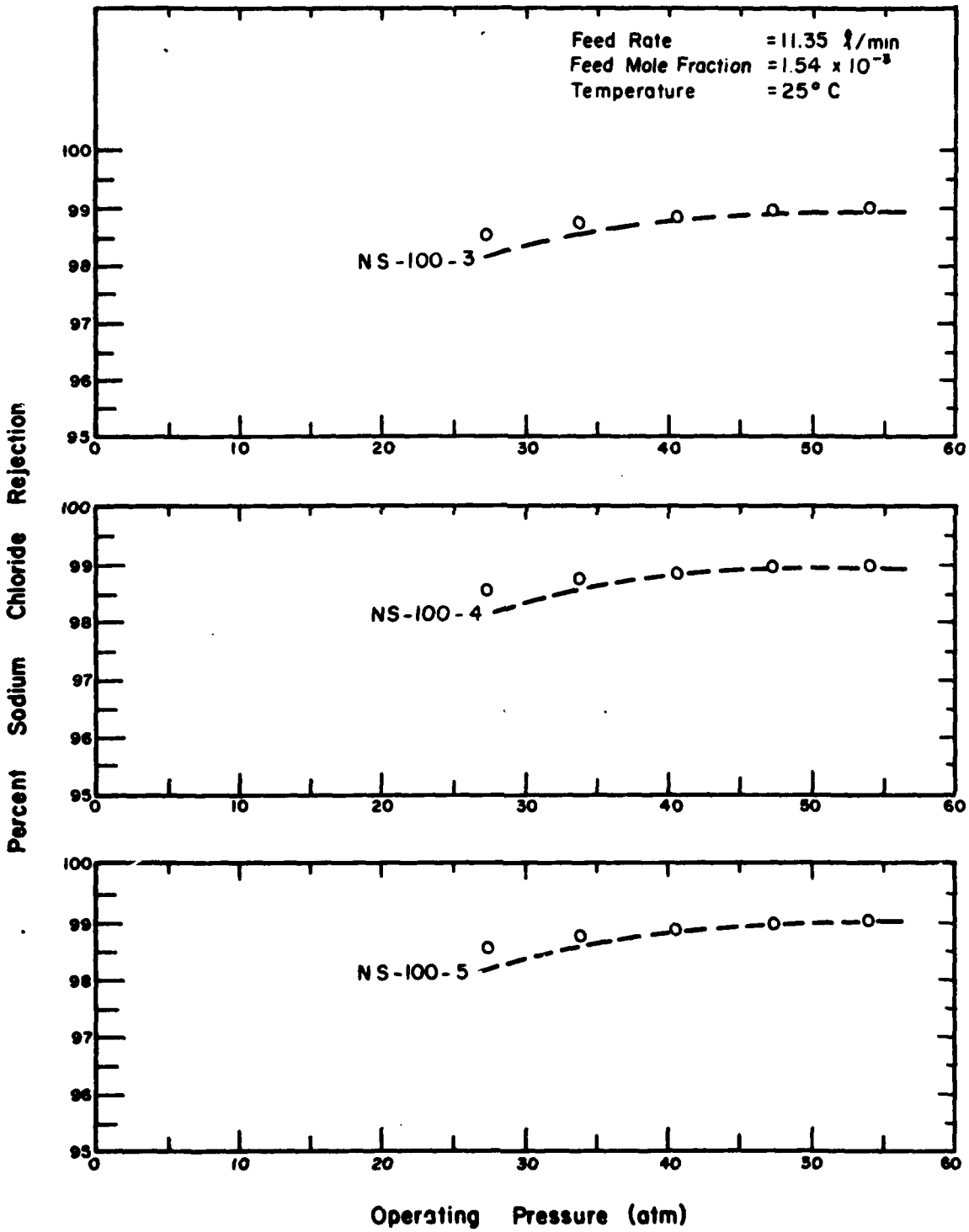

Figure 56. Comparison of Predicted and Experimental Sodium Chloride Rejection as a Function of Operating Pressure

Table 53

Comparison of Computer Predicted Values to Experimental Data

NS-100 Membrane	Average Deviation of Computer Prediction from Experimental Data		Corresponding Figure Number
	Product Rate	Rejection	
NS-100-1	9.1%	0.5%	
NS-100-3	8.4%	0.5%	
NS-100-1	6.2%	0.5%	
NS-100-3	4.1%	0.5%	
NS-100-1	4.8%	0.5%	
NS-100-3	3.6%	0.5%	

In view of the above discussion it is evident that the development of a general analytical technique capable of describing the performance of different membrane types and module geometries for different solute-solvent feed streams would be of great value. Such a technique could then be incorporated into an optimization code and thus, optimal plant layouts, processing conditions, and production costs could be compared for various membrane and module types.

10.6.1 An Analytical Model from Black-Box Experimentation

If the important operating variables (e.g. pressure, temperature, feed rate, feed concentration) of a process can be selected, but the model which relates the output variables (e.g. product rate, product quality) to the operating variables is either too complex or is not known, an empirical approach to model building is required. The development of empirical models to represent a continuous process involves postulation of a mathematical form for the model, black-box experimentation to collect empirical data, estimation of the unknown coefficients in the model, and evaluation of the results.

The term "nonlinear", when applied to empirical process modeling, indicates that the model is of order greater than one in the parameters (coefficients) to be estimated (and more than likely is also nonlinear in the independent variables).

The approximation function (model) relating the product characteristics (e.g. quantity, quality) to the operating variables (e.g. feed rate, pressure, feed concentration) may be represented as

$$\underline{Y} = \underline{Y}\,(\vec{X};\ \vec{\beta}) = \underline{Y}\,(X_1,\ X_2,\ \ldots\ X_n;\ \beta_0,\ \beta_1,\ \beta_2\ \ldots\ s) \qquad (64)$$

where X_i is a particular controllable input variable and β_j a particular unknown coefficient. If the true response function is too complex, or if it is unknown, knowledge of the process is ordinarily contained in tabulated form listing output characteristics for a range of input conditions. It is sometimes expendient to represent these tabulated data by an analytical approximation having sufficient accuracy so that it can be used to model the system in optimization studies. Berezin and Zhidkev (1965) have proposed a number of possible forms for the approximation function and have discussed their relative merits. If insufficient information is available to establish a preferred form for the approximating function, a general polynomial form may provide adequate representation and, in addition, has some real advantages in computational simplicity and susceptibility to statistical analysis. Other functions may well possess other advantages, but these depend upon the criterion used to judge the accuracy of the fit, as well as the nature of the true response. A generalized polynomial approximation would have the following form.

$$\underline{Y}(\vec{X};\vec{\beta}) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_n X_n + \beta_{11} X_1^2 +$$

$$\beta_{12} X_1 X_2 + \ldots + \beta_{nn} X_n^2 + \beta_{111} X_1^3 + \ldots + \beta_{112} X_1^2 X_2 +$$

$$\ldots + \beta_{nnn} X_n^3 + \ldots \qquad (65)$$

and the accuracy of this representation depends primarily upon the number of terms included in the polynomial and on the choice of the coefficients, β. The degree of a polynomial is the highest degree of any term appearing on the right hand side. Thus, if Equation 65 were truncated to

$$\underline{Y} = \beta_0 + \beta_1 X_1 + \beta_{22} X_2^2 \qquad (66)$$

the polynomial would be of the second degree.

Because the generalized polynomial form can be viewed as being a Taylor's series expansion to the true response function, the polynomial representation has in fact a certain theoretical justification. Thus, for a response depending upon a single variable, a Taylors expansion about the base point X_o is

$$Y(x) = Y_o + \left(\frac{\partial Y}{\partial X}\right)_o (X - X_o) + \frac{1}{2}\left(\frac{\partial^2 Y}{\partial X^2}\right)_o (X - X_o)^2 + \ldots \qquad (67)$$

and by retaining a sufficient number of terms, any smooth function can be represented by such a polynomial in a restricted region. If the range of interest is limited so that the quantity $(X - X_o)$ is small, Equation 67 reduces to

$$Y(x) \quad \underline{Y}(x) = \left[Y_o - \left(\frac{\partial Y}{\partial X}\right)_o X_o + \frac{1}{2}\left(\frac{\partial^2 Y}{\partial X^2}\right)_o X_o^2\right] +$$

$$\left[\left(\frac{\partial Y}{\partial X}\right)_o - \left(\frac{\partial^2 Y}{\partial X^2}\right)_o X_o\right] x + \frac{1}{2}\left(\frac{\partial^2 Y}{\partial X^2}\right)_o X^2 \qquad (68)$$

or

$$\underline{Y}(x) = \beta_0 + \beta_1 X + \beta_{22} X^2 \qquad (69)$$

Thus, the approximation $\underline{Y}(x)$ to the true response $Y(x)$ is valid over a limited range of X provided the coefficients are properly selected. The same conclusions are valid if higher than second order terms are retained,

except that the range of validity is extended. Certainly, as the range of variation is increased, a greater number of terms are required to adequately represent the model. The same remarks also apply to models of higher dimensionality.

As mentioned above, polynomial representation becomes applicable over a large range of inputs as the degree is increased. However, the amount of data required to determine the coefficients will also markedly increase. Due to the rapid increase in the minimum number of experiments necessary to evaluate the coefficients as the degree of the polynomial increases, inputs are ordinarily restricted to a limited region so that first, second, or at most third degree polynomials provide an accurate representation.

10.6.2 Nonlinear Coefficient Estimation by Least Squares

Suppose an observable dependant variable, the response, Y_k, $k = 1,2...r$, and several known independent (controllable) variables X_i, $i - 1,2...n$, exist for a certain process. Assume that both Y_k and X_i are continuous variables and let β_j, $j = 1,2...s$, be the unknown parameters in the approximating function (model)

$$\underline{Y}_k = \underline{Y}_k\,(X_{k,1}, X_{k,2} \cdots X_{k,n};\ \beta_0, \beta_1 \cdots \beta_s) \tag{70}$$

or in matrix notation

$$\vec{\underline{Y}} = \vec{\underline{Y}}\,(\vec{X}_{k,n};\ \vec{\beta}) \tag{71}$$

where

$$\vec{X}_{k,n} = \begin{matrix} X_{11} & X_{12} \cdots & X_{1n} \\ X_{21} & X_{22} & X_{2n} \\ \vdots & & \vdots \\ X_{r1} & X_{r2} & X_{rn} \end{matrix} \qquad \vec{\beta} = \begin{matrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_s \end{matrix} \tag{72}$$

with s + 1 coefficients to be determined from r > s experiments. Suppose that the r > s experiments have been performed with each experiment yielding a measured response $\hat{Y}_k$, so that we have r responses associated with the r sets of inputs $X_{k,1}, X_{k,2} \ldots X_{k,n}$, $k = 1,2 \ldots r$. If the experiments were to be repeated for any single set of inputs, a different $\hat{Y}$ might result owing to experimental error. It is important then to realize than an approximating function may fail to represent the observed responses for two

fundamental reasons: first, the data used to determine the approximation may include experimental error, and second, the mathematical form of the approximating function may not correspond to the true, but usually unknown, function.

For the kth experiment, the residual, R_k, may be defined as the difference

$$R_k = \hat{Y}_k - \underline{Y}\,(\vec{X}_k;\ \vec{\beta}) \tag{73}$$

between the observed response $\hat{Y}$ and that predicted by the approximating function, $\underline{Y}$. The parameters β_i obviously influence the magnitude of the residual, since the approximation is altered by changing the numerical values of these coefficients. The residual can, of course, be positive or negative.

Residuals for each of the r experiments may be formed and added in such a way that each contributes a positive quantity to the sum. For example,

$$G = \sum_{k=1}^{r} |R_k| \tag{74}$$

is one such possibility. An alternative summation is given by the sum E of the squares

$$E = \sum_{k=1}^{r} R_k^{\,2} \tag{75}$$

coefficients β_i in the approximating function should be chosen so that some measure of the total of the residuals is reduced. It is reasonable then to choose the β_i so that G, E or some other suitable sum is minimized. Thus, the "fit" of any approximating function is improved as the total of all residuals is reduced.

The least squares estimate is usually chosen as the preferred technique because of ease of computation and other beneficial statistical features (Himmelblau, 1970). Thus, we wish to

$$\text{Minimize } \phi = \sum_{k=1}^{r} w_k\,[\hat{Y}_k - \underline{Y}\,(\vec{X}_k;\ \vec{\beta})]^2 \tag{76}$$

where w_k represents the kth weighing factor, perhaps unity, and $\hat{Y}_k$ is the single observation of Y made at $\vec{X}_k$. Thus, the nonlinear estimation problem appears as an optimization problem in parameter space in which the observations $\hat{Y}_k$ and the independent variables $\vec{X}_k$ are known and the values of all

β_j are variables to be determined so that ϕ is minimized. Figure 57 illustrates the two dimensional geometric interpretation of the selection of β_1* and β_2*; values of β_1, β_2 for which ϕ is minimum.

10.6.3 Comparison of the Mechanistic and Regression Models

Figures 58, 59 and 60 compare simulated product rate and product quality data generated by the computer coded mechanistic model (previously listed in Figure 44) to data generated by the quadratic approximation functions

$$\begin{aligned}\%\ \text{Salt Rejection} = {} & 0.92295158 + 0.1973911 \times 10^{-2}P + 0.12252955 \\ & \times 10^{-5}F - 0.42360048 \times 10^{1}MF - 0.16134596 \times 10^{-4}P^2 + 0.3886053 \\ & \times 10^{-7}P\cdot F + 0.76303363 \times 10^{-1}P\cdot MF - 0.34366288 \times 10^{-9}F^2 \\ & - 0.8136734 \times 10^{-4}F\cdot MF - 0.15378944 \times 10^{3}MF^2 \end{aligned} \tag{77}$$

$$\begin{aligned}\text{PRODUCT RATE} = {} & - 0.31911087 \times 10^{2} + 0.3705265 \times 10^{1}P - \\ & 0.34236652 \times 10^{-2}F - 0.556425 \times 10^{4}MF - 0.8286573 \times 10^{-2}P^2 + \\ & 0.85154388 \times 10^{-4}P\cdot F - 0.40184357 \times 10^{2}P\cdot MF - 0.47012617 \times \\ & 10^{-6}F^2 + 0.22535348F\cdot MF + 0.36614645 \times 10^{5}MF^2 \end{aligned} \tag{78}$$

where P = Operating Pressure (in atm); F = Feed Rate (in gal/day; MF = Feed Salt Concentration in mole fraction. Resultant Product Rate is in gal/day and was converted to cm/sec for Figures 58, 59 and 60. These functions are simply a truncated form of the generalized polynomial shown in Equation 65. The ten coefficients in each of the two quadratic functions above were estimated by minimization of the multivariable least squares function

$$\phi = \sum_{k=1}^{r} w_k \left[\hat{Y}_k - \underline{Y}\,(\vec{X}_k;\ \vec{\beta})\right]^2 \tag{79}$$

using Marquardt's (1963) optimization method. The optimization code used is listed in Appendix IV and will be discussed later.

Sixty-four sets of simulated data (r-64) yielding product rate and product quality as a function of operating conditions (pressure, feed rate, feed concentration) were generated to form the basis for each of the two sets of ten coefficients (s=10) to be estimated for use in the quadratic

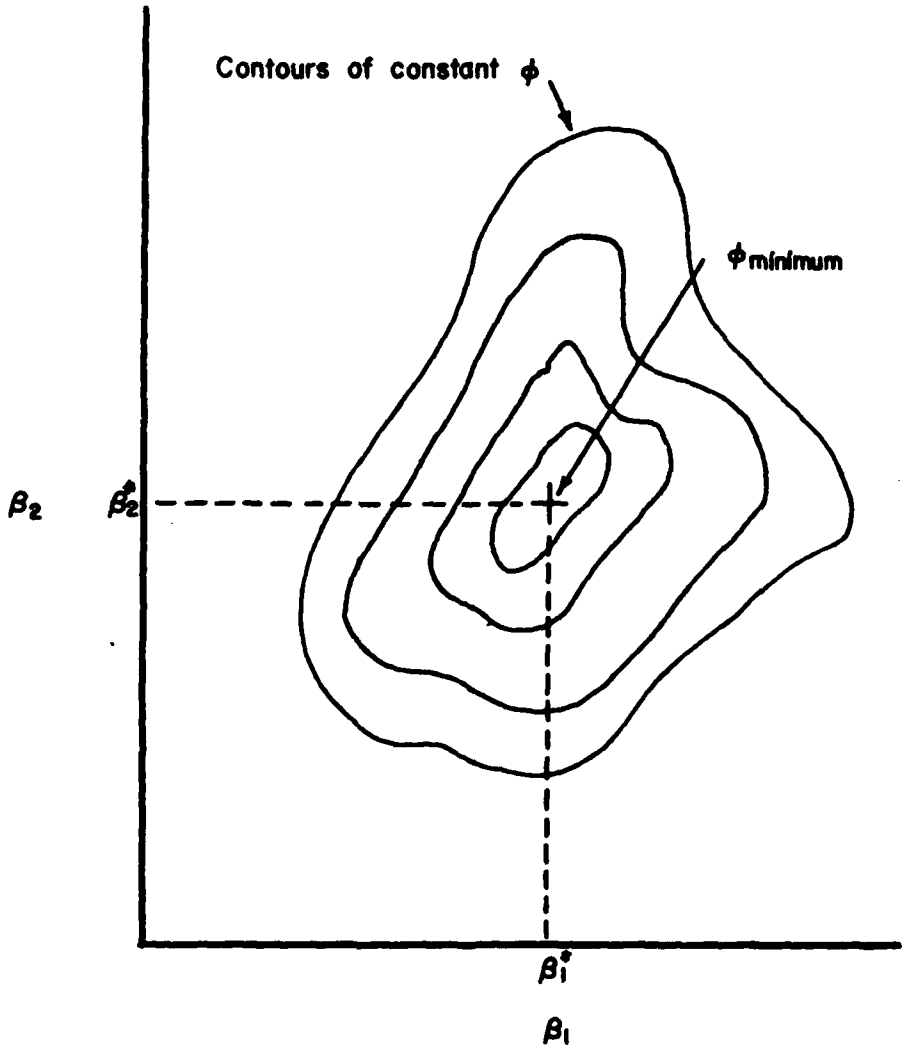

Figure 57. Two-Dimensional Selection of Least Squares Coefficients

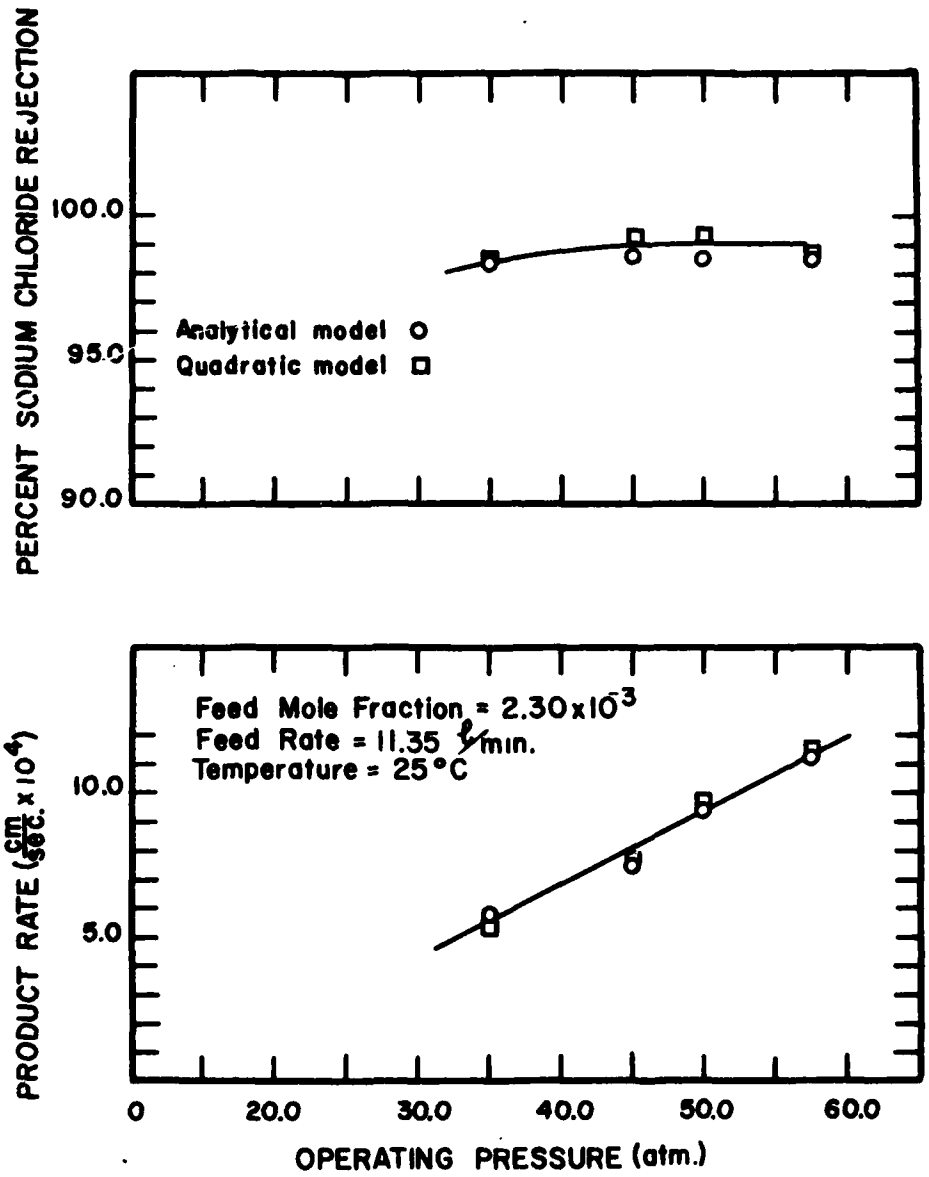

Figure 58. Comparison of Mechanistic and Quadratic Polynomial Models

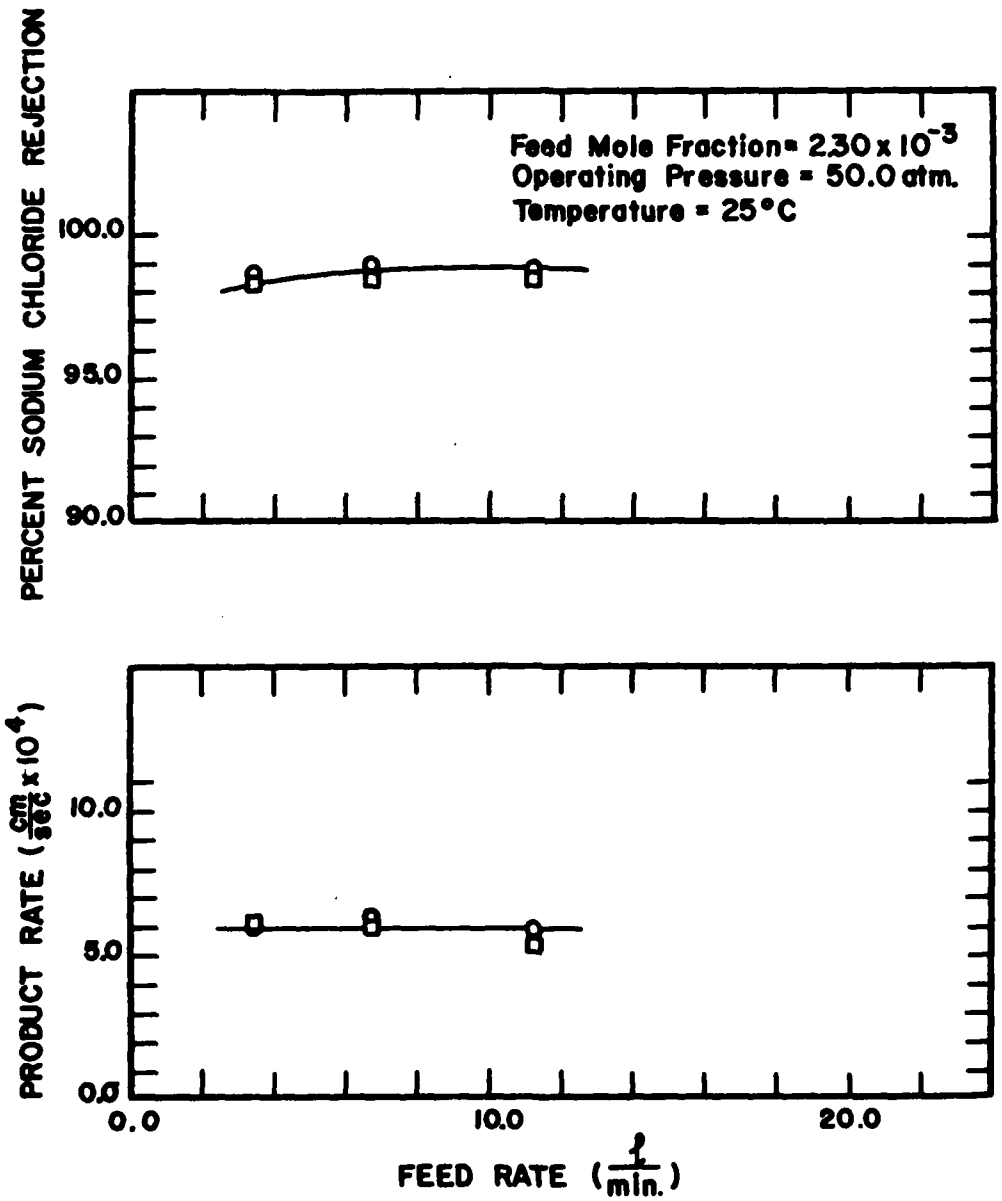

Figure 59. Comparison of Mechanistic and Polynomial Models

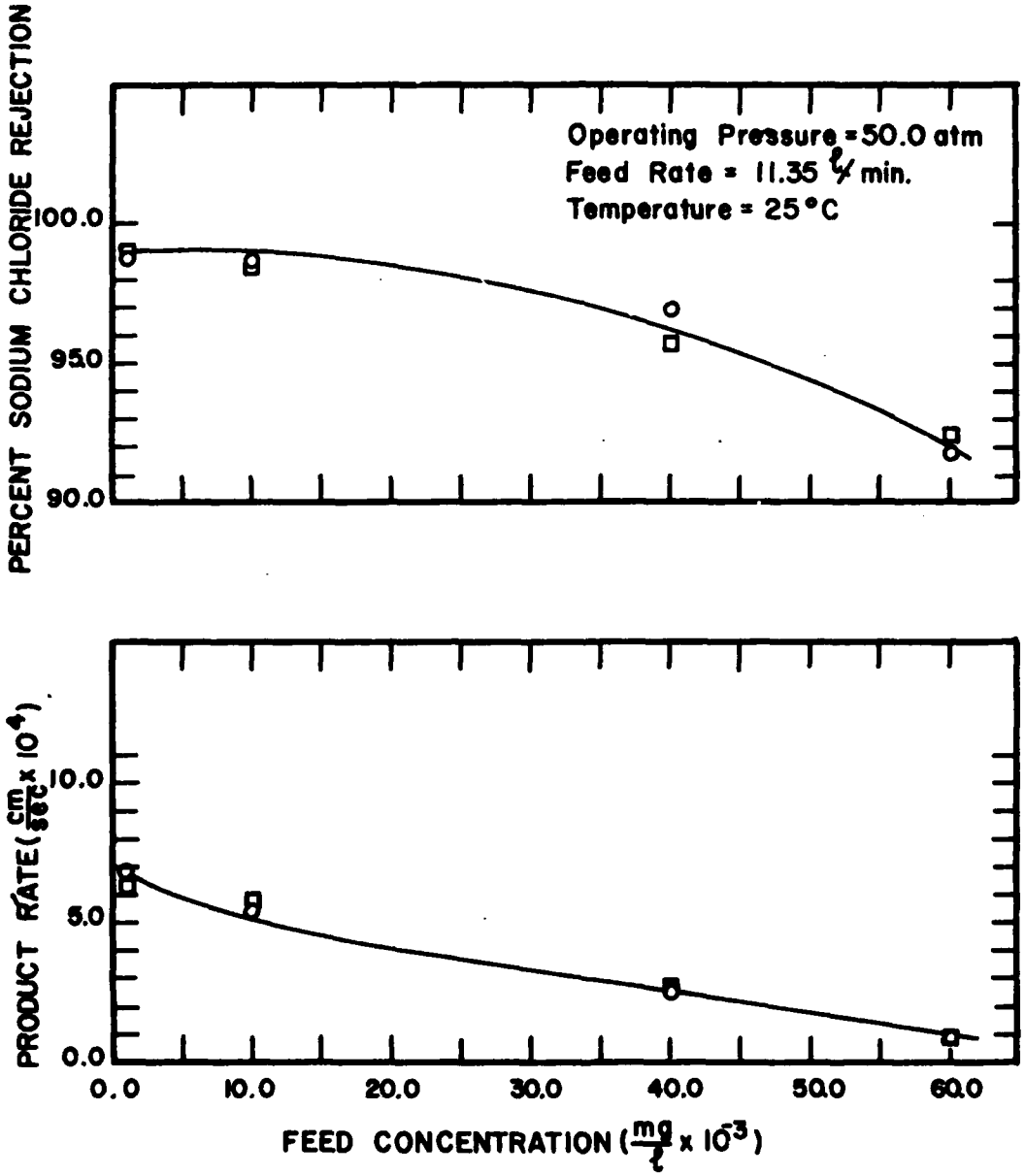

Figure 60. Comparison of Mechanistic and Quadratic Polynomial Models

approximation functions. Once the coefficients have been selected, the resulting Equations 77 and 78 were used to provide the data shown in Figures 58, 59 and 60. The actual comparison then, is between data generated by a mechanistic model (i.e. vertical path on left hand side of Figure 37) to a quadratic least squares fit of that data (i.e. horizontal and diagonal paths in Figure 37). However, if the analytical model used in data generation is assumed to closely represent an existing system (as it has been shown in Figures 45 to 56) then very similar data could be experimentally taken on the existing system and it is reasonable to expect that a quadratic approximation function fit to experimental data should be nearly as accurate as shown in Figures 58, 59 and 60.

It is important to realize that the fitting of an approximation function, be it a polynomial or otherwise, to experimental data taken in a black-box fashion on an existing system does not involve detailed knowledge of the system. In the case of the reverse osmosis process, estimation of the product water rate and product quality by an approximation function requires no knowledge of the membrane type, hydrodynamic regime, membrane geometry or solute-solvent-membrane interaction, provided sufficient experimental data is available.

In essence, if a suitable form for the approximation function can be found and if experimental data is available, the reverse osmosis process can be readily modeled via a surface fitting technique for any binary solution regardless of membrane geometry, membrane type or hydrodynamic conditions. Furthermore, the simple nature of the approximation function makes it amenable to incorporation into optimization schemes to provide information concerning the optimal design and operation of a reverse osmosis plant.

10.7 Optimization Techniques

The act of optimization frequently presents a mathematical problem of such a nature that a certain function of several variables is to be maximized or minimized subject to some constraints imposed on the variables. The function selected to be representative of the performance of the system is called the objective function. It is clear that the maximization or minimization of the objective function leads to optimization of the system. The optimizer has several variables under his control called decision variables. The problem then, is to find values of decision variables, within allowed constraints which maximize or minimize the value of the objective function.

In the particular case to be studied, perhaps the best indication of optimum reverse osmosis desalination plant operation would be the cost of producing a unit quantity of water meeting a predetermined quality specification. The objective becomes the minimization of cost through the manipulation of process variables; pressure, feed rate, feed concentration, tubular membrane diameter, etc. Once the process conditions have been selected which minimize water production cost, the system has been optimized.

10.7.1 Numerical Optimization of Nonlinear Multivariable Functions

The general organization of the search for an optimum value of a multivariable objective function can be summarized as a sequential search involving the successive calculation of new values of the objective function and the comparison of these values with the best values which has been so far obtained. With this iterative procedure in mind, the basic difference in the methods proposed in the literature lies in the philosophy dictating the choice of the next location for objective function evaluation. In any logical method, the selection of the new location for evaluation of the objective function is of major importance. The procedure for making such a choice is often described in terms of search strategy. In general, once a feasible base point is chosen, a set of exploratory experiments is carried out in the vicinity of this base point. This exploration is made, initially, to study the behavior of the objective function in the neighborhood of the starting location, thus providing information about those directions of movement which might yield favorable results.

Thus, one important feature of any search method is the choice of a direction of movement. If the direction can be chosen from only a finite number of experiments, the direction of movement will be in a favorable direction only, and not necessarily lying along the line of greatest improvement. If on the other hand, the choice is unrestricted, the direction along the line of steepest gradient may be taken.

The second essential feature of any multidimensional search is the distance of movement along the chosen direction. Only at this point does possible improvement occur in the values of the objective function, all previous work being required to lay the basis for efficient movement. The move in this selected direction can be a single step, or alternatively, a series of steps in which the objective function is tested at each step; the movement in this direction being continued as long as the objective function improves.

Using the final location of the previous move as the new base, the cycle of exploratory experiments, choice of direction for movement, and movement are repeated as long as necessary. In each cycle of the search the value of the objective function will improve, or at least remain constant. Eventually no further improvement will be obtained. Further optimization might, however, be attempted by reducing the step size in the search. The search for the desired optimum will then end if it has been located within the desired accuracy or if changes in its value have been found to fall within some preselected fraction of its value. The basic search procedure will thus allow movement to at least a local optimum. If constraints are present, an alternative routine will be necessary to allow movement to continue in valid regions only. In any case a special procedure will always be necessary to define the local optimum and stop the search.

In general, an optimum value, found by starting from an initial base point,will not be known to be a global optimum. If the objective function is not known to contain a single optimum, an accepted procedure is to begin the search at a number of initial base points widely separated; and if the same value is found for all tested cases, this value can be termed global with some degree of confidence. Numerical search in the presence of possible multiple optima is a subject of continuing research. As yet, however, a rigorous method of establishing the global optimum has not been proposed, except in certain restricted classes of functions. In general, there is no guarantee that present numerical multivariable optimization methods will achieve a global optimum when faced with a feasible region containing one or more local optima.

In most practical operations, it is unsafe to assume that the system operating variables can be altered without constraint and that the system itself can operate independently of all external requirements imposed its product. It is uncommon in practice to find an unrestricted problem.

Mathematically, all restrictions can be written in equality form

$$g_e = g_e\,(x_1, x_2, \ldots x_n) = 0 \tag{80}$$

or as an inequality,

$$g_m = g_m\,(x_1, x_2, \ldots x_n) \leq 0 \tag{81}$$

Restrictions of the form of equation 81, define an n-dimensional region in which acceptable values of x_1, x_2, ... x_n are found. This region has boundaries which are defined by the locus of points satisfying the equality given by the upper limit of these restrictions. All solutions x_1, x_2, ... x_n lying outside the region delineated by the restrictions are excluded from consideration in the optimization. Thus the absolute optimum may never be achieved due to the presence of restrictions. In such situations we must settle for the best possible optimum for these circumstances.

Methods which reduce the dimensionality of complex systems (e.g. Figure 66) by setting up subproblems, each of lower dimensionality, are called decomposition techniques. Such methods do not carry out the optimization itself, but provide a framework within a suitable optimization can be applied. Several decomposition methods have been proposed but no method has yet been developed for handling the general complex system; however, it is still a subject of active investigation.

Essentially, there are two basic principals in choosing subproblems from a compelx system: 1) a subsystem operating between specified interconnecting links (fixed links) with other subsystems must be operated

optimally. This concept is called the principle of splitting. 2) Whatever the course of action taken in the initial stages of a sequential system, the remaining stages must be conducted in an optimal manner with respect to the feed to those stages. This is called the principal of optimality. Mathematical formulation of the principle of optimality is known as dynamic programming.

In general, the optimum result from a system will not equal the sum of the optima determined from each of the subsystems comprising the total system. A subsystem can, however, be optimized separately if it is linked to other parts of the main system by invarient or fixed links. Systems can often be decomposed into smaller subsystems, even if fixed links are not present. Thus, if certain connections between subsystems are temporarily regarded as being specified by constants, each of the subsystems so isolated may be separately optimized. Finally, of course, a search must be conducted to determine the best feasible values of these links.

10.7.2 Estimation of Coefficients by Marquardt's Method

In order to solve for the unknown coefficients in a multivariable, nonlinear regression equation of the form

$$\underline{Y}_k = \underline{Y}_k\,(x_{k,1}, X_{k,2}, \ldots X_{k,n};\ \beta_o, \beta_1, \ldots \beta_s) \qquad (82)$$

utilizing r data points for the response Y, Marquardt (1963) proposed a method based upon linearization of the proposed least squares objective function

$$\text{Minimize } \phi = \sum_{k=1}^{r} w_k\,[\hat{Y}_k - \underline{Y}_k\,(\vec{X}_k;\ \beta)]^2 \qquad (83)$$

The model (Equation 82) is linearized by expanding $\underline{Y}_k$ in a Taylor's series about current trial values for the coefficients and retaining only the linear terms

$$\underline{Y}_k = Y_k^{(o)} + \left[\frac{\partial \underline{Y}_k}{\partial \beta_1}\right]_{(o)} \Delta\beta_1 + \left[\frac{\partial \underline{Y}_k}{\partial \beta_2}\right]_{(o)} \Delta\beta_2 + \ldots + \left[\frac{\partial \underline{Y}_k}{\partial \beta_s}\right] \Delta\beta_s \qquad (84)$$

where $\Delta\beta_j = [\beta_j - \beta_j^{(o)}]$, j = 1, 2, ... s and k = 1, 2, ... r. The notation (o) denotes quantities evaluated at the initial trial values.

The linearized model is substituted into the objective function and partial derivitives of the function with respect to each coefficient are taken and set equal to zero. These "normal equations"

$$\frac{\partial \phi}{\partial \beta_j} = 0 \qquad j - 1, 2, \ldots s \tag{85}$$

will be of the form

$$(\vec{A}^t \vec{A}) \vec{\Delta\beta} = \vec{A}^t \, (Y - \underline{Y}^{(o)}) \tag{86}$$

where

$$\vec{A} = \begin{matrix} \frac{\partial \underline{Y}_1}{\partial \beta_1} & \frac{\partial \underline{Y}_1}{\partial \beta_2} & & \frac{\partial \underline{Y}_1}{\partial \beta_s} \\ \frac{\partial \underline{Y}_2}{\partial \beta_1} & \frac{\partial \underline{Y}_2}{\partial \beta_2} & & \frac{\partial \underline{Y}_2}{\partial \beta_s} \\ \vdots & & & \vdots \\ \frac{\partial \underline{Y}_r}{\partial \beta_1} & \frac{\partial \underline{Y}_r}{\partial \beta_2} & \cdots & \frac{\partial \underline{Y}_r}{\partial \beta_s} \end{matrix} \tag{87}$$

$$\vec{\Delta\beta} = \begin{matrix} \beta_1 - \beta_1^{(o)} \\ \beta_2 - \beta_2^{(o)} \\ \vdots \\ \beta_s - \beta_s^{(o)} \end{matrix} \quad \text{and } (Y - \underline{Y}^{(o)}) = \begin{matrix} Y_1 - \underline{Y}_1^{(o)} \\ Y_2 - \underline{Y}_2^{(o)} \\ \vdots \\ Y_r - \underline{Y}_r^{(o)} \end{matrix} \tag{88}$$

$\vec{A}^t$ is the transpose of the $\vec{A}$ matrix. The derivitives in the $\vec{A}$ matrix may be evaluated analytically or numerically. If the normal equations are modified by adding the factor λ

$$[\vec{A}^t \vec{A} + \lambda^{(o)} \vec{I}] \, \vec{\Delta\beta} = \vec{A}^t \, (Y - \underline{Y}^{(o)}) \tag{89}$$

then λ is added to each term of the main diagonal of the $\vec{A}^t \vec{A}$ matrix. It can be shown (Himmelblau, 1970) that when $\lambda \to +\infty$ Marquardt's Method becomes identical to Steepest Descent. The Steepest Descent procedure ordinarily converges for poor starting guesses of β_j, but requires a lengthy solution time. As $\lambda \to 0$ Marquardt's Method reduces to the Gauss Newton approach which converges rapidly to a solution but only for good starting estimates of β. Thus, in the Marquardt procedure, the initial values of λ are large and are decreased toward zero as the optimum is approached.

The modified normal equations are a system of linear algebraic equations and may be solved by an appropriate technique for $\vec{\Delta\beta}$. The $\vec{\Delta\beta}$ vector and ϕ will approach zero as convergence is achieved. If convergence is achieved, the final coefficients are calculated from

$$\beta_j = \beta_j^{(o)} + \Delta\beta_j \quad j = 1, 2, \ldots s. \tag{90}$$

If convergence is not achieved, the old values of $\beta_j^{(o)}$ are replaced by the new estimates and the entire process is repeated.

The technique for reducing λ is discussed in the original article by Marquardt (1963)

10.7.3 Optimization by Steepest Descent

The gradient of a function

$$f = f_{(x_1, x_2, \ldots x_n)} \tag{91}$$

designated Δf is a vector at a point on the surface of the function which extends in the direction of the maximum increase in f at the given point. The negative of the gradient extends in the direction of steepest descent. Figure 61 illustrates the geometric interpretation of f, Δf and $-\Delta f$ in two dimensional space. The closed curves represent contours of constant f which are of increasing value proceeding from the minimum f*. Unfortunately, the direction of steepest descent is a local property, so that the direction of steepest descent generally varies from point to point, and the locus of infinitely small moves along the line of steepest descent will ordinarily be a curved line.

If we assume that f is a single value, continuous function with only a single minimum in the region of search, then by determining the components of $-\Delta f$ it is possible to carry out a succession of calculations to reduce the value of f to at least a local minimum.

The basic method of steepest descent is a cyclic or iterative search technique which does not follow the continuous line of steepest descent, but approximates it by a succession of straight lines as shown in Figure 62. Each line corresponds to a stage in the search in which the components of the negative of the local function gradient

$$-\nabla f = -(\frac{\partial f}{\partial x_1})\,\delta x_1 - (\frac{\partial f}{\partial x_2})\,\delta x_2 - \ldots - (\frac{\partial f}{\partial x_n})\,\delta x_n \tag{92}$$

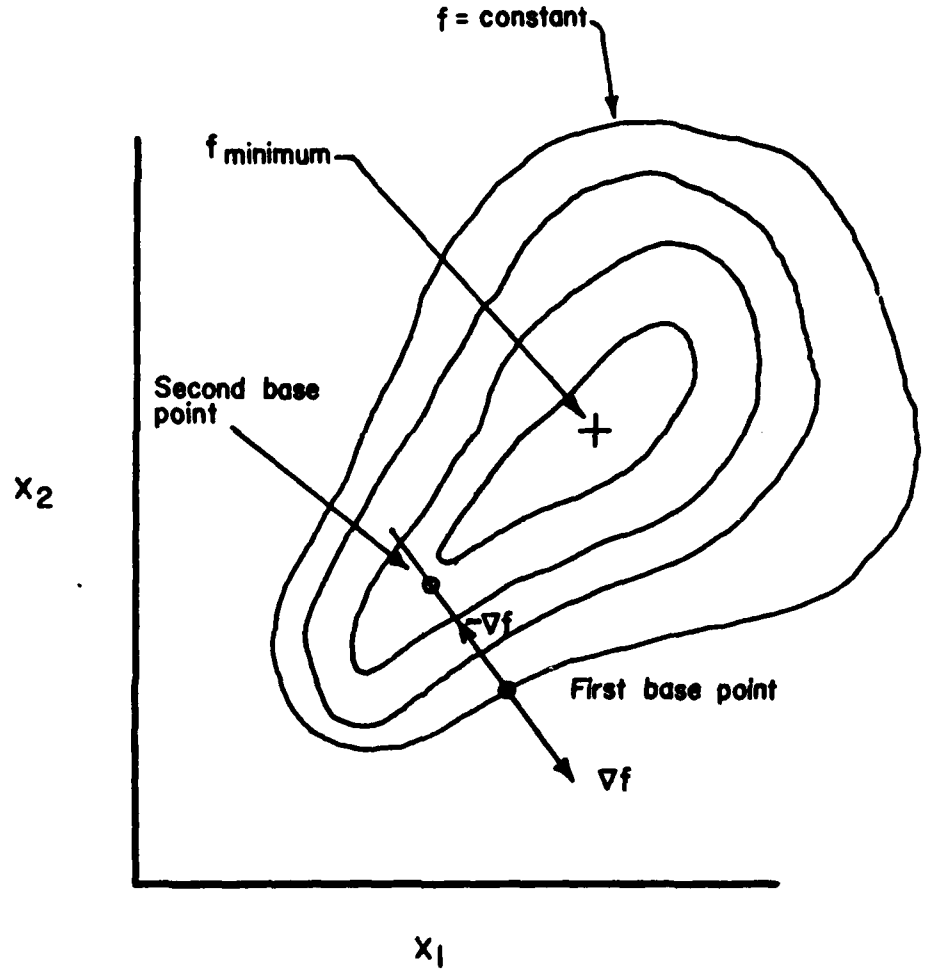

Figure 61. Two-dimensional Geometric Interpretation of the Gradient

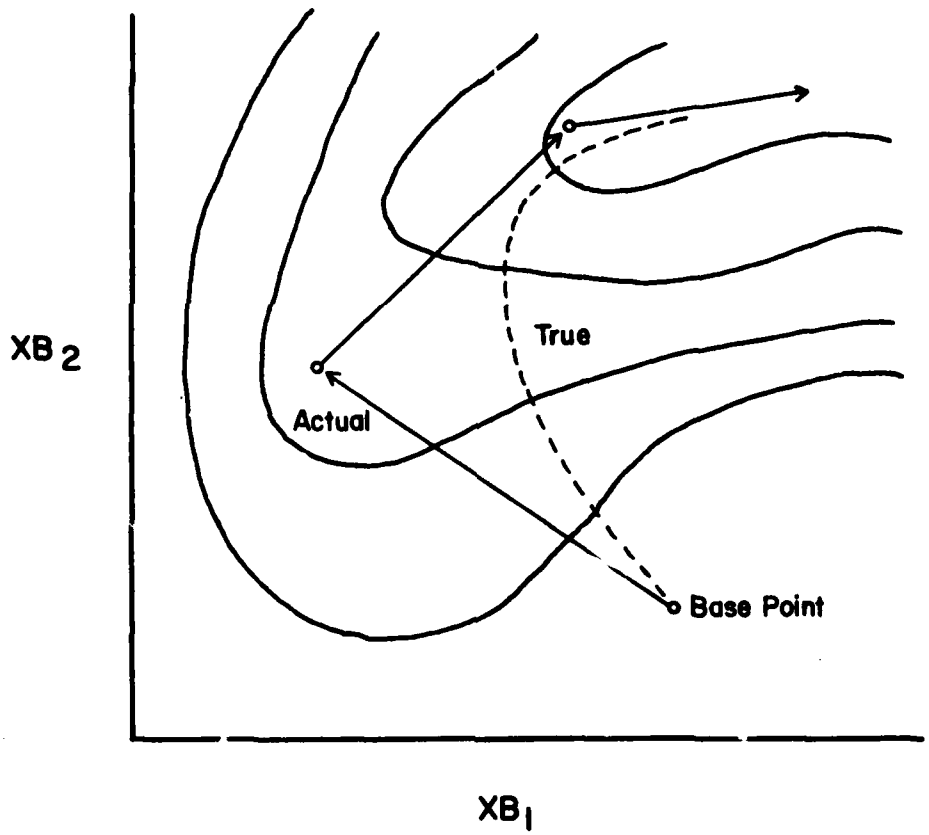

Figure 62. A Sequence of Steepest Descent Moves

are evaluated either analytically or numerically; the unit vector

$$\frac{-\nabla f}{|-\nabla f|} = \frac{-\frac{\partial}{\partial x_1}\vec{\delta x}_1 - \frac{\partial f}{\partial x_2}\vec{\partial x}_2 - \ldots}{\sqrt{(\frac{\partial f}{\partial x_1})^2 + (\frac{\partial f}{\partial x_2})^2 + \ldots}} \tag{93}$$

is computed to ascertain the direction of search, and this direction is searched one dimensionally for the approximate location of the restricted optimum. This point then serves as the base for the next stage. Figure 63 illustrates the numerical calculation of the components $\partial f/\partial x_1$ and $\partial f/\partial x_2$ of a two-dimensional gradient. From the initial base point (xB_1, xB_2) the x_1 component of the gradient is computed by evaluating the function at ($xB_1 + \zeta R1$, xB_2). In a similar manner, using xB_2, the x_2 component is determined. Here, ζ is a constant.

Assuming this line to be a gradient vector, a one-dimensional search is conducted in this direction until the optimum along the gradient is found. Many techniques for such a one-dimensional search are available in the literature (Johnson, 1966; Wilde, 1964). The particular method adopted by Copper and Kephart (1965) uses a geometric series to determine the step size. With this method one doubles the step size following each successful step along the gradient. These authors have shown that if a failure is encountered before the fourth function evaluation the two schemes are very similar. However, if more than four successful steps are required to find the one-dimensional optimum, the geometric scheme determines the optimum with fewer function evaluations than the Fibonacci search technique.

The geometric one-dimensional search can be described as follows. Once the gradient has been determined, one steps out along the gradient a distance ξ times the scale factor γ. The function is then evaluated at this point. If the evaluation is less (in the case of minimization) than the starting point, the search continues to move out along the gradient (see Figure 63), in a manner to be discussed later. However, should the function evaluation be greater than the value at the initial point, the search returns to the starting point and steps out a reduced distance, equal to the product of the reduced scale factor γ_r and the original distance. Note that this step returns the search to approximatly the point at which the partial derivitatives were calculated. Again, the function is evaluated at this new point. If the step is successful, the search continues along the gradient using the reduced scale factor. Should the reduced evaluation be a failure also, the constant factors ζ and ξ are reduced twenty-fold and the above process is repeated. Further failure following this reduction indicates that the optimum has been reached, and the procedure is terminated.

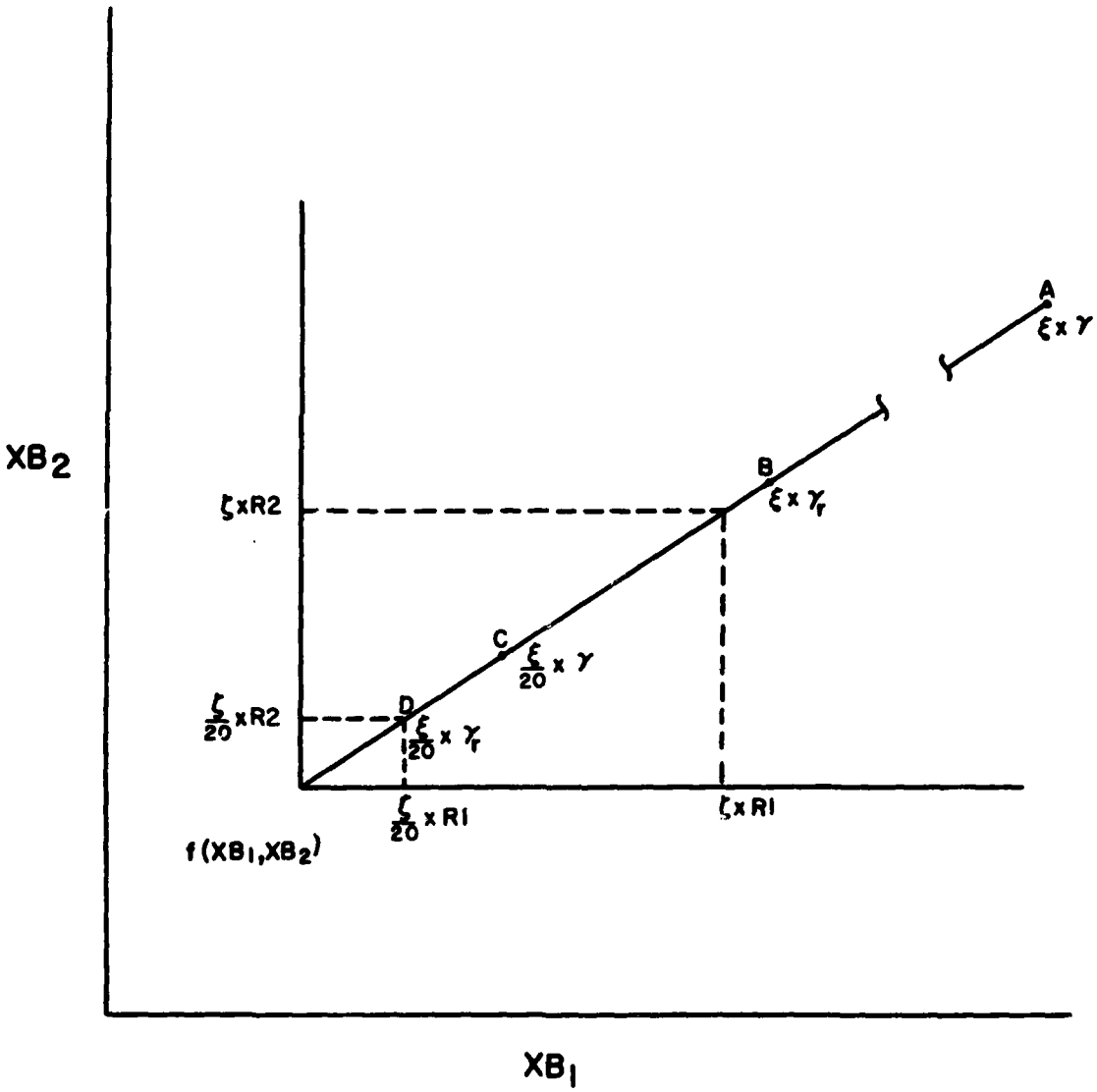

Figure 63. Calculation of a Two-Dimensional Gradient

It is felt (Copper and Kephart, 1965) that the magnitude of ζ and ξ are not important. However, their ratio ζ/ξ should be chosen to be approximately 1/5. The magnitudes of ζ and ξ are determined by the history constructed of the response surface. As previously indicated when a failure occurs the magnitudes are reduced. If, however, several steps (10 to 12) are taken without arriving at a one-dimensional optimum, ζ and ξ are increased.

It has been found (Zellnik, *et al.*, 1962) that one-sided difference approximations, as opposed to central-difference approximation, are sufficient to calculate the gradient. In order to evaluate the objective function, and calculate the gradient at some point X_i ($i = 1, 2, 3 \ldots N$), only $N + 1$ function evaluations are required compared to $2N + 1$ evaluations required by the central-difference method. The one-sided difference technique is sufficiently accurate, and a far more rapid method of approximating the partial derivitives. It should be observed that this calculation is only an approximation of the gradient. However, the error decreases as the optimum is approached and at optimum is negligible.

In the real physical situation, variables such as pressure, velocity, and product concentration have upper and lower bounds. One definite requirement of the optimization code is that it be capable of handling problems involving bounded variables.

As seen in Figure 64, for a two-dimensional case, the global optimum may lie outside the feasible region restricted by upper, XH_i, and lower XL_i, bounds on the variables. It is therefore necessary to determine an optimum within this area. An unconstrained gradient search would follow steps 1-2, 2-3, 3-6, 6-7, 7-8. However, the lower boundary on the variable XB_1 is encountered at point 4; not the true optimum within the bounded region. In computing the new gradient at point 4, it is observed that since the XB_1 variable has hit a boundary, it is unnecessary to include the component of this variable in the calculation. Further, it is found (Copper and Kephart, 1965) that holding a bound variable constant for two or three gradient calculations (points 4 and 5) proves successful in speeding up the search. It is important, however, to include this variable in later gradient calculations as Figure 65 will indicate.

The unconstrained search would follow the dotted path, thus reaching the global optimum at point 11. In the bounded search, though, the upper bound XH_2 of variable XB_2 is encountered at point 5. Thus, the component of the XB_2 variable is not considered in the gradient calculations at point 5 and 6. Since at point 7 the XB_2 variable remains at the upper boundary, it again is not considered in the gradient calculation at points 7 and 8. Calculation of the gradient at point 9, which includes the XB_2 variables, carries the search back within the feasible region and the global optimum is finally reached at point 11. Choice of the number of calculations to remain on the boundary is arbitrary, however, three such calculations seem to be very efficient.

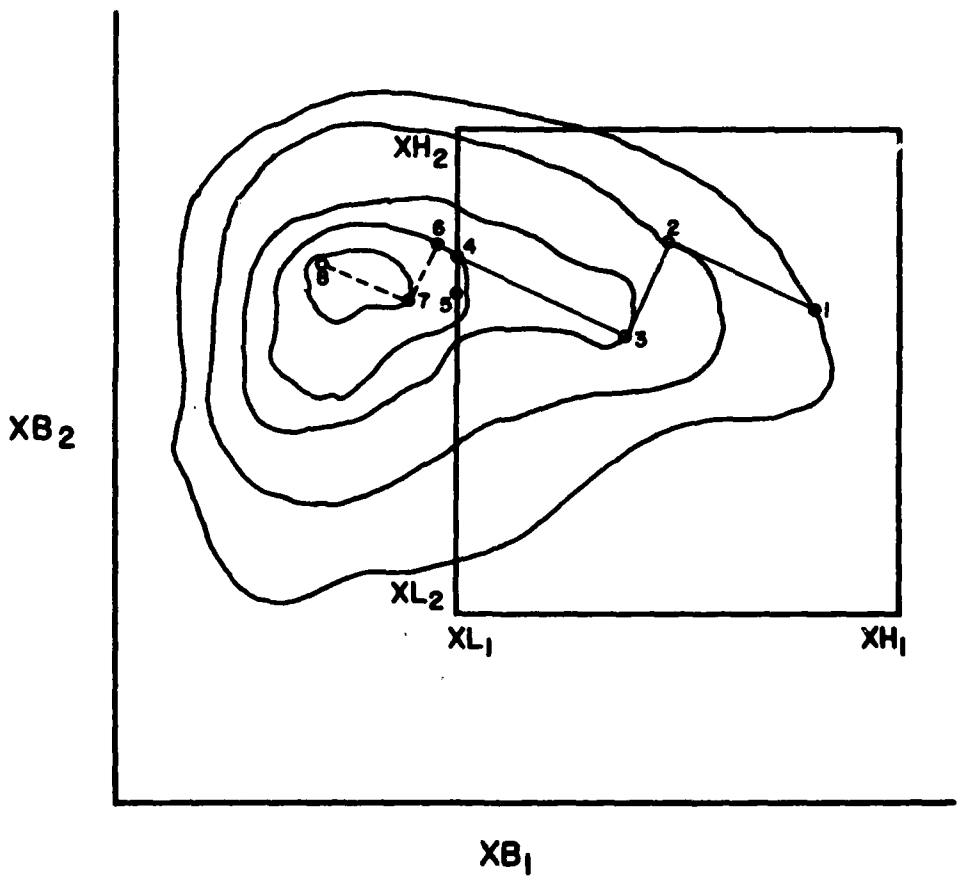

Figure 64. Two-Dimensional Steepest Descent with Optimum at a Boundary

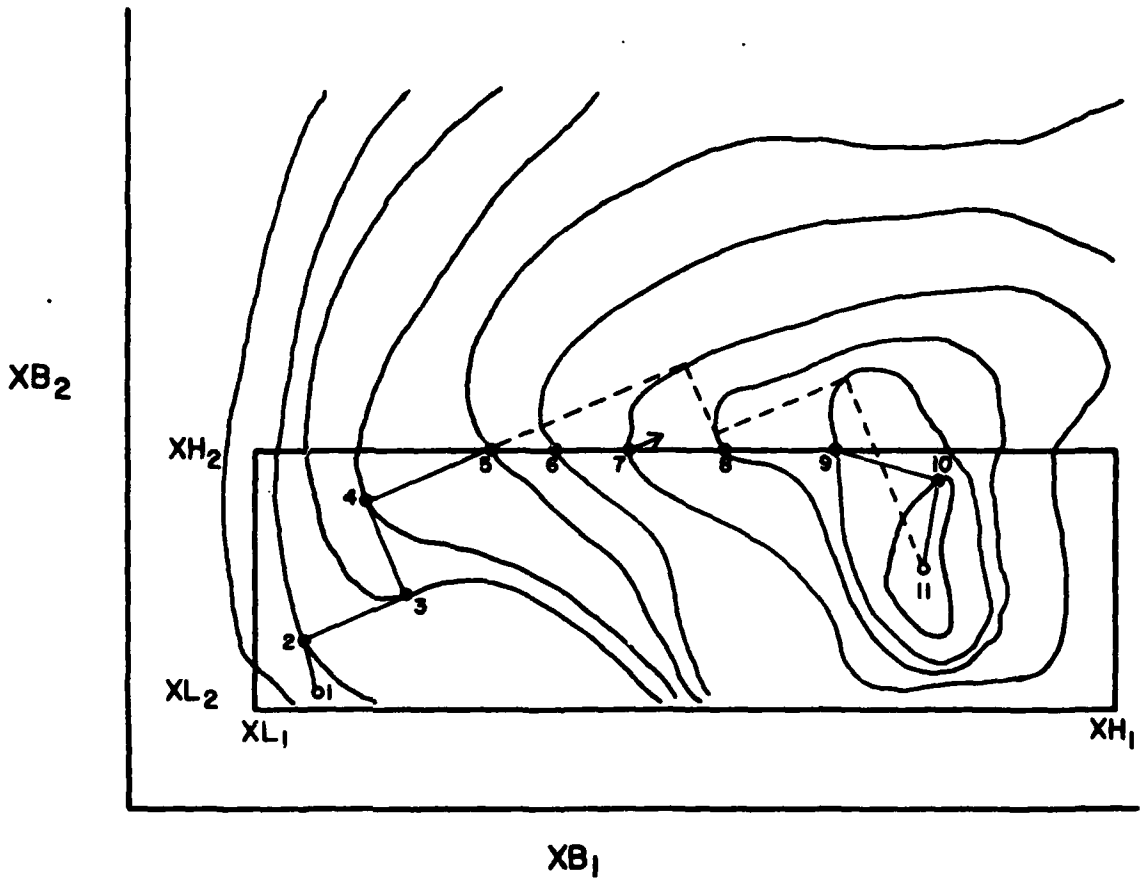

Figure 65. Two-dimensional Steepest Descent with Variable Held on Boundary and Released

A major deficiency of the Steepest descent method of optimization is its inefficient optimization along a ridge (or valley in the case of minimization). This inefficiency arises from the tendency of the gradient to "sawtooth" across the ridge. Copper and Kephart (1965), Booth (1965) have outlined techniques which help overcome the ridge problem. When sufficient knowledge of the surface has been accumulated to detect the presence of a ridge, an attempt can be made to de-emphasize the strongest gradient components. This procedure results in skewing the gradient vector to follow the ridge more closely.

10.8 Plant Optimization Technique

Previous investigators (Fan, *et al.*, 1968; Griffith and Kraus, 1968; Perona and Dillon, 1972) who have studied optimization of the reverse osmosis process have found that the multivariable objective function (cost function) to be minimized is ordinarily non-linear, while restrictions on the decision variables are often linear inequality constraints. Several general methods are available for optimization problems of this sort.

Fan *et al.* (1968) used a combined optimization technique based on a discrete analog of the maximum principle and a gradient search technique to study the optimization of a single stage plant containing one, two, or three banks in series. Some workers (Horn and Jackson, 1965; Jackson and Horn, 1965) have challenged the maximum principle when applied to the discrete case, citing examples wherein the discrete form of the maximum principle fails. A second disadvantage to the use of the discrete maximum principle arises when the mathematical model is incorporated into this technique. Ordinarily the desired structure of a model for use in optimization is an expression (transformation equation) which explicitly gives the output from a unit as a function of its input variables. To achieve this structure, some mathematical rearrangement or simplification of the analytical model is required. This rearrangement of the model is always possible in principle, but in most practical situations it is too difficult to be attempted without substantial simplification of the model. Complex analytical models often associated with the reverse osmosis process ordinarily cannot survive the degree of simplification needed to form explicit transformation equations. Such simplification produces a model of dubious value. For this reason, any optimization procedure, such as the discrete analog of the maximum principle, requiring recursive transformation equations which may be incorporated into the objective function are likely to have limited application in reverse osmosis studies. McCutchan and Goel (1974) used the decomposition technique of dynamic programming to arrive at optimum operating parameters for two and three-stage designs. In order to develop the recursive transformation equations essential to this technique, the plant geometry selected did not allow for division of each stage into module banks. Consequently, the feed stream could not be repressurized throughout the plant and no tapering of flow was possible. In addition, the analytical model described in their study was used to model an entire stage; a simplification of unknown validity. Griffith and Kraus (1968) used a general

non-linear optimization procedure based on steepest descent as developed by Copper and Kephart (1965) to study the optimization of a single stage reverse osmosis plant. Inequality constraints such as minimum velocity and pressure or maximum product salt concentration were imposed to restrict these parameters to specific domains. The mathematical model used by Griffith and Kraus (1968) was complex in nature and no explicit transformation equations were required.

Extension of the non-linear steepest descent technique (Copper and Kephart, 1965), together with the application of the principle of temporarily fixed links to complex multistage plant layout (Figure 66), has been the selected method of optimization. Information concerning this extension is presented in the following discussion.

10.9 Plant Layout

In the design of a large scale reverse osmosis plant using tubular membranes grouped in modular form, it becomes necessary to predict the correct number of modules required for the desired product water quality and quantity, and the optimal arrangement of modules in a combination of parallel and series flows. Previous investigators studying the cost minimization of a reverse osmosis desalination plant producing purified water have often selected plant layouts lacking the flexibility necessary to provide for all features of engineering concern. Griffith and Kraus (1968) studied a single stage process with turbulent flow inside cylindrical tubes. Provisions were made to consider varying the number of parallel tubes "continuously" from inlet to outlet to increase velocity and decrease concentration polarization. However this study did not provide for multistage operation, modular grouping of membrane tubes, or dividing stages into sections to permit the repressurization of feed. Fan *et al.* (1968) studied one, two and three bank layouts but did not include provisions for modular grouping of membrane tubes, addition of a second stage, or tapering of flow area to increase flow velocity within a stage. McCutchan and Goel (1974) used the technique of dynamic programming to optimize the operating parameters for two-stage and three-stage designs but did not consider modular groupings of membranes, division of stages into sections, and tapering of flow area. McCutchan and Goel (1974) did, however, consider a variable membrane permeability model allowing the adjustment of membrane permeability to optimum conditions. Hodgson (1972) conducted a comparison of operating data and computer simulated data for a tubular two-stage desalination plant for seawater. As part of a test program on the 2,500 gpd pilot plant, a computer simulation was performed for various arrangements of modules to determine their optimum arrangement in both stages. Tapering of flow within a stage was found to increase product quality and quantity by decreasing concentration polarization but larger pressure drops per stage resulted. No economic analysis was presented to determine which arrangements provided the minimum cost of water production. Perona and Dillon (1972) investigated one- and two-stage reverse osmosis plants for

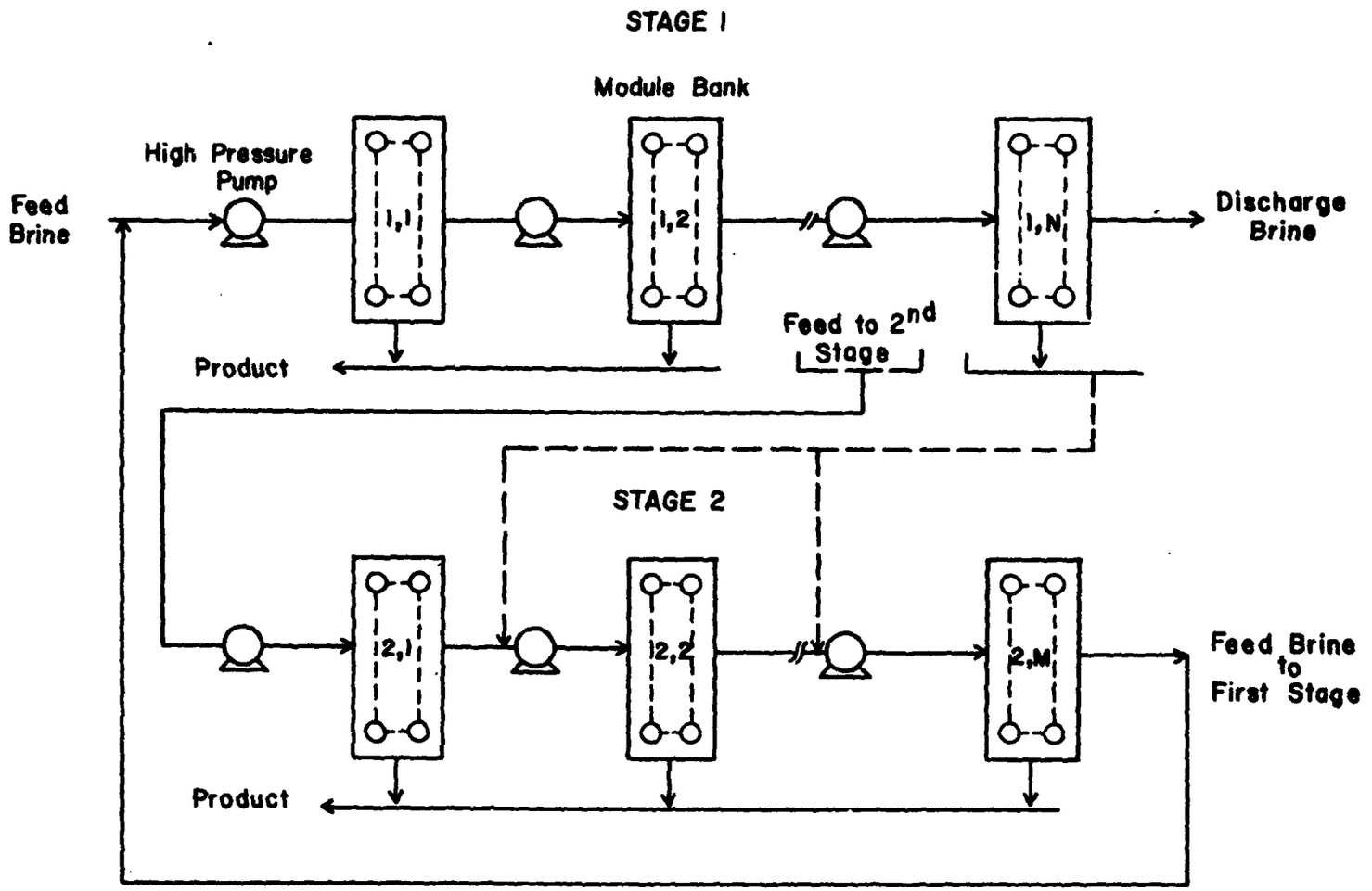

Figure 66. Generalized Reverse Osmosis Desalinization Plant Layout

the desalination of brackish water. The plant layout incorporated almost all features of engineering concern but failure to group membrane tubes into modular form resulted in extremely small pressure drops per section and tube lengths too large to be practical.

Product water from the first stage which meets a specified quality criteria is withdrawn from the cascade and undergoes no further processing. If the product from at least one section of the first stage has a lower concentration than the product specification, it is blended with product from sections of the first stage having a higher than specific concentration. The blended product which meets specification is withdrawn from the cascade. If the product water concentration from any of the sections of the first stage exceeds product specification and cannot be blended, it is fed to the section of the second stage where its concentration is most closely matched.

The inlet concentration to the first section of the second stage is the lowest product concentration from the first stage which exceeds product specification and was not completely used in blending. The salt solution in the second stage may be taken to the concentration of the feed to the first stage and recycled to it.

It is believed that this plant layout provides the flexibility necessary to study all parameters of economic and engineering interest while remaining simple enough to be incorporated in optimization techniques.

10.10 Economic Analysis

Ordinarily, the criteria used to determine the operating conditions and the plant geometry in any separations process is the production of the product at minimum cost subject to certain technological constraints. For this reason, product water cost has been selected as the factor to be minimized in finding the optimum operation and layout of a reverse osmosis plant. Cost relationships used to estimate costs in the more highly developed separation process (e.g. distillation, electrodialysis) are of a somewhat detailed and sophisticated nature owing to the large number of economic studies available. A simplified cost equation has been used throughout the early stages of the development of this computer optimization code to provide formore efficient program debugging. In addition, selection of the equipment for reverse osmosis has not yet become a standardized policy, leading to a somewhat undecided basis for capital, operating and maintenance cost estimation Therefore, only two cost parameters: (1) a daily change, C_A, per square foot of membrane area, and (2) a unit cost for pumping energy, C_E, have been used. With these considerations, the unit cost, C_W, of product water becomes

$$C_W = \frac{C_A A_M + C_E P_E}{W} \tag{94}$$

This simplified equation is most meaningful if the costs are considered to be relative rather than absolute. Thus, the effect of changing plant size, module arrangement, or operating parameters will result in a relative variation of cost from optimum conditions. To obtain total absolute water costs, terms not proportional to area or pumping energy will have to be included.

A more detailed economic analysis should be undertaken as soon as sufficient cost information becomes available.

10.11 Comparison of Plant Optimization to Non-Optimum Results

The computer optimization code previously described and listed in Appendix IV was run in the non-optimization mode using inlet pressures and feed rates selected to be a good approximation to the optimum operating conditions for seawater desalination using modules comprised of fourteen 1.27 centimeter diameter tubular NS-100 membrane sections. Inlet pressures, feed rates, and concentrations for each module bank in the two-stage plant are listed in Table 54 along with corresponding computer calculated results for the product rate, product concentration and water cost. Figure 67 shows a schematic diagram of the non-optimized plant geometry. The selection of a constant inlet pressure (100 atm) for each module bank requires the addition of a pressure booster pump at each bank. Evident in this figure is the tapering of flow to each successive module bank. Only the second module bank in the second stage requires an expanded number of modules in parallel due to the injection of permeate from the first stage. The plant capacity has been selected to be 0.5 million gallons per day treating a salt water feed containing 35,000 parts per million of sodium chloride. The average product concentration listed in Table 54 is well below the prechosen 500 parts per million limit.

To illustrate the usefullness of attempting to optimize the operating variables and geometry of a hyperfiltration plant, the computer optimization code was run in the optimization mode using as a base point the inlet conditions (100 atm, 3.00 ft/sec) selected for the non-optimization case. Listed in Table 55 are the optimum inlet pressures, inlet feed rates and concentrations for each module bank in the two stage plant. Optimum plant arrangement (Figure 68) suggests tapering of flow to approximately the same degree as found for the non-optimum plant arrangement (Figure 67). As can be seen from Tables 54 and 55 the optimum feed rate to each module bank is approximately constant and is nearly equal to the estimated non-optimum feed rate (3.00 ft/sec). If the optimum feed rate had varied significantly from one module bank to the next, or if the estimated non-optimum feed rate had not been chosen so accurately, the plant arrangements shown in Figures 67 and 68 would not have been similar.

Repressurization pumps have not been added between each module bank in the plant optimization case since, in some instances, it was found that the addition of a subsequent module bank operating at a lower pressure (no repressurization) was economically more feasible than operating fewer modules at elevated pressures.

Table 54

Tabulation of Non-Optimum Operating Conditions and Results (Corresponding to Figure 67)

Stage	Module Bank	Inlet Pressure (atm)	Inlet Velocity (ft/sec)	Inlet Mole Fraction	Product Rate (gal/day)	Product Mole Fraction	Cost (cents/kgal)
1	1	100.00	3.00	0.010667	0.2086×10^{6}	0.2692×10^{-3}	140.38
1	2	100.00	3.00	0.013420	0.1386×10^{6}	0.3819×10^{-3}	91.96
1	3	100.00	3.00	0.016166	0.0941×10^{6}	0.5322×10^{-3}	112.15
1	4	100.00	3.00	0.018786	0.0765×10^{6}	0.7720×10^{-3}	144.86
2	1	100.00	3.00	0.000269	0.15031×10^{6}	0.8003×10^{-5}	61.11
2	2	100.00	3.00	0.000590	0.22837×10^{6}	1.4863×10^{-5}	43.67
2	3	100.00	3.00	0.001530	0.03728×10^{6}	2.7045×10^{-5}	47.62
2	4	100.00	3.00	0.002076	0.03478×10^{6}	3.9912×10^{-5}	46.34
2	5	100.00	3.00	0.003120	0.01668×10^{6}	5.7510×10^{-5}	59.57
2	6	100.00	3.00	0.004119	0.01195×10^{6}	7.8100×10^{-5}	59.18
2	7	100.00	3.00	0.005350	0.00859×10^{6}	10.5306×10^{-5}	62.80
2	8	100.00	3.00	0.006823	0.00428×10^{6}	13.2979×10^{-5}	67.57
2	9	100.00	3.00	0.007910	0.00503×10^{6}	16.9619×10^{-5}	66.08
2	10	100.00	3.00	0.009738	0.00255×10^{6}	21.1577×10^{-5}	78.75

Cost = 178.63 ¢/kgal; Total Product Rate = 0.4998×10^{6} gpd; Product Mole Fraction = 2.35×10^{-5};

No. of Modules = 6824

Table 55

Tabulation of Optimum Operating Conditions and Results Corresponding to Figure 68

Stage	Module Bank	Inlet Pressure (atm)	Inlet Velocity (ft/sec)	Inlet Mole Fraction	Product Rate (gal/day)	Product Mole Fraction	Cost (cents/kgal)
1	1	110.00	2.72	0.01677	0.26114×10^6	0.2819×10^{-3}	123.35
1	2	102.81	2.37	0.01434	0.0879×10^6	0.4063×10^{-3}	73.82
1	3	110.00	2.55	0.01622	0.1031×10^6	0.5083×10^{-3}	90.62
1	4	110.00	2.71	0.01916	0.0678×10^6	0.8774×10^{-3}	104.41
2	1	103.63	2.94	0.000282	0.1993×10^6	0.9523×10^{-5}	59.21
2	2	110.00	1.75	0.000641	0.2224×10^6	2.5551×10^{-5}	39.61
2	3	107.73	1.59	0.002018	0.0179×10^6	4.2596×10^{-5}	37.48
2	4	106.87	2.06	0.002453	0.0218×10^6	5.1111×10^{-5}	38.90
2	5	104.26	2.97	0.003331	0.0153×10^6	6.2935×10^{-5}	42.33
2	6	96.08	2.96	0.004460	0.0098×10^6	8.4997×10^{-5}	48.96
2	7	87.62	2.19	0.005710	0.0059×10^6	11.8074×10^{-5}	56.94
2	8	104.87	2.72	0.006872	0.0067×10^6	14.9562×10^{-5}	63.49
2	9	97.86	2.99	0.008941	0.0026×10^6	18.8576×10^{-5}	58.94
2	10	91.42	2.96	0.010153	0.0020×10^6	22.8810×10^{-5}	69.51

Cost = 158.63 ¢/kgal; Total Product Rate = 0.5038×10^6 gpd; Product Mole Fraction = 2.76×10^{-5}

No. of Modules - 5915

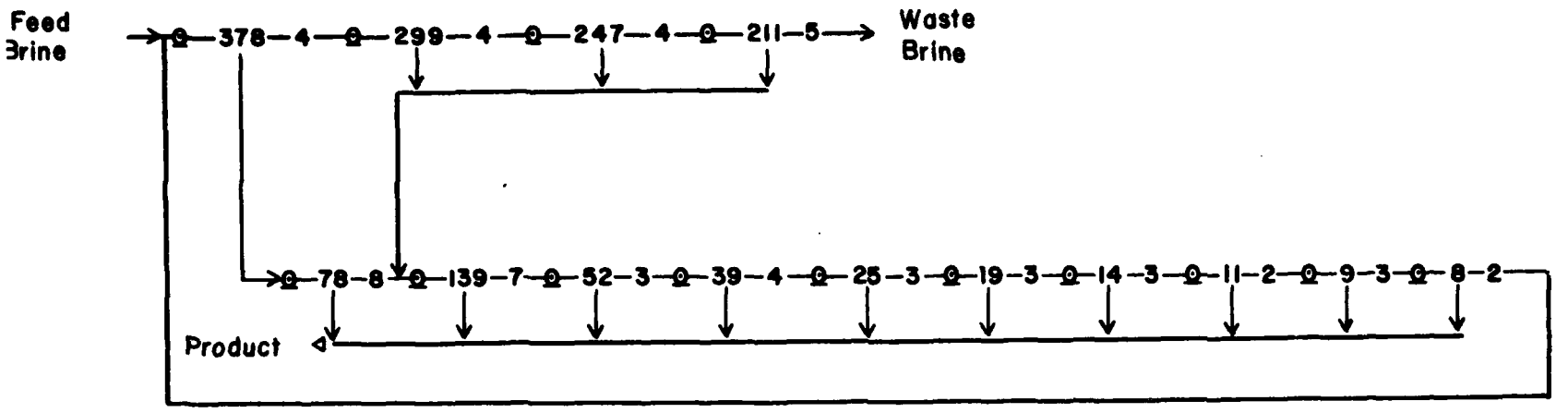

Figure 67. NON-OPTIMUM PLANT GEOMETRY

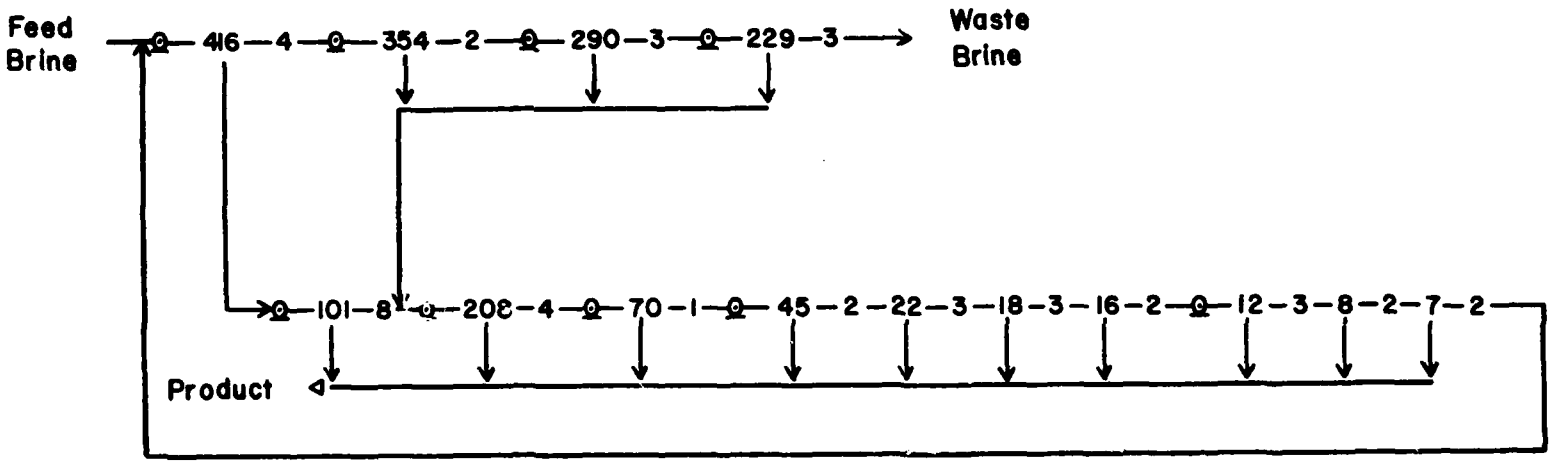

Figure 68. OPTIMUM PLANT GEOMETRY

To illustrate the accuracy and usefulness of process modeling by the black-box experimentation least-squares surface fitting technique described in Section 10.6, the plant optimization code was modified to include extimation of the product rate and product quality by the quadratic polynomial approximations, Equations 77 and 78. Figure 69 in conjunction with Table 56 shows the close correspondence between optimization with the mechanistic model and optimization using the quadratic approximations. Once again it should be emphasized that the modified computer code involving the application of surface fitting techniques can be used to optimize the plant arrangement and operating conditions for a reverse osmosis plant utilizing any module configuration or membrane type if sufficient experimental data is available.

It may be concluded from these results that optimization of reverse osmosis geometry and operating conditions using steepest descent is a viable technique to reduce water production costs for the desalination of seawater. Information concerning the optimum plant geometry, feed rates, operating pressures, degree of taper, degree of feed stream concentration and other design parameters may be collected and modified to aid in the design of desalination systems. With the inclusion of a nonlinear least squares technique for determining the unknown coefficients in a surface fitting model the steepest descent method of plant optimization can be used to optimize a two-stage reverse osmosis plant utilizing any type of membrane module.

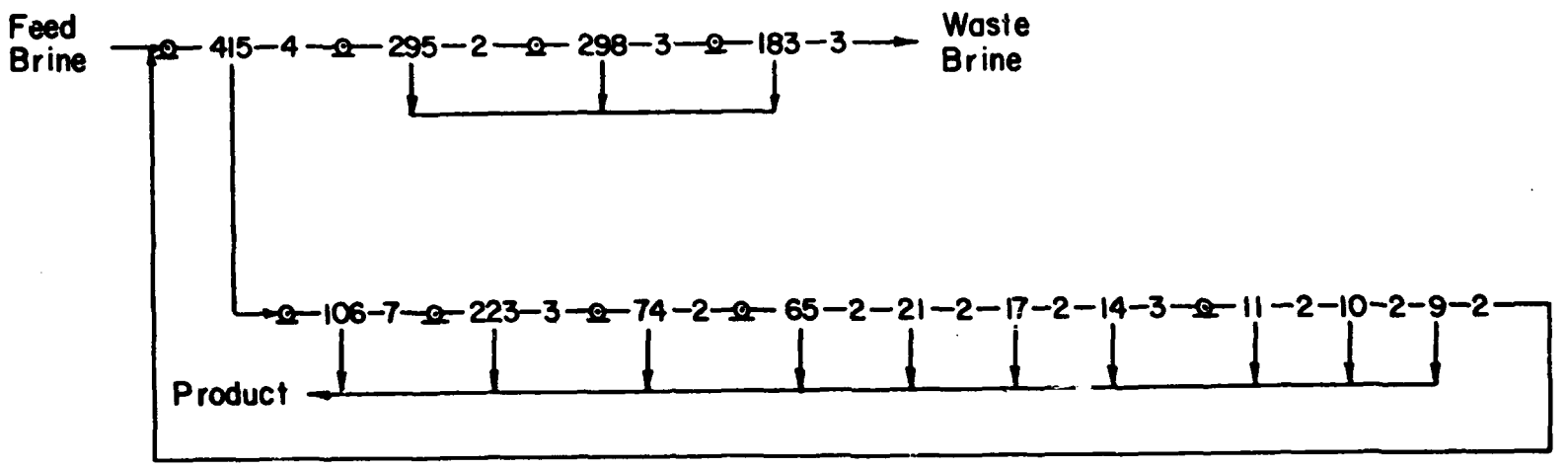

Figure 69. OPTIMUM PLANT GEOMETRY - QUADRATIC MODEL

Table 56

Tabulation of Optimum Operating Conditions and Results (Corresponding to Figure 77)
(Quadratic Model)

Stage	Module Bank	Inlet Pressure (atm)	Inlet Velocity (ft/sec)	Inlet Mole Fraction	Product Rate (gal/day)	Product Mole Fraction	Cost (cents/kgal)
1	1	110.00	2.73	0.010677	0.2608×10^{6}	0.2979×10^{-3}	120.65
1	2	101.22	2.83	0.014363	0.0778×10^{6}	0.3941×10^{-3}	78.06
1	3	110.00	2.52	0.016016	0.1117×10^{6}	0.4981×10^{-3}	89.87
1	4	110.00	3.40	0.019173	0.0578×10^{6}	0.8338×10^{3}	99.40
2	1	104.01	2.76	0.000298	0.1997×10^{6}	1.1732×10^{-5}	59.55
2	2	110.00	1.56	0.000674	0.1922×10^{6}	2.4931×10^{-5}	39.31
2	3	108.44	1.93	0.002109	0.0294×10^{6}	4.0232×10^{-5}	36.88
2	4	106.27	1.50	0.00258	0.0333×10^{6}	5.2715×10^{-5}	38.50
2	5	105.06	2.83	0.00352	0.0105×10^{6}	6.2074×10^{-5}	41.73
2	6	97.12	2.83	0.00412	0.0089×10^{6}	8.6530×10^{-5}	47.76
2	7	87.33	2.79	0.00530	0.0063×10^{6}	11.1109×10^{-5}	56.38
2	8	104.82	2.74	0.00602	0.0071×10^{6}	14.794×10^{-5}	62.07
2	9	97.80	2.64	0.00892	0.0024×10^{6}	18.476×10^{-5}	58.15
2	10	92.11	2.38	0.01088	0.0021×10^{6}	$22,656 \times 10^{-5}$	65.68

11. RECOMMENDATIONS

It is recommended that the economic analysis of the reverse osmosis process for seawater desalination be extensively revised from the simple form used in this study as soon as capital, operating, and maintenance costs become established. Estimation of equipment, land, and indirect costs such as (1) engineering and design (2) construction supervision (3) administrative expenses (4) interest during construction should all be based on information supplied by manufacturers. Operation and mainenance costs for a reverse osmosis plant should include (1) operating and maintenance labor (2) general overhead (3) supplies and maintenance materials (4) membrane replacement (5) electric pumping power (6) chemicals.

Additional studies should be undertaken to confirm the applicability of the general regression technique to various commercial sized reverse osmosis modules. This research should involve different membrane types (NS-100, Cellulose Acetate, Polyamide etc.), different membrane configurations (e.g. spiral wound, hollow fiber, tubular) and different solutes (organic, inorganic) for all hydrodynamic flow conditions.

NOMENCLATURE

$\Delta P(x)$ = local applied pressure difference across the membrane, atm.

$\Delta\pi(x)$ = local osmotic pressure difference across the membrane, atm.

$N_B(x)$ = local flux of water through the membrane, g-mole $H_2O/cm^2 \cdot sec$

A = pure water permeability coefficient, g-mole $H_2O/cm^2 \cdot sec \cdot atm$.

N_{BP} = local flux of water through the membrane with pure water as feed, g-mole $H_2O/cm^2 \cdot sec$.

$N_A(x)$ = local flux of salt through the membrane, g-mole $NaCl/cm^2 \cdot sec$.

B = local salt permeability coefficient, cm/sec.

c = molar density of solution, g-mole/cm^3.

$X_{A2}(x)$ = local mole fraction of salt at the membrane surface, dimensionless.

$X_{A3}(x)$ = local mole fraction of salt in the permeate, dimensionless.

r = radial coordinate in cylindrical coordinate system, cm.

L = length of membrane tube, cm.

$N_{Ar}(x)$ = local flux of salt in the radial direction, g-mole $NaCl/cm^2 \cdot sec$.

Δr = incremental radial distance, cm.

$N_{Br}(x)$ = local flux of water in the radial direction, g-mole $H_2O/cm^2 \cdot sec$.

R = radius of tubular membrane, cm.

$N_{A2}(x)$ = local flux of salt at the membrane surface, g-mole $NaCl/cm^2 \cdot sec$.

$''$ (x) = local flux of water at the membrane surface, g-mole $H_2O/cm^2 \cdot sec$.

= mole fraction of salt, dimensionless.

$-_{AB}$ = Diffusivity of salt through water, cm^2/sec.

X_{A1} = local mole fraction of salt at the film edge, dimensionless.

δ_{AB} = thickness of the film, cm.

ΔX_A = salt mole fraction difference, dimensionless.

$k^{o}_{x,loc}$ = local mass transfer coefficient in the presence of transpiration, g-mole/cm^2·sec.

$k_{x,loc}$ = local mass transfer coefficient at moderate transpiration rates, g-mole/cm^2·sec.

k_1 = mass transfer coefficient as ordinarily applied in film theory, cm/sec.

V_w = transpiration velocity, cm/sec.

θ_{AB} = correction factor for finite interfacial velocity, dimensionless.

ϕ_{AB} = rate factor, dimensionless.

Pe_w = wall Peclet number, dimensionless.

Re_w = wall Reynolds number, dimensionless

Ar = reference pure water permeability coefficient, g-mole H_2O/cm^2·sec·atm.

α = empirical constant equal to slope from Figure 8, atm^{-1}.

ΔP = pressure difference across the membrane, atm.

ΔP_r = reference pressure difference across the membrane, atm.

θ = proportionality factor relating osmotic pressure to solution mole fraction, atm.

M = empirical constant equal to slope from Figure 10, cm/sec.

X_{A2}^{*} = reference mole fraction of salt at the interface, dimensionless.

B^{*} = reference salt permeability coefficient, cm/sec.

$\underline{Y}$ = response determined by mathematical approximation.

$\vec{X}$ = vector of inputs, $(X_1, X_2, \ldots X_n)$.

$\vec{\beta}_s$ = vector of coefficients, $(\beta_0, \beta_1, \ldots \beta_s)$.

x_i = particular input variable.

β_j = particular coefficient

x_0 = initial or base location for the variable X.

Y(x) = true single variable response function.

Y_k = true response to the kth experiment.

k = index for a particular experiment.

$\vec{X}_{k,n}$ = square matrix of inputs as defined by Equation 51.

r = number of experiments run.

Y_k = measured response to the kth experiment.

R_k = residual to the kth experiment.

G = sum of the absolute values of the residuals.

E = sum of the squares of the residuals.

w_k = k^{th} weighting factor.

β_1^* = optimum value of β_1 coefficient for two-dimensional response function.

β_2^* = optimum value of β_2 coefficient for two-dimensional response function.

g_e = the eth equality constraint.

g_m = the mth inequality constraint.

$\Delta\beta_j$ = denotes base or initial case.

$\vec{A}$ = square matrix of partial derivatives with respect to the unknown coefficients

$\overrightarrow{Y-\underline{Y}}^{(o)}$ = vector of the quantity $Y_k-Y_k^{(o)}$ for $k=1,2,3,\ldots r$.

Φ = least squares objective function to be minimized.

λ = modification factor.

$\vec{I}$ = identity matrix.

f = general multivariable function.

∇f = gradient of the general multivariable function.

$\vec{\delta x_1}$ = unit vector in the x_1 direction.

ζ = variable distance used for gradient evaluation.

ξ = range factor

γ = scale factor for movement along the gradient.

γ_r = reduced scale factor

X_{Hi} = upper bound on the ith variable being optimized.

XB_1 = a variable to be optimized in the sample two-dimensional case.

XB_2 = a variable to be optimized in the sample two-dimensional case.

C_A = daily charge per membrane area, cents/cm^2.

C_W = total cost of water production, cents/kgal.

A_m = membrane area, cm^2.

C_E = unit cost for pumping power, cents/kwh.

P_E = energy consumed per day, kwh/day.

W = product volume, kgal/day.

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APPENDIX I

Correspondence

DIVISION OF CHEMISTRY
DIVISION DE CHIMIE

CABLE ADDRESS
ADRESSE TÉLÉGRAPHIQUE "RESEARCH"

PLEASE QUOTE FILE No
No DE DOSSIER À RAPPELER

NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA, CANADA
K1A 0R9

August 3, 1973

Dr. E. S. K. Chian,
Environmental Engineering,
Department of Civil Engineering,
University of Illinois,
Urbana, Illinois 61801,
U. S. A.

Dear Dr. Chian:

Thank you very much for sending me a copy of your recent paper on "Evaluation of New Reverse Osmosis Membranes for the Separation of Toxic Compounds from Water". Needless to say, that Dr. Matsuura and I are very pleased to see your references to our work on the subject. Thank you very much.

May I know what response you had from the audience when you presented your paper at Detroit? I regard your paper as a very valuable and timely contribution both to the science of reverse osmosis and to its application for waste water treatment. I would appreciate receiving further reprints of your publications in the field.

With my best wishes,

Yours sincerely,

S Sourirajan

S. Sourirajan.

SS/dn

National Research Council Canada
Conseil national de recherches Canada

Division of Chemistry
Division de chimie

File Référence

July 14, 1975

Professor E.S.K. Chian
Department of Civil Engineering
University of Illinois at
Urbana-Champaign
Urbana, Illinois 61801
U.S.A.

Dear Professor Chian:

I must first apologize to you for being so slow in acknowledging receipt of your letter dated June 17, 1975, along with the enclosures. I am impressed by the tremendous amount of good work on reverse osmosis being done in your laboratory. All your work has a practical bearing, and the new approaches and conclusions arising from your work represent a major contribution to the science and engineering of reverse osmosis.

I see that there are at least a few areas in which your work and the work of this laboratory have some common ground. Therefore I believe that continued contacts between us should be mutually beneficial.

You are always most welcome to this laboratory. I regard it a privilege for me to share thoughts with you on reverse osmosis.

With my best regards.

Yours sincerely,

S Sourirajan

SS/cf

S. Sourirajan

Ottawa, Canada
K1A 0R9

APPENDIX II

Publications

1. Chian, E. S. K. and Fang, H. H. P., "Evaluation of New Reverse Osmosis Membranes for Separation of Toxic Compounds from Water," *AIChE Sym. Series 136, Water-1973*, pp. 497-507 (1974).

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12. Fang, H. H. P. and Chian, E. S. K., "Reverse Osmosis Separation of Polar Organic Compounds in Aqueous Solution," *Environ. Sci. & Technol.* (1976).

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14. Aschauer, M. N. and Chian, E. S. K., "Modelling of a Tubular NS-100 Membrane Module for Sea Water Desalination," paper submitted to *Am. Inst. Chem. Engr. Jour.* for publication, 1976.

15. Aschauer, M. N. and Chian, E. S. K., "A Practical Modeling Technique for the RO Process," paper submitted to *Environ. Eng. Div.*, *ASCE*, for publication, 1976.

16. Chian, E. S. K., Aschauer, M. N. and Fang, H. H. P., "A Practical Use of Modeling and Optimization for Reverse Osmosis Plant Design," paper submitted to *Desalination* for publication, 1976.

17. Chian, E. S. K., Fang, H. H. P. and Aschauer, M. N., "Physicochemical Criteria of Reverse Osmosis Separation of Solutes - A Review," paper submitted to *Water Res.* for publication, 1976.

18. Chian, E. S. K., "Physicochemical Criteria of Removal Trace Organics by Reverse Osmosis," paper accepted for presentation at the 69th Annual Meeting, *AIChE*, Chicago, Illinois, November 28 - December 2, 1976.

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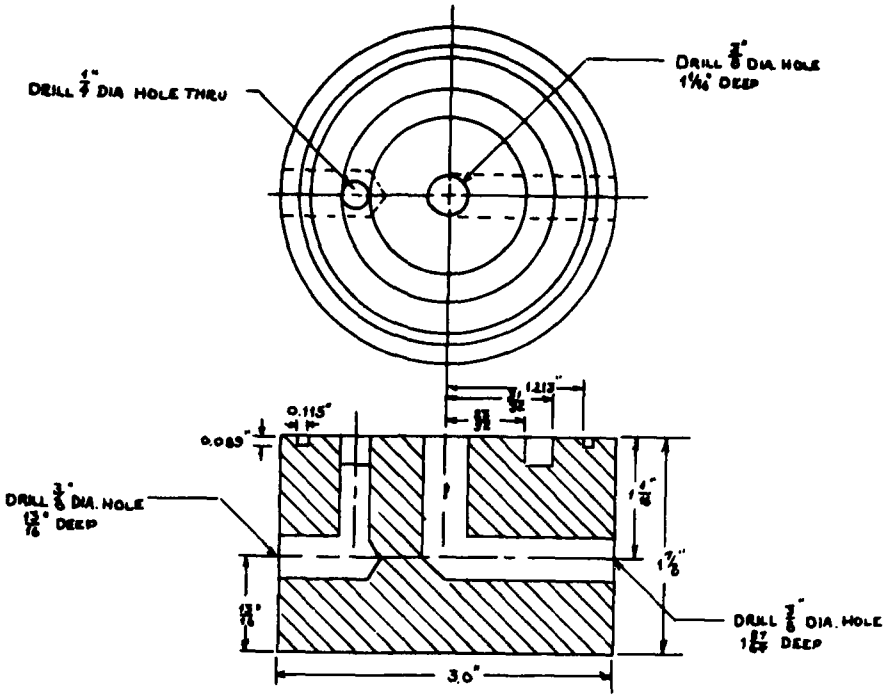
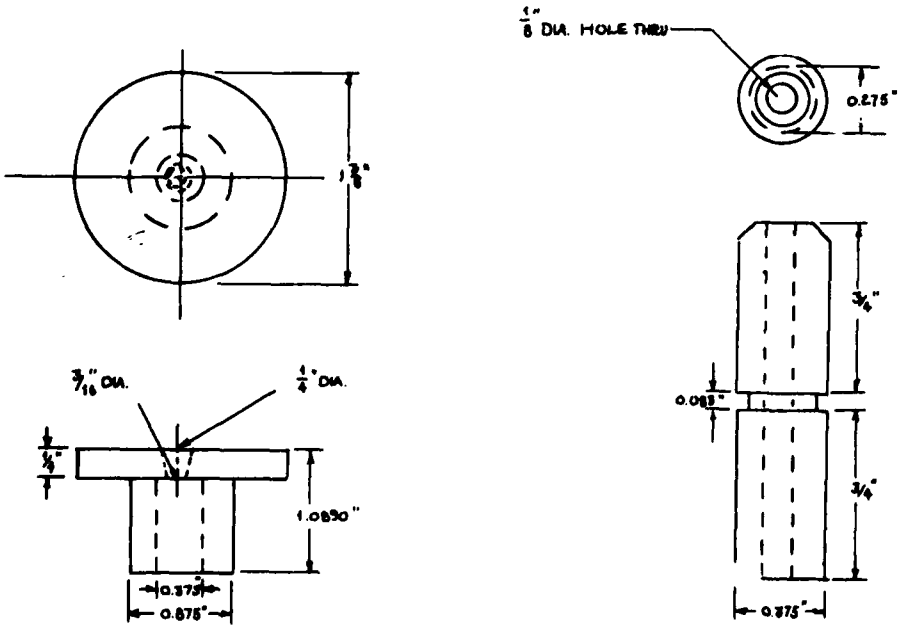
BEST AVAILABLE

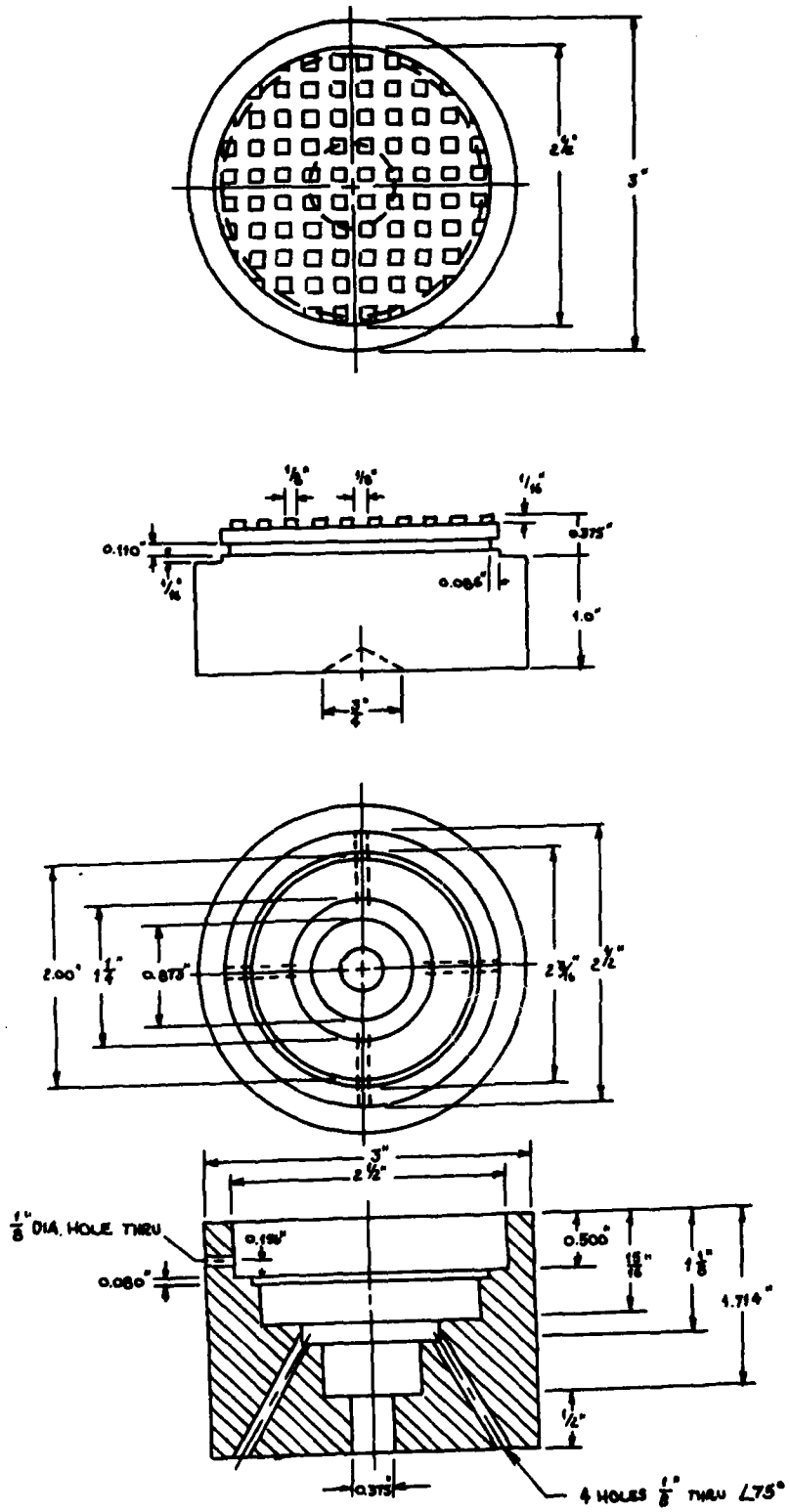
APPENDIX III

Equipment

BEST AVAILABLE


DRILL 1/4" DIA HOLE THRU
DRILL 3/8" DIA HOLE 1 1/16" DEEP
1.213"
0.115"
0.089"
DRILL 3/8" DIA. HOLE 13/16" DEEP
1 1/16"
1 7/8"
DRILL 3/8" DIA. HOLE 1 27/64" DEEP
3.0"


1/8" DIA. HOLE THRU
0.275"
1 3/8"
3/4"
0.089"
3/4"
7/16" DIA.
1/4" DIA.
1/4"
1.0850"
0.375"
0.875"
0.375"


3"
0.110"
0.375"
1.0"
2.00"
0.873"
3"
2 1/2"
1/8" DIA. HOLE THRU
0.080"
0.500"
1.714"
1/2"
0.375"
4 HOLES 1/8" THRU ∠75°

APPENDIX IV

Computer Codes

Computer Program for Optimizing the Membrane Performance

Mathematical Approach

The purpose of the program is to optimize a response $F(X_1, X_2, X_3 --- X_n)$ at a constrainted value, S_c, of another response $S(X_1, X_2, --- X_n)$. Both F and S are functions of n variables $X_1, --- X_n$. At the optimum of F

$$dF = F_1\, dX_1 + F_2\, dX_2 --- + F_n\, dX_n = 0$$

where $dX_1, --- dX_n$ are not independent since they must to satisfy the following equation

$$dS_c = S_1\, dX_1 + S_2\, dX_2 --- + S_n\, dX_n = 0$$

where S_i and F_i are partial derivatives of S and F with respect to X_i respectively. By introducing a Lagrange Multiplier, X_{n+1}, the optimum F and the corresponding values of n variables can be determined by solving the following n + 1 simultaneously equations.

$$F_1 + x_{n+1}\, S_1 = 0$$

$$F_2 + x_{n+1}\, S_2 = 0$$

$$\vdots$$

$$F_n + x_{n+1}\, S_n = 0$$

$$S_c - S(X_1, \cdots X_n) = 0$$

There are n + 1 unknowns in these n + 1 equations. With the aid of a digital computer, the solutions can be easily found using numerical analysis.

First, a new set of dependent variables are defined as follows:

$$G^1 = F_1 + x_1 S_1 = 0$$

$$\vdots$$

$$G^n = F_n + x_n S_n = 0$$

$$G^{n+1} = S - S_c = 0$$

The Taylor series expansion of G^j, by neglecting terms of second order or higher, around the optimum becomes

$$G^j + \sum_{i=1}^{n+1} G_i^j \ \Delta X_i = 0$$

where G_i^j is the partial derivative of G^j with respect to X_i, and ΔX_i is the difference of X_i, the value of the trial and that of the optimum. In order to find the value of each variable at the optimum, an initial guess should be first made. Values of S, and the first derivatives of S and F are therefore calculated. $G^1, \cdots G^{n+1}$ and $(n+1)^2$ first derivatives (such as G_i^j) can also be determined. Since for n + 1 unknown, $\Delta X_1 \cdots \Delta X_{n+1}$, can be determined from the following n + 1 linear equations by Cramer's Rule or other numerical methods.

$$\begin{array}{l} \sum_{i=1}^{n+1} G_i^1 \ \Delta X_i = -G^1 \\ \vdots \qquad\qquad\qquad \vdots \\ \sum_{i=1}^{n+1} G_i^{n+1} \ \Delta X_i = -G^{n+1} \end{array}$$

After $\Delta X_1, \cdots \Delta X_{n+1}$ are known, second guesses of the variables are $X_1 + \Delta X_1, \cdots X_{n+1} + \Delta X_{n+1}$. The iteration process keeps on until at certain trial all the ΔX_i become negligible. At the point, the value of each variable is the condition at which the maximum response F is obtained under the constraint S_c.

Program

```
C   THIS PROGRAM IS WRITTEN FOR FINDING THE VALUE OF EACH FACTOR TO GET
C   AN OPTIMUM RESPONSE BY USING ANOTHER RESPONSE AS A CONSTRAINT.  THE
C   REGRESSION EQUATIONS OF BOTH RESPONSES SHOULD BE EXPRESSED IN
C   QUADRATIC FORM.  NO EFFECT HIGHER THAN SECOND ORDER EFFECT CAN BE
C   INVOLVED.  OPTIMIZATION IS CONDUCTED BY "CALCULUS OF VARIATIONS".
C   SOLUTIONS OF N1 SIMULTANEOUS LINEAR EQUATIONS ARE SOLVED BY A PROGRAM
C   "GAUSZ" IN THE LIBRARY OF THE COMPUTING SERVICES OFFICE AT THE
C   UNIVERSITY OF ILLINOIS.  THE PROGRAM IS WRITTEN IN FORTRAN IV BY DR.
C   HERBERT H. P. FANG OF THE ENVIRONMENTAL ENGINEERING AT THE UNIVERSITY
C   OF ILLINOIS.  JULY 24, 1973
C   IN THIS PROGRAM THE NUMBER OF FACTORS IS LIMITED TO TWENTY   HOWEVER,
C   IT CAN BE EASILY ADJUSTED FOR MORE FACTORS BY SIMPLY CHANGING THE SIZE
C   OF ELEMENTS IN DIMENSION.
C   TOTAL INPUT DATA CARDS = 2N+10
C
C   DEFINITIONS OF SOME VARIABLES
C
C   N        # OF FACTORS
C   M        # OF TRIALS
C   MMAX        MAXIMUM NUMBER OF TRIALS
C   DXALLW        MAXIMUM ALLOWED DX(I)
C   X(I), I=1,N        N FACTORS
C   X(N+1)        LAGRANGE MULTIPLIER
C   DX        DIFFERENCE BETWEEN X(GUESS) AND X(OPTIMUM)
C   F        RESPONSE TO BE OPTIMIZED
C   S        RESPONSE SERVED AS A CONSTRAINT
C   SCON   CONSTRAINED VALUE OF RESPONSE S
C   DF(I)        DERIVATIVE OF F WITH RESPECTED TO X(I)
C   DS(I)        DERIVATIVE OF S WITH RESPECTED TO X(I)
C   F0,S0        CONSTANT TERMS IN REGRESSION EQUATIONS OF F AND S
C        RESPECTIVELY.
C   F1(I),S1(I)        LINEAR TERMS" COEFFICIENTS.
C   F2(I,J),S2(I,J)        QUADRATIC TERMS" COEFFICIENTS
C
      REAL*8 DG(4,4),G(4),DX(4)
      DIMENSION X(4),DF(4),DS(4),F1(4),
     1   F2(20,20),S1(20),S2(20,20),XMID(20),XUNIT(20),IDUM(21)
C
C   INPUT
C
  8    FORMAT(I5)
  10   FORMAT(8F10.5)
       READ (5,8)N
       READ(5,8) MMAX
       READ(5,10)DXALLW
       READ(5,10)SCON
       READ(5,10)F0
       READ(5,10)S0
       READ(5,10) (F1(I),I=1,N)
       READ(5,10) (S1(I),I=1,N)
       DO 100 I=1,N
       F2(I,I)=0.
       IF(I.GE.N) GO TO 100
```

```
      I1=I+1
      READ(5,10)(F2(I,J),J=I1,N)
      DO 100 J=I1,N
  100  F2(J,I)=F2(I,J)
      DO 101 I=1,N
      S2(I,I)=0.
      IF(I.GE.N) GO TO 101
      I1=I+1
      READ(5,10)(S2(I,J),J=I1,N)
      DO 101 J=I1,N
  101 S2(J,I)=S2(I,J)
      READ(5,10) (X(I),I=1,N)
      READ(5,10)X(N+1)
      READ(5,10)(XUNIT(I),I=1,N)
      READ(5,10)(XMID (I),I=1,N)
C
C END OF INPUT
C
C  EVALUATIONS OF RESPONSES AND THEIR DERIVATIVES
C
      WRITE(6,199)
  199 FORMAT("********** TRIAL  1 **********"//)
      M=1
       N1=N+1
      XMID(N1)=0.
      XUNIT(N1)=1.
      F=F0
      S=S0
      DO 201 I=1,N
      F=F+F1(I)*X(I)
      S=S+S1(I)*X(I)
      IF(I.EQ.N)GO TO 201
      I1=I+1
      DO 200 J=I1,N
      F=F+F2(I,J)*X(I)*X(J)
      S=S+S2(I,J)*X(I)*X(J)
  200  CONTINUE
  201 CONTINUE
  210  DO 300 I=1,N
      DF(I)=F1(I)
      DS(I)=S1(I)
      DO 90 J=1,N
      DF(I)=DF(I)+F2(I,J)*X(J)
      DS(I)=DS(I)+S2(I,J)*X(J)
  90  CONTINUE
      G(I)=DF(I)+X(N1)*DS(I)
  300 CONTINUE
      M=M+1
      G(N1)=S-SCON
      DO 401 I=1,N
      DO 400 J=1,N
      DG(I,J)=F2(I,J)+X(N1)*S2(I,J)
  400 CONTINUE
```

```
      DG(I,N1)=DS(I)
  401 CONTINUE
      DO 405 J=1,N
      DG(N1,J)=DS(J)
  405 CONTINUE
      DG(N1,N1)=0.
C
C  END OF CALCULATIONS OF RESPONSES AND THEIR DERIVATIVES
C
      WRITE(6,980) X
      WRITE(6,981)F,S
      WRITE(6,980) DF
      WRITE(6,980) DS
      WRITE(6,980)DG
  980 FORMAT(4F20.5)
      WRITE(6,981)G
  981 FORMAT(/4F20.5//)
      IER=1
      CALL GAUSS(DG,N1,4,G,DX,IDUM,IER)
      WRITE(6,900)M
  900 FORMAT(//"********** TRIAL  ",I2," **********"//
     1 "          X                DX              XCAL "/)
      DO 500 I=1,N1
      X(I)=X(I)-DX(I)
      XCAL=XMID(I)+X(I)*XUNIT(I)
       WRITE(6,901)I,X(I),DX(I),XCAL
  901 FORMAT(I2,6F12.5)
  500  CONTINUE
      F=F0
      S=S0
      DO 502 I=1,N
      F=F+F1(I)*X(I)
      S=S+S1(I)*X(I)
      IF(I.EQ.N)GO TO 502
      I1=I+1
      DO 501 J=I1,N
      F=F+F2(I,J)*X(I)*X(J)
      S=S+S2(I,J)*X(I)*X(J)
  501 CONTINUE
  502 CONTINUE
      WRITE(6,1000)F,S
 1000 FORMAT(//" OPTIMIZED RESPONSE F = ",F10.5//" CALCULATED CONSTRAINT
     1 S =",F10.5////)
      IF(M.GE.MMAX) GO TO 700
      DO 600 I=1,N1
      IF(DABS(DX(I)).GT.DXALLW) GO TO 210
  600 CONTINUE
      WRITE(6,902)
  902 FORMAT(//" THE ITERATION PROCESS HAS BEEN COMPLETED")
      GO TO 800
  700 WRITE(6,903)MMAX
  903 FORMAT(//" THE ITERATION PROCESS IS TERMINATED BECAUSE OVER ",I2,
     1 " TRIALS")
  800 CALL EXIT
      END
```

Input

```
00003
00020
0.001
10.0
97.244
10.6917
-2.40625   -0.16375   2.16131
9.29499    -2.875     -5.6
-0.161251   2.65675
0.33625
-0.792499  -6.7925
-0.0375
0.         0.         0.
-5.5
0.1        6.         4.
0.3        10.        86.
```

Output

********* TRIAL 1 **********

0.0	0.0	0.0	-5.50000
97.24399	10.69170		
-2.40625	-0.16375	2.16131	-0.00000
9.29499	-2.87500	-5.60000	-0.00000
0.0	4.19749	40.01747	9.29499
4.19749	0.0	0.54250	-2.87500
40.01747	0.54250	0.0	-5.60000
9.29499	-2.87500	-5.60000	0.0
-53.52869	15.64875	32.96129	0.69170

********* TRIAL 2 **********

	X	DX	XCAL
1	-0.07052	0.07052	0.29295
2	-0.21004	0.21004	8.73977
3	0.11430	-0.11430	86.45718
4	-0.13835	-5.36165	-0.13835

OPTIMIZED RESPONSE F = 97.66319

CALCULATED CONSTRAINT S = 10.04391

-0.07052	-0.21004	0.11430	-0.13835
97.66319	10.04391		
-2.06849	-0.11395	1.90318	-0.00000
8.68509	-2.82340	-5.11310	-0.00000
0.0	-0.05161	3.59850	8.68509
-0.05161	0.0	0.34144	-2.82340
3.59850	0.34144	0.0	-5.11310
8.68509	-2.82340	-5.11310	0.0
-3.27009	0.27668	2.61059	0.04391

********* TRIAL 3 **********

	X	DX	XCAL
1	-0.38897	0.31845	0.26110
2	-2.05954	1.84951	-2.35727
3	0.60324	-0.48894	88.41295
4	0.02459	-0.16294	0.02459

OPTIMIZED RESPONSE F = 98.65015

CALCULATED CONSTRAINT S = 10.62477

-0.38897	-2.05054	0.60324	0.02459

98.65016	10.62477		
-0.47028	0.10181	0.43460	-0.00000
6.82967	-2.58936	-2.88066	-0.00000
0.0	-0.18074	2.49171	6.82967
-0.18074	0.0	0.33533	-2.58936
2.49171	0.33533	0.0	-2.88066
6.82967	-2.58936	-2.88066	0.0

-0.30233	0.03813	0.36376	0.62477

********* TRIAL 4 *********

	X	DX	XCAL
1	-0.49289	0.10392	0.25071
2	-2.13784	0.07830	-2.82706
3	0.64413	-0.04069	88.57459
4	0.05187	-0.02728	0.05187

OPTIMIZED RESPONSE F = 98.69513

CALCULATED CONSTRAINT S = 10.02253

-0.49289	-2.13784	0.64413	0.05187

98.69513	10.02253		
-0.34894	0.13232	0.13198	-0.00000
6.61397	-2.50854	-2.17186	-0.00000
0.0	-0.20236	2.30643	6.61397
-0.20236	0.0	0.33430	-2.50854
2.30643	0.33430	0.0	-2.17186
6.61397	-2.50854	-2.17186	0.0

-0.00588	0.00220	0.01933	0.02253

********* TRIAL 5 *********

	X	DX	XCAL
1	-0.49921	0.00632	0.25008
2	-2.14428	0.00644	-2.86568
3	0.64269	0.00144	88.57074

```
4      0.05306     -0.00120      0.05306

OPTIMIZED RESPONSE F =    98.69633

CALCULATED CONSTRAINT S =    9.99990


          -0.49921            -2.14428            0.64269            0.05306

          98.69633             9.99990
          -0.35174             0.13285            0.11301           -0.00000
           6.62888            -2.50347           -2.12867           -0.00000
           0.0                -0.20330            2.29831            6.62888
          -0.20330             0.0                0.33426           -2.50347
           2.29831             0.33426            0.0               -2.12867
           6.62888            -2.50347           -2.12867            0.0

           0.00002             0.00001            0.00005           -0.00010


********* TRIAL    6 *********

        X            DX           XCAL

1     -0.49923     0.00001      0.25008
2     -2.14434     0.00006     -2.86603
3      0.64267     0.00002     88.57066
4      0.05307    -0.00000      0.05307

OPTIMIZED RESPONSE F =    98.69532

CALCULATED CONSTRAINT S =   10.00000


THE ITERATION PROCESS HAS BEEN COMPLETE
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Plant Optimization Code

```
C       OPT - MAIN PROGRAM TO HANDLE INPUT, OPTIMIZATION FOR HYPERFILT-
C       RATION PLANT STUDIES.
C       OPTIMIZATION PROGRAM AUTHORS, W.L. KEPHART, K.F. CROSS,J.R. COPPER
C       COMPUTING TECHNOLOGY CENTER, OAK RIDGE, TENN.
C       MODIFIED THROUGH  07/75 BY M.N. ASCHAUER
C       UNIVERSITY OF ILLINOIS, CHAMPAIGN, ILLINOIS.
C       WRITTEN IN FORTRAN IV, FOR THE IBM 360/75
C
C       ACCELERATION SCHEME WITH RIDGE RESTRAINTS.
C       SF1      FIRST VECTOR STEP SIZE FACTOR.
C       SF2      SUB-INTERVAL STEP SIZE FACTOR.
C       RF       REDUCTION FACTOR AFTER UNSUCCESSFUL STEP.
C       ALPHA    VARIABLE RANGE OF DERIVITIVE EVALUATION.
C       BET      RANGE FACTOR OF VARIAELE CHANGING MOST RAPIDLY.
C       KNT(J)   NUMBER OF TIMES VARIABLE IS HELD ON BOUNDARY.
C
C       INEQUALITY CONSTRAINTS
C       XPM, XPLIM  MAXIMUM CUMULATIVE PRODUCT SALT CONCENTRATION.
C       REM, RELIM  MINIMUM REYNOLDS NUMBER ALLOWED.
C       PRM, PRLIM  MINIMUM PRESSURE ALLOWED.
C
C       ******************************************************************
        IMPLICIT REAL*8(A-H,O-Z)
C       NAME OF COMMON TELLS WHICH ROUTINES USE IT...O=OPT,L=LINCON,
C       E=EVAL, B=BANK, C=ECON.
C
        COMMON / COMOB /TEMP,CRA,RP,RV,RXF,RXP,RFLX,RPWFLX,RA,RSPC,ZETA,
       1 SIGMA,PHI
        COMMON / CMOBCN /FEEDIN,XFONE,XFORIG,FDORIG,XFDIS,FDOUT,VOUT,POUT,
       1XFOUT,VLAST,PLAST,XPRMIT,CA,CE,EP,ET,AXPAVE,ASMFLX,STGNUM,BNKNUM,
       2NEANKS
        COMMON / CMOLBC /STEP,XPLIM,RELIM,PRLIM,VLIM,LIST1,LIST6,LINES
        COMMON / COMOL /R(20),KON(10),K
        INTEGER BNKNUM,STGNUM
C
        REAL*8 X(20),XB(20),XL(20),XH(20),DX(20),ACC1(20),ACC2(20),
       1 ANUM(20),FP(20),FP1(20),FPC(20,10),SLEFAC(20),KONST,INCRMT
        DIMENSION KNT(20),LIM(20),WT(20),AXPAVE(2,10),ASMFLX(2,10)
        DATA STEPA,STEPG,STEPI,STEPL / 1HA,1HG,1HI,1HL /
C       LOWER LIMITS, UPPER LIMITS EQUIVALENCED TO XB,XL,XH ARRAYS.
        EQUIVALENCE (XB(1),PIN),(XL(1),PL),(XH(1),PU),(XB(2),VIN),
       1(XL(2),VL),(XH(2),VU),(XB(3),CR),(XL(3),CRL),(XH(3),CRU),
       2(XB(4),DIA),(XL(4),DIAL),(XH(4),DIAU),(WT(1),PWT),(WT(2),VWT),
       3(WT(3),CRWT),(WT(4),DIAWT)
C
C
C       ******************************************************************
C
C       SECTION TO INITIALIZE STARTING VARIABLES TO BASE CONDITIONS
C       WHICH ARE USED UNTIL BEGINNING OF NEW BANK. RESET FOR EACH NEW
C       STAGE. SEE FORMAT 6001 FOR UNITS OF VARIABLES.
C
C       ******************************************************************
C
        NOPT = 1
C       SET VALUES OF WEIGHTING FACTOR TO BE USED.
        PWT = 10.0D0
        VWT = 1.0D0
        CRWT = 0.0D0
```

```
      DIAWT = 1.0D0
      FEEDIN = 1.0D6
      XFONE = 1.0677D-2
      XFORIG = 1.0677D-2
      FDORIG = FEEDIN
      XFDIS = 2.1354D-2
      INCRMT = 0.20D0
      STGNUM = 0
      IF(NOPT .EQ.0) GO TO 1400
C
      CALL NONOPT
C
1400  CONTINUE
      STGNUM = STGNUM+1
      IF(STGNUM .GT. 2) GO TO 8024
C
C     SET XB STARTING VALUES FOR P,V,CR,DIA.
C     ONE OR MORE VARIABLES ARE OPTIMIZED STARTING WITH THE FIRST-P.
      BNKNUM = 1
      XB(1) = 80.0D0
      XB(2) = 2.0D0
      XB(3) = 1.25D0
      XB(4) = 0.50D0
      IF(NOPT .EQ. 0) READ(5,1401) (XB(I),I=1,4)
1401  FORMAT(4D10.0)
      XFORIG = XFONE
      PLAST = 0.0D0
      VLAST = 0.0D0
      XFOUT = XFORIG
      IF(NOPT .EQ. 0) GO TO 1421
C
      CALL STGADR(XB,PWT,VWT,CRWT,DIAWT)
C
1421  GO TO 1493
C     ****************************************************************
C     BEGIN LOOP 1
C     1492 IS RETURN LOOP WHICH BEGINS NEW MODULE BANK IN STAGE.
C     ONE OR MORE OPTIMIZATIONS MAY BE DONE IN 8010 LOOP.
C     ****************************************************************
C
1492  CONTINUE
      IF(STGNUM .EQ. 1) NBANKS = BNKNUM
      IF(STGNUM .EQ. 2) XFDIS = 1.0677D-2
      IF(STGNUM .EQ. 2) INCRMT = 0.50D0
      IF(XFOUT .GT. XFDIS) GO TO 8022
      BNKNUM = BNKNUM + 1
      XB(1) = POUT
      XB(2) = VOUT
      XB(3) = (XFOUT/XFORIG)+(INCRMT+0.05D0)
      XB(4) = 0.50D0
      IF(NOPT .EQ. 0) READ(5,1401) (XB(I),I=1,4)
      XFONE = XFOUT
      FEEDIN = FDOUT
      VLAST = VOUT
      PLAST = POUT
      IF(NOPT .EQ. 0) GO TO 1422
C
      CALL BNKADR(XB,PWT,VWT,CRWT,DIAWT)
C
```

```
1422  GO TO (1493,1491),STGNUM
C
1491  CALL DLEND
C     SET XL LOWER LIMITS EQUIVALENT TO PL,VL,CRL,DIAL.
1493  XL(1) = 27.218D0
      XL(2) = 0.C1D0
      XL(3) = (XFOUT/XFORIG)+INCRMT
      XL(4) = 0.0D0
C     SET XH UPPER LIMITS EQUIVALENT TO PU,VU,CRU,DIAU.
      XH(1) = 110.0D0
      XH(2) = 20.CDC
      XH(3) = 10.0DC
      XH(4) = 3.CDC
C
C     SET LOWEST AND HIGHEST NO. OF VARIABLES TO BE OPTIMIZED.
      NVARL = 2
      NVARU = 2
C     SET LIMITS FOR PRODUCT SALT CONC., REYNOLDS NO., AND PRESSURE.
      XPLIM = 1.0C-2
      XPRMIT = 1.54157C-4
      VLIM = 0.20D0
      RELIM = 210C.0D0
      PRLIM = 20.414D0
      TEMP = 77.0D0
C     SET REFERENCE CONDITICNS TO FIT EMPIRICAL EQUATIONS. BASE CASE.
      RP = 40.826ED0
      RV = 3.2682D0
      RXF = 1.6624D-3
      RXP = 1.6624D-5
      RFLX = 11.123D0
      RPWFLX = 12.123DC
C     SET EMPIRICAL CONSTANTS, BASE CASE.
      ZETA = 1.084D-3
      SIGMA = 5.05652D-5
      PHI = C.8510D0
C     SET ECONOMIC PARAMETERS. CA=AREA COST(CENTS/SQFT DAY),
C     CE=ELECTRICITY CCST(CENTS/KWH), EP= PUMP EFFICIENCY.
C
      CA = 1.0D0
      CE = 1.0D0
      EP = 0.7D0
      ET = 0.0D0
C     LIST1=(0-PRINT DETAILED PROGRESS OF OPTIMIZATION , 1=SKIP)
C     LIST6=(0-PRINT 1 LINE /CALL TC SECTION, 1-SKIP)
      LIST1 = 1
      LIST6 = 0
C     LOGCR MEANS(1=ADJUST CR, 0= NC), CRADJ = FACTCR.
      LOGCR = 0
      CRADJ = 0.9D0
C     STEP SIZES AND WEIGHTING FACTCRS.
      ALPH = 0.001D0
      BETA = 0.005D0
      MAXTIM = 60000
C     LOOPS=(1-DO 9010 LOOP CNCE PER N) (2-TWICE PER N TO SAVE TIME).
      LOCPS = 1
C
C     SET TIMING ROUTINE.
      M = 0
      CALL STIMEZ(6C000,M)
```

```
C
C
C     CCMPUTE REFERENCE PURE WATER PERMEABILITY AND REFERENCE SOLUTE
C     PERMEABILITY COEFFICIENTS.
      RA = RPWFLX/RP
C     CONVERT TEMPERATURE TC DEGREES CENTIGRADE.
      TDEGC = (TEMP+40.0D0)/1.8D0 - 40.0D0
      PIRXP = (82.05DC*(TDEGC+273.16D0)*2.0D0*18.01534D0)*(55.5082SD0*
     1 0.932D0*RXP)/((1.0D0-RXP)*1.0D3*18.0695D0)
      PIRXW = (RP+PIRXP)-(RFLX/RA)
      KONST = (PIRXW*18.0685DC*1.0D3)/(82.05D0*(TDEGC+273.16D0)*2.0D0*
     1 18.01534D0*0.932D0)
      RXW = KONST/(55.5C825D0+KCNST)
      RSPC = (RFLX*1.547D-6)/(((1.0D0-RXP)/ RXP)*(RXW-RXP))
C
C     NOW PRINT OUT NAMELIST VARIABLE VALUES.
      WRITE(6,6001) STGNUM,BNKNUM,FIN,PL,PU,PWT,VIN,VL,VU,VWT,CR,CRL,
     1CRU,CRWT,DIA,DIAL,DIAU,DIAWT
6001  FORMAT( 1H1/'0  HYPERFILTRATICN DESIGN CPTIMIZATION-INPUT VARIABLE
     1S FOR STAGE NO.',I2,' MODULE BANK NO.',I3/
     A'0   INITIAL VALLE',9X,'LOWER LIMIT',11X,'UPPER LIMIT',10X,
     1'WEIGHTING FACTOR',5X,'VARIABLE', / 1H /
     2 4X,6HPIN    ,F12.6, 4X,6HPL     ,F12.6, 4X,6HPU     ,F12.6          ,
     3 3X,6HPWT    ,F12.6,3X,'INLET PRESSURE (ATM) '                       /
     4 4X,6HVIN    ,F12.6, 4X,6HVL     ,F12.6, 4X,6HVU     ,F12.6          ,
     5 3X,6HVWT    ,F12.6,3X,'INLET VELOCITY (FT/SEC) '                    /
     6 4X,6HCR     ,F12.6, 4X,6HCRL    ,F12.6, 4X,6HCRU    ,F12.6          ,
     7 3X,6HCRWT   ,F12.6,3X,'CONCENTRATION RATIO'                         /
     8 4X,6HDIA    ,F12.6, 4X,6HDIAL   ,F12.6, 4X,6HDIAU   ,F12.6          ,
     9 3X,6HDIAWT  ,F12.6,3X,'INSIDE TUBE DIAMETER (INCHES '               )
      WRITE(6,6003) NVARL,NVARU,XPLIM,RELIM,PRLIM,TEMP,FEEDIN,XFONE,RP,
     1 RV,RXF,RXP,RFLX,RPWFLX,RA,RSPC,ZETA,SIGMA,PHI
6003  FORMAT(1H /1H / 2(4X,'VARIABLE     VALUE   DESCRIPTION',29X)/1H /
     14X,6HNVARL ,I12  ,3X,40HMIN NUM OF VARIABLES TO BE OPTIMIZED        ,
     24X,6HNVARU ,I12  ,3X,40HMAX NUM OF VARIABLES TO BE OPTIMIZED       /
     34X,6HXPLIM ,F12.6,3X,40HMAX SALT CONC. CF PROD. (MOLE FRACTION)    ,
     44X,6HRELIM ,0PF12.6,3X,35HMIN REYNOLDS NUMBER ALLOWABLE            /
     54X,6HPRLIM ,F12.6,3X,40HMIN PRESSURE ALLOWABLE                     ,
     64X,6HTEMP  ,F12.6,3X,40HTEMPERATURE (DEGREES F)                    /
     74X,6HFEEDIN,1PD12.2,3X,35HFEED FLOW RATE (GAL/DAY)                 ,
     89X,6HXFIN  ,0PF12.6,3X,35HFEEC CONCENTRATION (MCLE FRACTION)       /
     94X,6HRP    ,F12.6,3X,40HREFERENCE PRESSURE (ATM)                   ,
     X4X,6HRV    ,F12.6,3X,40HREFERENCE VELOCITY (FT/SEC)                /
     14X,6HRXF   ,F12.6,3X,40HREFERENCE FEED MOLE FRACTION               ,
     24X,6HRXP   ,F12.6,3X,40HREFERENCE PERMEATE MOLE FRACTION           /
     34X,6HRFLX  ,F12.6,3X,40HREFERENCE FLUX (GFD)                       ,
     44X,6HRPWFLX,F12.6,3X,40HREFERENCE PURE WATER FLUX (GFD)            /
     54X,6HRA    ,D12.6,3X,40HREFERENCE PURE WATER PERMEABILITY COEFF.,
     64X,6HRSPC  ,D12.6,3X,40HREFERENCE SOLUTE PERMEABILITY COEFF        /
     74X,6HZETA  ,D12.6,3X,40H                                           ,
     84X,6HSIGMA ,D12.6,3X,40H                                           /
     94X,6HPHI   ,D12.6,3X,40H                                           )
      WRITF(6,6004) CA,CE,EP,LIST1,LIST6,LOGCR,CRADJ,ALPH,BETA,MAXTIM
6004  FORMAT(                                                            /
     X4X,6HCA    ,F12.6,3X,40HUNIT CCST OF MEMB AREA (CENTS/SQFT*DAY)    ,
     14X,6HCE    ,F12.6,3X,40HUNIT COST OF ELEC POWER (CENTS/KWH)        /
     24X,6HEP    ,F12.6,3X,40HPUMP EFFICIENCY (FRACTION)                 ,
     34X,6HLIST1 ,I12  ,3X,40H(0=LIST ON TAPE,1=SKIP)                    /
     44X,6HLIST6 ,I12  ,3X,40H(0=LIST ON TAPE 6,1=SKIP)                  ,
```

```
      54X,6HLOGCR ,I12  ,3X,40HADJUST CR (0=NO,1=YES)                  /
      64X,6HCRADJ ,F12.6,3X,40HCR ADJUSTMENT FACTOR                    .
      74X,6HALPH  ,F12.6,3X,40HSTEP SIZE FOR GRADIENT                  /
      84X,6HBETA  ,F12.6,3X,40HSTEP SIZE FOR SEARCHING                 .
      94X,6HMAXTIM,I12  ,3X,40HMAX TIME PER CASE (IN .01 SEC)          )
C     CHECK STARTING VALUES. IF ZERO SKIP TO NEXT CASE.
      IF(XB(1).LE.0.0D0) GO TO 8020
      IF(XB(2).LE.0.0D0) GO TO 8020
      IF(XB(3).LE.0.0D0) GO TO 8020
      IF(XB(4).LE.0.0D0) GO TO 8020
      IF(XFONE.LE.0.0D0) GO TO 8020
C
C     CALL SETUP IN TUBE TO INITIALIZE VARIABLES FOR THIS CASE.
      CALL SETUP
C
C     ****************************************************************
C
C     BEGIN LOOP 2.
C     DO 8010 N LOOP. ONE OR MORE OPTIMIZATIONS MAY BE DONE. FIRST TIME
C     OPTIMIZE NVARL VARIABLES STARTING WITH P. ORDER OF VARIABLES = P,
C     V,CR,TAPER,C. LOOP IS DONE ((NVARU-NVARL)+1) TIMES.
C
C     ****************************************************************
C
      DO 8010 N=NVARL,NVARU
C
      LOOP=0
90    LINES=100
      LOOP=LOOP+1
      GO TO (91,92), LOOP
C     LOWER CR IF LOOP IS DONE MORE THAN ONCE.
91    IF(N.NE.NVARL.OR.LOGCR.EQ.1) XB(3)=(XB(3)-1.0D0)*CRADJ + 1.0D0
      IF(N.NE.NVARL.OR.LOGCR.EQ.1) WRITE(6,6006) CR
6006  FORMAT( 1H1/ '**CR HAS BEEN ADJUSTED TO',F9.4,'**'/1H )
92    LIST6=0
93    ALPHA=ALPH
      BET=BETA
      CMM=-1.0D0
      SF1=1.5D0
      SF2=0.9D0
      RF=0.25D0
      RMAX=0.0D0
      STEP=STEPI
      K=0
      ISTOP=1
      KNTVEC=-1
      KT2=3
      KT5=1
      DO 73 I=1,N
      KNT(I)     =0
      FP1(I)      =0.0D0
      SLEFAC(I) =1.0D0
      R(I)=CABS((XH(I)-XL(I))*WT(I))
      RMAX=DMAX1(RMAX, R(I))
      LIM(I)=0
      IF(R(I).EQ.0.0D0) LIM(I)=1
73    CONTINUE
      IF(RMAX.LE.0.D0) RMAX=1.0D0
      DO 29 I=1,20
```

```
29      X(I)= XB(I)
        K=K+1
C       CALL EVAL WHICH CALLS BANK, ECON TO GET INITIAL COST.
337     CALL EVAL(XB,FB,C,IER,XPM,REM,PRM)
C
        IF(IER.NE.1) GO TO 340
        IF(XPM.LE.XPLIM+1.0D-10 .AND. REM.GE.RELIM-0.02D0 .AND. PRM.GE.
       1 PRLIM) GO TO 341
        IF(N.LT.3 .OR. R(3).LE.0.0D0) GO TO 338
C
C       CALL ADJUST TO SET PRESSURE,VELOCITY TO ACCEPTABLE VALUES.
340     CALL ADJUST(XB)
C
        IF(XB(1) .GT. XH(1)) XB(1) = XH(1)
        IF(XB(2) .GT. XH(2)) XB(2) = XH(2)
        GO TO 337
C       338 IS ERROR. CALL EVAL. GO TO NEXT CASE.
338     CALL EVAL(XB,FB,1,IER,XPM,REM,PRM)
C
        GO TO 8024
CC      TXPE=XPE
341     TXPM=XPM
        TREM=REM
        TPRM=PRM
C       INITIALIZATION FOR THIS CASE IS DONE.
C
C       ***************************************************************
C
C       BEGIN A NEW VECTOR DIRECTION STARTING AT POINT XB.
C       EITHER GRADIENT OR ACCELERATION (PARALLEL TANGENT) DIRECTION.
C
C       ***************************************************************
3       L=0
        KT=4
        KNTVEC=KNTVEC+1
        SF=SF1
        SCALE=CMM
        XPM=TXPM
        REM=TREM
CC      XPE=TXPE
        PRM=TPRM
        IF(LIST1.EQ.0) WRITE(6,100) K,L,FB,(XB(I),I=1,N)
C       ***************************************************************
C
C       STORE ACCELERATION VECTOR COORDINATES OF CALC ITS DIRECTION.
C
C       ***************************************************************
        GO TO (200,204,201),KT5
200     IF(KNTVEC-1)5,201,201
201     DO 202 I=1,N
        ACC1(I)=ACC2(I)
202     ACC2(I)=XB(I)
        IF(KNTVEC.EQ.1) GO TO 5
        KT5=2
        GO TO 5
C       CALCULATE ACCELERATION VECTOR DIRECTION.
204     DO 205 I=1,N
        IF(R(I).NE.0.0D0) ANUM(I)=(XB(I)-ACC1(I))*CMM*RMAX / R(I)
        IF(R(I).EQ.0.0D0) ANUM(I)=0.0D0
```

```
205   CONTINUE
      KT5=3
      STEP=STEPA
      IFLAG=3
      IF(M.EQ.1) GO TO 7111
C     CALL LINCON TO ADJUT THE ACCELERATION VECTOR DIRECTION.
      CALL LINCON(ANUM,XB,XH,XL,KNT,N,IFLAG,CMM,FPC,FL,XPM,REM,PRM)
C
      GO TO 89
C     ACCELERATION VECTOR SKIPS RESTRAINING FACTOR SLEFAC.GO TO STEP
C     SIZE
C     ***************************************************************
C
C     APPROXIMATING PARTIALS BY ONE-SIDED DIFFERENCES.
C
C     ****************************************************************
CC    SXPE=XPE
5     SXPM=XPM
      SREM=REM
      SPRM=PRM
      STEP=STEPG
      IF(LIST1.EQ.0) WRITE(6,6008)
6008  FORMAT(10X,1H )
      LINES=LINES+1
      IF(LIST1 .EQ. 0) WRITE(6,1409) REM,XPM,PRM
1409  FORMAT(5HOREM=,E15.8,5X,4HXPM=,E15.8,5X,4HPRM=,E15.8)
      DO 4 I=1,N
4     X(I)=XB(I)
C
C     IF VARIABLE IS ON BOUNDARY , IT IS HELD THERE FOR 5 GRADIENT
C     VECTOR CHANGES BEFORE IT IS USED AGAIN. THE NUMBER OF VARIABLES
C     IS REDUCED BY ONE FOR THE NEXT 5 GRADIENT VECTOR DIRECTION
C     CHANGES.
C
      DO 984 J=1,N
      SL=FB
      IF(LIM(J)-1)969,72,969
969   IF((X(J)-XH(J))*(X(J)-XL(J)))68,67,67
67    KNT(J)=KNT(J)+1
      IF(KNT(J)-5)72,68,68
68    KNT(J)=0
C     ARBITRARY STEP ALPHA*R FOR EACH VARIABLE.
      X(J)=X(J) + ALPHA*R(J)
      K=K+1
      IF(M.EQ.1) GO TO 7111
      IF(LOOP.EQ.1 .AND. M.EQ.1 .AND. LOOPS.EQ.2) GO TO 7111
C     CALL EVAL WHICH CALL BANK, ECON TO GET COST.
      CALL EVAL(X,FH,0,IER,XPM,REM,PRM)
C
      IF(LIST1 .EQ. 0) WRITE(6,1409) REM,XPM,PRM
      IF(LIST1.EQ.0) WRITE(6,106) K,L,FH,(X(I),I=1,N)
      GO TO 6
72    FH=0.0D0
      SL=0.0D0
6     IF(R(J).EQ.0.0D0) GO TO 7
C     PARTIAL DERIVITIVE OF COST FUNCTION, 3 CONSTRAINTS.
      FP(J)= (FH-SL)/ALPHA
      FPC(J,1)= -(XPM-SXPM)/ALPHA
      FPC(J,2)=(REM-SREM)/ALPHA
```

```
      FPC(J,3)= (PRM-SPRM)/ALPHA
      GO TO 35
7     FP(J)=0.0D0
      FPC(J,1)=0.0D0
      FPC(J,2)=0.0D0
      FPC(J,3)=0.0D0
35    ANUM(J)=FP(J)
      X(J)=XB(J)
984   CONTINUE
      STEP=STEPL
      IF(LIST1.EQ.0) WRITE(6,107) (FP(I),I=1,N)
107   FORMAT(1H0,42HPARTIAL DERIVITIVES OF GRADIENT EVALUATION/
     11H ,7E16.8/1H ,7E16.8/1H,7E16.8)
      IFLAG=3
      DO 69 I=1,10
69    KCN(I)=0
      IF(M.EQ.1) GO TO 7111
C     CALL LINCCN TO ADJUST THE PARTIALS (GRADIENT VECTOR DIRECTION).
      CALL LINCCN(ANUM,XB,XH,XL,KNT,N,IFLAG,CMM,FPC,FL,XPM,REM,PRM)
C     ***************************************************************
C
C     RIDGE ANALYSIS. SLEFAC RESTRAINS OSCILLATING VARIABLES.
C
C     ***************************************************************
      DO 14 I=1,N
      IF(FP1(I)*ANUM(I)) 12,14,13
12    SLEFAC(I)=SLEFAC(I)*0.64D0
      GO TO 14
13    SLEFAC(I)=SLEFAC(I)*1.25D0
      SLEFAC(I)=DMIN1(SLEFAC(I),1.0D0)
14    FP1(I)=ANUM(I)
      IF(LIST1.EQ.0) WRITE(6,1429) (SLEFAC(J),J=1,N)
1429  FORMAT(8H SLEFAC=,7E15.6)
209   DO 80 J=1,N
80    ANUM(J)=ANUM(J)*SLEFAC(J)
C
89    CONTINUE
      IFLAG=3
C     CALL LINCCN TO ADJUST THE DIRECTION (GRADIENT OR ACCELERATION).
      CALL LINCCN(ANUM,XB,XH,XL,KNT,N,IFLAG,CMM,FPC,FL,XPM,REM,PRM)
C
C     ****************************************************************
C
C     CALCULATE DX. TERM TO BE USED IN STEP SIZE (DX(I)*SCALE*BOUND).
C
C     ****************************************************************
      IF(KT5.EQ.3) GO TO 11
C     GRADIENT VECTOR.
      AMAX=0.0D0
      DO 8 J=1,N
      AMAX=DMAX1(AMAX, DABS(ANUM(J) ))
8     CONTINUE
      DO 9 J=1,N
      IF(AMAX.GT.0.0D0) DX(J)=ANUM(J)*R(J)*BET / AMAX
      IF(AMAX.LE.0.0D0) DX(J)=0.0D0
      IF(LIST1 .EQ. 0) WRITE(6,4193) DX(J),ANUM(J),R(J),BET,AMAX
4193  FORMAT('0','CHECK VALUES',D12.6,2X,D12.6,2X,D12.6,2X,D12.6,2X,
     1 D12.6)
9     CONTINUE
```

```
      GO TO 20
C     ACCELERATION (PARALLEL TANGENT) VECTOR. 0.05 DISTANCE BETWEEN
C     POINTS.
11    DO 10 J=1,N
10    DX(J)=ANUM(J)*R(J)*0.05D0 / RMAX
C
C     ****************************************************************
C
C     CALCULATES NEW VECTOR AND CHECKS PREDICTED VECTOR IS EXTERIOR
C     TO BOUND DOMAIN. MULT STEP BY BOUND (SMALLEST VALUE 0-1)
C     TO PUT ALL VARIABLES IN OR ON BOUNARY.
C
C     ****************************************************************
20    IBOUND=0
      BOUNDT=1.0D0
      BOUND=1.0D0
85    IBOUNT=0
21    DO 22 I=1,N
      IF(I-IBOUND)83,22,83
C     STEP FROM XB TO X
83    X(I)=XB(I) +DX(I)*SCALE*BOUND
      IF(KTS.EQ.3) GO TO 56
      IF(KNT(I))22,56,22
56    IF(X(I)-XH(I))43,43,44
44    IF(X(I)-XB(I) .NE. 0.0D0) BOUNDT=(XH(I)-XB(I))/(X(I)-XB(I))
      IF(X(I)-XB(I) .EQ. 0.0D0) BOUNDT=0.0D0
      X(I)=XH(I)
      GO TO 42
43    IF(X(I)-XL(I)) 45,42,42
45    IF(XB(I)-X(I) .NE. 0.0D0) BOUNDT=(XB(I)-XL(I))/(XB(I)-X(I))
      IF(XB(I)-X(I) .EQ. 0.0D0) BOUNDT=0.0D0
      X(I)=XL(I)
42    IF(BOUND-BOUNDT)22,22,82
82    BOUND=BOUNDT
      IBOUND=I
      IBOUNT=I
22    CONTINUE
      IF(IBOUNT)85,86,85
86    CONTINUE
C
C     ****************************************************************
C
C     EVALUATION OF POINT ON PREDICTED VECTOR.
C
C     ****************************************************************
      IFLAG=1
      IF(M.EQ.1) GO TO 7111
C     CALL LINCON TO ADJUST THE VARIABLES TO SATISFY THE CONSTRAINTS.
      CALL LINCON(ANUM,X,XH,XL,KNT,N,IFLAG,CMM,FPC,FL,XPM,REM,PRM)
      IF(LIST1 .EQ. 0) WRITE(6,1009) REM,XPM,PRM
      IF(LIST1.EQ.0) WRITE(6,1006) K,L,F,(X(I),I=1,N)
106   FORMAT(3H0   ,I4,2X,I4,10X,E16.8,/3H    ,7E16.8/3H    ,7E16.8)
      F=FL
C     CHECK VALUE OF F FOR IMPROVEMENT. 23 IF BETTER, 30 IF WORSE.
      IF(CMM*(F-FB))30,30,23
C
C     ****************************************************************
C
C     GOOD MOVE ALONG VECTOR. STEP IMPROVED POSITION.
```

```
C
C     ******************************************************************
23    L=L+1
      ISTOP=1
      FB=F
      TXPM= XPM
      TREM= REM
CC    TXPE= XPE
      TPRM= PRM
      CO 24 I=1,N
24    XB(I)=X(I)
      IF(KT5.EQ.3) GO TO 26
      IF(L.NE.30) GO TC 71
C
C     VARIABLES ARE RELATIVE INSENSITIVE, WE ARE MOVING TOO SLOWLY,
C     LETS SPEED THINGS ALONG
C
C     AFTER 30 GOOD STEPS INCREASE ALPHA,BET, START NEW VECTOR DIRECTION
      ALPHA=ALPHA*5.0DC
      BET=BET*5.0D0
      IF(LIST1.EQ.0) WRITE(6,65)
65    FORMAT(1H0,48HPRCCEEDING TOC SLOWLY, INCREASING ALPHA AND BETA,
     127H,BEGIN ANEW FRCM THIS POINT)
      KT2=3
      GO TO 3
C
71    IF(L.NE.10 .AND. L.NE.20) GO TO 26
C     AFTER 10 GOCD STEPS INCREASE ALPHA, BET OR RESET SF=SF1,
C     AFTER 20 GOOD STEPS INCREASE ALPHA,BET.
      IF(SF.NE.SF2) GO TO 74
      SF=SF1
      GO TO 26
74    ALPHA=ALPHA*2.0D0
      BET=BET*2.0D0
C     MULT SCALE BY 1.5 TO INCREASE STEP SIZE (OR BY C.9 TO DECREASE).
26    SCALE=SCALE*SF
      KT2=3
      IF(LIST1.EQ.0) WRITE(6,64) L
64    FORMAT(1H0,19HSUCCESSFUL STEP NO.,I2)
      IF(IBOUNC.LE.C) GC TC 89
88    ANUM(IBOUND)=C.0D0
      KNT(IBOUND)=KNT(IBOUND)+1
      GO TO 89
C     ******************************************************************
C
C     THIS SEARCH WAS A FAILURE; DETERMINE COURSE OF ACTION.
C     KT5=3 WHEN ACCELERATICN STEP IS BEING TAKEN.
C
C     ******************************************************************
30    KT=KT-1
      GO TO (34,34,31),KT
C     KT=3, FIRST FAILURE. 20 IF NO GOOD STEPS, 3 IF GOOD STEPS.
31    CONTINUE
      IF(LIST6.EQ.0 .AND. L.LE.0) WRITE (6,6009)
      IF(LIST6.EQ.0 .AND. L.GT.C) WRITE (6,6010) ALPHA
6009  FORMAT('0FIRST STEP FAILED. REDUCE STEP, TRY AGAIN.')
6010  FORMAT('0THIS STEP FAILEC. ALPHA=', F12.9)
      LINES=LINES+2
      IF(L.GE.1) GO TO 3
```

```
      SF=SF2
      SCALE=SCALE*RF
      IF(LIST6.EQ.0) WRITE(6,59)
59    FORMAT(1H0,  'FIRST SEARCH FAILURE ALONG VECTOR DIRECTION.' ,
     1     ' NOW SCANNING LAST INTERVAL.'  )
      GO TO 20
C     KT=2 (NEVER 1) SECOND FAILURE. GO BACK TO 3. RESTART UNLESS DONE.
34    IF(LIST6.EQ.0) WRITE(6,6010) ALPHA
      LINES=LINES+1
      IF(KT5.EQ.3) GO TO 3
      IF(L.GE.1) GO TO 3
C     BACK TO 3 IF ACCELERATION OR ANY GOOD STEPS.
      ALPHA=ALPHA/20.0D0
      BET=BET/20.0D0
217   DO 213 I=1,N
213   ACC2 (I)=ACC1 (I)
      IF(KNTVEC-3)214,215,215
214   KT5=1
      KNTVEC=KNTVEC-1
      GO TO 216
215   KT5=3
216   CONTINUE
      IF(LIST6.EQ.0) WRITE(6,62)
      KT2=KT2-1
62    FORMAT(1H0,39HUNSUCCESSFUL FIRST STEP WHILE SCANNING ,
     152HWITH REDUCED SF AFTER UNSUCCECCFUL FIRST STEP WHILE,
     225HSCANNING WITH ENLARGED SF/  1H ,
     354HREDUCE ALPHA,BETA,RE EVALUATE ELSE OPTIMUM IS OBTAINED)
      GO TO (46,3),KT2
C     PARABOLIC FIT CANNOT BE USED BECAUSE OF INEQUALITY CONSTRAINTS.
C
C     CASE HAS BEEN COMPLETED, UNLESS INDEPENDENT VARIABLE WAS
C     HELD ON BOUNDARY FOR LAST VECTOR EVALUATION
C     RELEASE VAR 1 TIME FOR ONE MORE GRADIENT CALCULATION.
C
46    GO TO (15,18),ISTOP
C     QUIT WHEN KT=2, KT2=1, ISTOP=1(KNT=0) OR ISTOP=2.
15    DO 17 I=1,N
      IF(KNT(I))17,17,16
16    ISTOP=2
      KT2=2
      KT5=3
17    KNT(I)=5
      GO TO (18,3),ISTOP
18    GO TO 7112
C
C     WRITE NOTE WHEN QUITTING ON TIME LIMIT. CALL EVAL FOR LIST.
7111  WRITE(6,6005)
6005  FORMAT(1H1/'** THIS CASE PULLED ON TIME. ** ANSWER NOT OPT.')
C     ************************************************************
C
C     CASE IS TERMINATED, OPTIMUM FOUND. POINT XB,FB.
C
C     ************************************************************
C     CALL EVAL LAST TIME TO PRINT OUT OPTIMUM RESULTS IN BANK, ECON.
7112  CALL EVAL(XB,FB,1,IER,XPM,REM,PRM)
C
      IF(LIST1.EQ.0) WRITE(6,1409) REM,XPM,PRM
      IF(LIST1.EQ.0) WRITE(6,100) K,L,FB,(XB(I),I=1,N)
```

```
100   FORMAT(3H0 *,I4,2X,I4,10X,E16.8/3H *,7E16.8/3H  *,
     17E16.8/3H  *,7E16.8)
      IF(LIST1.EQ.0) WRITE(6,47)
47    FORMAT(1H1,9HEXCELSIOR)
C
      IF(LOCPS.EQ.2 .AND. LCOP.EQ.1) GO TO 90
C     ***************************************************************
C
8010  CONTINUE
C     8010 END N LOOP. NVARL,NVARU. *** GO TO 1492 FOR NEW MODULE BANK.
C     END OF LOOP 2 WITHIN LOOP1.
C
      GO TO 1492
8020  WRITE(6,8021)
8021  FORMAT(' 0 ONE OF THE STARTING VALUES XE(I) .LE. 0... STOP')
      GO TO 8024
8022  WRITE(6,8023) STGNUM
8023  FORMAT('0       DISCHARGE BRINE EXCEEDS LIMIT. LAST MODULE BANK HAS
     1BEEN ADDED TO STAGE NO.',I4/'0  NOW CALL-ENTRY ACCUM-TO DETERMINE
     2PERMEATE QUALITY,QUANTITY IN EACH STAGE AND FEED OR RECYCLE TO NEX
     3T STAGE.')
C
      CALL ACCUM
      GO TO 1400
8024  CONTINUE
      END
```

```
C
      SUBROUTINE LINCON(FP,X,XH,XL,KNT,N,IFLAG,CHM,FPC,FL,XPM,REM,PRM)
C
C     IF IFLAG=1 ADJUST THE VARIABLES TO SATISFY THE CONSTRANTS.
C     IF IFLAG=2 SECOND PASS AT ADJUSTING VARIABLES.
C     IF IFLAG=3 ADJUST THE PARTIALS (VECTOR DIRECTION).
C     FPC(I,J)=PARTIAL OF CONSTRAINT J WITH RESPECT TO VARIABLE I.
C     N=NO. OF VARIABLES.
C     NLINEQ= 0 EQUALITY CONSTRAINTS.
C     NNOTEQ= 3 INEQUALITY CONSTRAINTS.
C     INEQUALITY CONSTRAINTS.
C     XPM,XPLIM MAXIMUM PRODUCT SALT CONCENTRATION.
C     REM,RELIM MINIMUM REYNOLD'S NO. ALLOWED.
C     PRM,PRLIM MINIMUM PRESSURE ALLOWED.
C
      IMPLICIT REAL*8(A-H,O-Z)
C
C     NAME OF COMMON TELLS WHICH ROUTINES USE IT...O=OPT=HYPFIL.
C     L=LINCON. E=EVAL. B=BANK. C=ECON.
      COMMON / CMCLBC /STEP,XPLIM,RELIM,PRLIM,VLIM,LIST1,LIST6,LINES
      COMMON / CONOL / R(20),KON(10),KFLG
C
      DIMENSION NLINLD(10),                    BSUMNT(10)
      DIMENSION FP(20),FPC(20,10),BSUM(10),AX(10,10)
      DIMENSION X(20),XH(20),XL(20),KNT(20)
C
C     ******************************************************************
C
      IF(LIST1.EQ.0 .AND. IFLAG.LT.3) WRITE(6,6001)
6001  FORMAT(30X,1H )
      IF(IFLAG.LT.3) LINES=LINES+1
      ITER=0
      NLINEQ=0
      NNOTEQ= 3
C     2 IS TOP OF LOOP FOR ADJUSTMENT OF VARIABLES.
2     CONTINUE
      NLIN=NLINEQ
      IF(IFLAG.EQ.3) GO TO 111
C     CALL EVAL WHICH CALLS BANK, ECON TO GET COST.
C     ADJUSTMENT OF VARIABLES ONLY (IFLAG=1,2).
      CALL EVAL(X,FH,0,IER,XPM,REM,PRM)
C
      KFLG=KFLG+1
      FL=FH
      IF(IER.NE. 1) GO TO 50
C     QUIT IF IER NOT 1, ERROR IN BANK.
9     CONTINUE
C
C     LIST FPC(I,J) WITH EQUALITY CONSTRAINTS FOR LOW VALUES OF J AND
C     CONTINUE J TO INCLUDE INEQUALITY CONSTRAINTS.
C     ORDER BSUMNT FOR INEQUALITY CONSTRAINTS IN SAME ORDER.
C     THIS VERSION OF THE PROGRAM USES ONLY 2 CONSTRAINTS.
C
      BSUMNT(1)= XPLIM-XPM
      BSUMNT(2)= REM-RELIM
      BSUMNT(3)= PRM-PRLIM
      DO 15 I=1,NNOTEQ
      IF(BSUMNT(I))16,16,15
16    KON(I)=1
```

```
15      CONTINUE
111     CONTINUE
C       ADJUSTMENT OF EITHER VARIABLES OR VECTOR DIRECTION.
        IF(NLINEQ.EQ.0) GO TO 112
        DO 12 I=1,NLINEQ
12      NLINLD(I)=I
112     CONTINUE
        DO 13 I=1,NNOTEQ
        IF(KON(I))13,13,14
14      NLIN=NLIN+1
        NLINLD(NLIN)=I+NLINEQ
13      CONTINUE
        IF(NLIN)50,50,3
3       CONTINUE
        GO TO (21,21,4),IFLAG
4       CONTINUE
C       4 IS TOP OF LOOP FOR ADJUSTMENT OF PARTIALS, VECTOR DIRECTION.
C       ADJUSTMENT OF VECTOR DIRECTION ONLY. (IFLAG=3)
C
C       IF PARTIAL OF I VARIABLE IS ZERO THEN PARTIAL OF ALL CONSTRAINTS
C       WITH RESPECT TO THE I-TH VARIABLE ARE SET TO ZERO.
C
        DO 10 I=1,N
        IF(KNT(I))5,10,5
5       DO 6 J=1,NLIN
        JT= NLINLD(J)
6       FPC(I,JT) =0.0D0
10      CONTINUE
C
C       COMPUTES THE VECTOR OF CONSTANTS.
C
        DO 400 J=1,NLIN
        BSUM(J)=0.0D0
        DO 400 I=1,N
        JT=NLINLD(J)
400     BSUM(J)=BSUM(J)+(FPC(I,JT)*FP(I))
        DO 399 I=1,NLIN
399     BSUM(I)=-BSUM(I)
        GO TO 385
C       ADJUSTMENT OF VARIABLES ONLY (IFLAG=1,2).
21      IF(NLINEQ)125,123,125
123     DO 124 I=1,NNOTEQ
        IF(BSUMNT(I))125,124,124
124     CONTINUE
        GO TO (125,50,50),IFLAG
125     IF(ITER-4)20,28,20
20      CONTINUE
C
C       PUT VARIABLES ON THE BOUNDRIES IF OUT, SETS THOSE PARTIALS=0
C
        DO 29 I=1,N
        IF(X(I)-XH(I))24,23,23
23      X(I)=XH(I)
        GO TO 26
24      IF(XL(I)-X(I))29,25,25
25      X(I)=XL(I)
26      DO 27 J=1,NLIN
        JT=NLINLD(J)
27      FPC(I,JT)=0.0D0
```

```
29      CONTINUE
28      CONTINUE
        ITER=ITER+1
C       QUIT IF NO CONVERGENCE IN 10 PASSES, SET COST LARGE.
        IF(ITER-10)330,330,384
384     FL=101000.0D0
        IF(LIST6.EQ.0) WRITE(6,410) ITER
410     FORMAT('0','DID NOT CONVERGE AFTER',I4,'ITERATIONS IN LINCON'     )
        LINES=LINES+2
        GO TO 50
330     CONTINUE
        IF(NLIN-NLINEQ)333,333,331
331     ITEMP=NLINEQ+1
        DO 332 I=ITEMP ,NLIN
        K=NLINLD(I)-NLINEQ
332     BSUM(I)=-BSUMNT(K)
333     CONTINUE
C       THIS VERSION OF PROGRAM USES ONLY TWO CONSTRAINTS.
C       MUST BE WITHIN TOLERANCE BAND OF CONSTRAINT.
        IF(BSUMNT(1)+1.0D-10)385,501,501
501     IF(BSUMNT(2)+0.02D0)385,502,502
502     IF(BSUMNT(3)+1.0D-4)385,503,503
503     CONTINUE
        GO TO (385,50,50),IFLAG
385     CONTINUE
C       ADJUSTMENT OF EITHER VARIABLES OR VECTOR DIRECTION.
C
C       COMPUTES THE A MATRIX.
C
        DO 401 J=1,NLIN
        DO 401 L=1,NLIN
        AX(J,L)=0.0D0
        DO 401 I=1,N
        JT=NLINLD(J)
        LT=NLINLD(L)
401     AX(J,L)=AX(J,L)+(FPC(I,LT)*FPC(I,JT))
C
C       IF A(I,I) IS ZERO THEN THE I-TH COLUMN AND ROW ARE ZERO,
C       SET A(I,I)=1
C
        DO 390 I=1,NLIN
        IF(AX(I,I))390,389,390
389     AX(I,I)=1.0D0
390     CONTINUE
C       CALL AMATQ4, LINEAR SIMULTANEOUS EQUATION SOLVING ROUTINE, IF
C       NLIN GT 1.
        IF(NLIN.LE.1) BSUM(1)=BSUM(1)/AX(1,1)
        IF(NLIN.GT.1) CALL AMATQ4(AX,BSUM,NLIN,1,10)
C
C       THE SOLUTION VECTOR IS IN BSUM(I)
C
        GO TO (30,30,395),IFLAG
C       ADJUSTMENT OF VARIABLES ONLY (IFLAG=1,2).
C       ADJUST THE X(I) TO SATISFY CONSTRAINTS.
30      DO 35 I=1,N
        DO 35 J=1,NLIN
        JT=NLINLD(J)
CC 35   X(I)=X(I)+BSUM(J)*FPC(I,JT)
35      X(I)=X(I)+BSUM(J)*FPC(I,JT)*R(I)
```

```
      IFLAG=2
      DO 36 I=1,N
      X(I)=DMAX1(XL(I),X(I))
36    X(I)=DMIN1(XH(I),X(I))
      GO TO 2
C     TRANSFER TO TOP OF VARIABLE ADJUSTMENT LOOP, 2.
395   CONTINUE
C     ADJUSTMENT OF VECTOR DIRECTION ONLY (IFLAG=3).
C
C     THIS AREA CHECKS PARTIALS GOING OUT OF BOUNDS AND SETS=0. HOLDS
C     LARGEST ON BOUNDS.
C
      FPMAX=0.0D0
      ISET=0
      DO 404 I=1,N
      DO 405 J=1,NLIN
      JT=NLINLD(J)
      FP(I)=FP(I)+BSUM(J)*FPC(I,JT)
405   CONTINUE
      IF(FP(I)*CMM)41,404,45
41    IF(X(I)-XL(I))49,49,404
45    IF(XH(I)-X(I)-1.0D-9)49,49,404
49    IF(DABS(FP(I))-FPMAX)48,48,46
46    FPMAX=DABS(FP(I))
      ISET=I
48    FP(I)=0.0D0
404   CONTINUE
      IF(LIST1.EQ.0) WRITE(6,100) (FP(I),I=1,N)
100   FORMAT(17HCPART. IN LINCON      ,7E15.8/7E15.8/7E15.8)
      IF(ISET)50,50,47
47    KNT(ISET)=KNT(ISET)+1
      GO TO 4
C     TRANSFER TO TOP OF VECTOR DIRECTION ADJUSTMENT LOOP, 4.
C
50    RETURN
      END
```

```
C
      SUBROUTINE AMATQ4(A,B,III,JJJ,ID)
C
C     LINEAR SIMULTANEOUS EQN SOLVING ROUTINE.
C     CALLED BY LINCON.  REAL*8 PRECISION.
C     DETERMINANT D REMOVED, CHANGED TO SUBROUTINE. RMK 5/68.
C     AUTHORS R.G. EDWARDS AND R.E. FUNDERLIC.
C     COMPUTING TECHNOLOGY CENTER, K-25
C     OAK RIDGE, TENNESSEE.
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(ID,1),B(IC,1)
C
      KK=III
      NV=IABS(JJJ)
      KKM=KK-1
      DO 20 I=1,KKM
      S=0.0D0
      DO 2 J=I,KK
      R=DABS(A(J,I))
      IF(R-S)2,1,1
1     S=R
      L=J
2     CONTINUE
      IF(L-I)3,8,3
3     DO 4 J=I,KK
      S=A(I,J)
      A(I,J)=A(L,J)
4     A(L,J)=S
      IF(NV)8,8,5
5     DO 6 J=1,NV
      S=B(I,J)
      B(I,J)=B(L,J)
6     B(L,J)=S
8     IF(A(I,I))9,20,9
9     IPO=I+1
      DO 14 J=IPO,KK
      IF(A(J,I))10,14,10
10    S=A(J,I)/A(I,I)
      A(J,I)=0.0D0
      DO 11 K=IPO,KK
11    A(J,K)=A(J,K)-A(I,K)*S
      IF(NV)14,14,12
12    DO 13 K=1,NV
13    B(J,K)=B(J,K)-B(I,K)*S
14    CONTINUE
20    CONTINUE
      IF(NV)19,19,16
16    KMO=KK-1
      DO 18 K=1,NV
      B(KK,K)=B(KK,K)/A(KK,KK)
      DO 18 I=1,KMO
      N=KK-I
      DO 17 J=N,KMO
17    B(N,K)=B(N,K)-A(N,J+1)*B(J+1,K)
18    B(N,K)=B(N,K)/A(N,N)
19    RETURN
      END
```

```
C
      SUBROUTINE EVAL(X,F,ICU,IBJ,XPM,REM,PRM)
C
C     SUBROUTINE EVAL CALLED FROM MAIN PROGRAM OPT OR LINCON.
C     SET VARIABLES. CALL SECTION WHICH CALLS ECON TO GET COST.
C
      IMPLICIT REAL*8(A-H,O-Z)
C     NAME OF COMMON TELLS WHICH ROUTINES USE IT...O=OPT,L=LINCON,E=EVAL
C     B=BANK,C=COST
      COMMON / COMEBC / PIN,VIN,CR,DIA,COST,REMIN,XPMAX,PMIN,NFLAG,IOUT
      DIMENSION X(20)
C
      XPMAX= 0.0D0
      REMIN= 1.0D6
      PMIN= 1.0D6
CC    XPE= 0.0D0
      IOUT= IOU
      PIN= X(1)
      VIN= X(2)
      CR= X(3)
      DIA= X(4)
C
      CALL BANK
C
      F= COST
      IBJ= NFLAG
      XPM= XPMAX
      REM=REMIN
      PRM= PMIN
CC    XPE= XPCUM
      RETURN
      END
```

```
C
      SUBROUTINE BANK
C
C     SUBROUTINE BANK CALCULATES CONCENTRATION,PRESSURE, AND VELOCITY
C     VARIATION FROM MODULE TO MODULE IN A MODULE BANK. THE SUBROUTINE
C     ALSO DETERMINES THE NUMBER AND ARRANGEMENT OF MODULES BASED ON
C     GIVEN INLET VARIABLES. IN ADDITION, THE SUBROUTINE CALLS ECON FOR
C     A COST ESTIMATE.
C
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER STGNUM,BNKNUM,CNTR
      REAL*8 LOBETA,LOEX,LOREX,LOSBFN,LOFN,MDAREA,MUF,OSMOT,MTK,LAMDA,
     1 LOG10T,LOGT2,MUEAR
      DIMENSION APIN(50),AVIN(50),AXFIN(50),AXPBAR(50),AXWBAR(50),
     1 AREBAR(50),ARHOBR(50),AMUBAR(50),AFLXBR(50),AREJN(50),AXPCUM(50),
     2 APBAR(50),AXPAVE(2,10),ASMFLX(2,10),AXPSAV(2),AVLSAV(2),
     3 XPBLND(2),BLNDRT(2),XBA(20)
C     NAME OF COMMON TELLS WHICH ROUTINES USE IT...O=OPT, L=LINCON,
C     E=EVAL, B=BANK, C=COST
C
      COMMON / COMOB /TEMP,CRA,RP,RV,RXF,RXP,RFLX,RPWFLX,RA,RSPC,ZETA,
     1 SIGMA,PHI
      COMMON / CMCLBC /STEP,XFLIM,RELIM,PRLIM,VLIM,LIST1,LIST6,LINES
      COMMON / CCMEBC /PONE,VONE,CR,DIA,CCST,REMIN,XPMAX,PMIN,NFLAG,IOUT
      COMMON / CCMBC /PI,SUMFLX,SALT,ARHOBR,DIFXP,DIFRE,DIFPR,CNTR
      COMMON / CMOBCN /FEEDIN,XFONE,XFORIG,FDORIG,XFDIS,FDOUT,VOUT,POUT,
     1XFOUT,VLAST,PLAST,XPRMIT,CA,CE,EP,ET,AXPAVE,ASMFLX,STGNUM,BNKNUM,
     2NBANKS
C
      EQUIVALENCE (TEMP,T)
C
C     STATEMENT FUNCTIONS FOR PROPERTIES OF SALT SOLUTIONS.
C     CONVERT MOLE FRACTION TO WEIGHT FRACTION.
      WTFRAC(Y)=(Y/(1.0D0-Y))/((Y/(1.0D0-Y))+0.3083614D0)
C     KELLOGG DENSITY FIT (LB/CUFT). Z=WT. FRACTION.
      RHOF(Z)=(C1*Z+B1)*Z+A1
C     KELLOGG VISCOSITY FIT (LB/FT SEC) Z= WT. FRACTION.
      MUF(Z)=((C2*Z+B2)*Z+A2)
C     OSMOTIC PRESSURE (ATMOS.) FOR LOW SALT CONCENTRATION.
      OSMOT(Z)= CTAB*CMWF*Z/(1.0D0-Z)
C     SCHMIDT NUMBER**0.667
      SC667(Z)= DEXP(AA+BB*Z)
C
C     ******************************************************************
C     INITIALIZATION FOR LOOP 1 (MODULE COUNTER LOOP) AND LOOPS WITHIN
C     LOOP 1. SET CONDITIONS FOR UPSTREAM END OF FIRST MODULE (=MODULE
C     INLET).
C     ******************************************************************
C     SET ERROR FLAG.
      NFLAG=1
      IF(CR .LE. 1.0D0) GO TO 8000
C     STORE FEED VARIABLES.
      XFIN= XFONE
      PIN=PONE
      VIN=VONE
      AXFIN(1)=XFIN
      APIN(1)=PIN
      AVIN(1)=VIN
      DIAFT=DIA/12.0D0
```

```
C       AX= TUBE CROSS-SECTIONAL AREA. (FT**2)
        AX= PI*DIAFT**2/4.0D0
        MDAREA=9.5D0
        IF(IOUT .EQ. 0) GO TO 8
C
C       ****************************************************************
C       PRINT HEADING FOR FINAL OPTIMUM CONDITIONS AND SOME INPUT CONDIT-
C       IONS. DONE ONLY IF FLAG IOUT=1.
C       ****************************************************************
        WRITE(6,1)
1       FORMAT(72H1HYPERFILTRATION DESIGN OPTIMIZATION    TUBULAR CHANNEL-
       1 TURBULENT FLOW     / 16HINPUT VARIABLES  )
        WRITE(6,2) PONE,VONE,XFONE,CR,XPLIM,RELIM,DIA,FEEDIN
2       FORMAT(45H0INLET PRESSURE. PONE (ATM)                    ,F15.4,
       1     48H     INLET VELOCITY. VONE (FT/SEC)               ,F15.4/
       2        45H FEED CONCENTRATION. XFONE (MOLE FRACTION)    ,F15.6,
       3     48H     CONCENTRATION RATIO                         ,F15.4/
       4        45H MAX SALT CONC OF PROD. XPLIM (MOLE FRACTION) ,F15.6,
       5     48H     MINIMUM REYNOLDS NUMBER ALLOWED. RELIM      ,F15.0/
       6        45H INSIDE TUBE DIAMETER. DIA (INCHES)           ,F15.4,
       7     48H     FEED RATE TO PLANT. FEEDIN (GPD)            ,1PE15.6)
        WRITE(6,3) CA,EP,CE
3       FORMAT(45H UNIT AREA COST (CENTS/SQFT*DAY)               ,F15.3,
       1     48H     PUMP EFFICIENCY. EP                         ,F15.3/
       2        45H ELEC POWER UNIT COST. CE (CENTS/KWH)         ,F15.3)
        WRITE(6,4)
4       FORMAT(1H0,'MOD.NO.',5X,'PRES',8X,'XFIN',11X,'XWBAR',9X,'XPBAR',
       1 8X,'REBAR',4X,'RHOBAR',5X,'MUBAR',6X,'FLXBAR',4X,'REJN'/1H )
C
C       SET MODULE COUNTER. COUNTS NO. OF MODULES IN SERIES PER BANK.
C
8       CNTR=0
C       INITIALIZE VARIABLES WHICH SUM THE WATER AND SALT PASSING THROUGH
C       EACH MODULE.
        SUMFLX=0.0D0
        SALT=0.0D0
C
C       AS A FIRST APPROXIMATION...PBAR=PIN,VBAR=VIN,XFBAR=XFIN.
C
C       ****************************************************************
C       800 CONTINUE IS A RETURN POINT FOR THE LOOP WHICH ADDS MODULES.
C       ****************************************************************
800     CONTINUE
        CNTR=CNTR+1
        IF(CNTR .GE. 50) WRITE(6,810) CNTR
810     FORMAT('0',' ELEMENTS IN ARRAYS=',I4,'.  EXCEEDS DIMENSION.')
        PBAR=PIN
        VBAR=VIN
        XFBAR=XFIN
C
C       SET AVERAGES COUNTER.
        NAVE=0
C
C       INITIALIZE VARIABLES USED IN CONVERGENCE TEST.
        FLXOLD=0.0D0
        XPOLD=0.0D0
C
C       ****************************************************************
C       1000 CONTINUE IS A RETURN POINT FOR THE LOOP WHICH SEEKS AVERAGE
```

```
C       OPERATING CONDITIONS FOR A MODULE.
C       ******************************************************************
1000    CONTINUE
        NAVE=NAVE+1
        IF(NAVE .GT.50) GO TO 8100
        ARG=WTFRAC(XFBAR)
        RHOBAR= RHOF(ARG)
        MUBAR= MUF(ARG)
        ARG3= SC667(ARG)
        REBAR=DIAFT*VBAR*RHOF(ARG)/MUF(ARG)
        MTK=0.023D0*MUF(ARG)*REBAR**0.80/(RHOF(ARG)*SC667(ARG)*DIAFT)
        IF(LIST1 .EQ. 0) WRITE(6,50) RHOBAR,MUBAR,ARG3,MTK
50      FORMAT(1H0,4D9.3)
C
C       CORRECT PURE WATER PERMEABILITY COEFFICIENT FROM REFERENCE VALUE.
        A=RA/DEXP(ZETA*(PBAR-RP))
        IF(DABS(RXF-XFBAR).LE.1.0E-4) GO TO 60
C
C       CORRECT SOLUTE PERMEABILITY COEFFICIENT FROM VALUE AT REFERENCE
C       CONCENTRATION.
        SPC= SIGMA*(XFBAR-RXF)+RSPC
60      IF(DABS(PBAR-RP).LE.1.0D-2) GO TO 70
C
C       CORRECT SOLUTE PERMEABILITY COEFFICIENT AT REFERENCE PRESSURE.
        CONST= DLOG(RSPC)
        POWER = PHI*DLOG(PBAR/RP)+CONST
        SPC= DEXP(POWER)
C
C       INITIALIZE THE EXPECTED RANGE OF BETA = XW/XP.
70      LOBETA= 1.0D0
        HIBETA= 100.0D0
C
C       KNTR COUNTS THE NUMBER OF ITERATIONS ON THE MATHEMATICAL MODEL
C       BEFORE CONVERGENCE IS OBTAINED.
        KNTR= 1
        IF(LIST1 .EQ. 0) WRITE(6,71) SPC
71      FORMAT(1H0,D9.3)
        LAMDA= MTK/SPC
        GAMMA= (A*82.05D0*(TEMP+273.16D0)*2.0D0*0.932D0)/18.01534D0
        LOEX= DEXP((LOBETA-1.0D0)/LAMDA)
        HIEX= DEXP((HIBETA-1.0D0)/LAMDA)
        LOREX= 1.0D0/LOEX
        HIREX= 1.0D0/HIEX
        LOSBFN= ((LOBETA-1.0D0)*LOREX+1.0D0-LOBETA*XFBAR)
        HISBFN= ((HIBETA-1.0D0)*HIREX+1.0D0-HIBETA*XFBAR)
        LOFN= A*PBAR+GAMMA*((1.0D0-LOBETA)*XFBAR/LOSBFN)-646315.2D0*SPC*
       1 (LOBETA-1.0D0)
        HIFN= A*PBAR+GAMMA*((1.0D0-HIBETA)*XFBAR/HISBFN)-646315.2D0*SPC*
       1 (HIBETA-1.0D0)
100     BETA= (HIBETA+LOBETA)/2.0D0
        KNTR= KNTR+1
        IF(KNTR .GT. 50) GO TO 8200
        EX= DEXP((BETA-1.0D0)/LAMDA)
        REX= 1.0D0/EX
        SBFN= ((BETA-1.0D0)*REX+1.0D0-BETA*XFBAR)
        FN= A*PBAR+GAMMA*((1.0D0-BETA)*XFBAR/SBFN)-646315.2D0*SPC*(BETA-
       1 1.0D0)
C
C       TEST FOR ABNORMAL SHAPE OF FUNCTION.
```

```
      IF(LOFN .LT. 0.0D0 .OR. HIFN .GT. 0.0D0) GO TO 8300
C     BEGIN CHOPPING THE RANGE.
      IF(FN)140,160,150
140   HIBETA= BETA
      HIFN= FN
      IF((HIBETA-LOBETA).LE.1.0D-3) GO TO 160
      GO TO 100
150   LOBETA= BETA
      LOFN= FN
      IF((HIBETA-LOBETA).LE.1.0D-3) GO TO 160
      GO TO 100
C
C
C     COMPUTE PREDICTED FLUX (GFD) AND PERMEATE MOLE FRACTION.
160   XPBAR= XFBAR/((BETA-1.0D0)*REX+1.0D0)
      XWBAR= BETA*XPBAR
      FLXBAR= 646315.2D0*SPC*(1.0D0-XPBAR)/XPBAR*(XWBAR-XPBAR)
      IF(DABS(FLXBAR-FLXOLD).LE.0.1D0 .AND. DABS(XPBAR-XPOLD).LE.3.0D-6)
     1 GO TO 2000
C     USE MASS BALANCES TO DETERMINE MODULE OUTLET CONDITIONS...VOUT.
C     POUT,XFOUT
C
      POUT= PIN-0.27218D0*((VBAR/0.81705D0)**2)
      IF(POUT .LE. 20.414D0 .AND. CNTR .EQ. 1) GO TO 8500
      IF(POUT .LE. 20.414D0) GO TO 1300
      VOUT= VIN-0.0107798D0*FLXBAR
      XFOUT= (XFIN*VIN-0.0107798D0*XPBAR*FLXBAR)/VOUT
C
C     COMPUTE NEW VALUES OF XFBAR,PBAR,VBAR.
C
      VBAR= (VIN+VOUT)/2.0D0
      XFBAR= (XFOUT+XFIN)/2.0D0
      PBAR= (PIN+POUT)/2.0D0
      IF(LIST1 .EQ. 0)WRITE(6,161) FLXBAR,XPBAR,XWBAR,VOUT,VIN,POUT,PIN,
     1 PBAR
161   FORMAT(1H0,8D9.3)
C
C     STORE OLD VALUES OF FLUX AND PERMEATE MOLE FRACTION TO USE IN
C     CONVERGENCE TEST.
C
      FLXOLD= FLXBAR
      XPOLD= XPBAR
C     GO BACK TO 1000 AND TRY AGAIN.
      GO TO 1000
2000  GPD= FLXBAR*MDAREA
      SUMFLX= SUMFLX+GPD
      REJN= (XFBAR-XPBAR)/XFBAR
      SALT= SALT+GPD*XPBAR
      XPCUM= SALT/SUMFLX
C
C     ******************************************************************
C     STORE INLET VELOCITY,PRESSURE,FEED MOLE FRACTION,,AVERAGE WALL
C     MOLE FRACTION,PERMEATE MOLE FRACTION,REYNOLDS NO.,DENSITY,AND
C     VISCOSITY FOR EACH MODULE. FOR EACH CALL TO SUBROUTINE BANK.
C     PRINT ONLY IF OPTIMUM VALUES HAVE BEEN FOUND.
C     ******************************************************************
      AVIN(CNTR)= VIN
      APBAR(CNTR)= PBAR
      APIN(CNTR)= PIN
```

```
      AXFIN(CNTR)= XFIN
      AXWBAR(CNTR)= XWBAR
      AXPBAR(CNTR)=XPBAR
      AREBAR(CNTR)= REBAR
      ARHOBR(CNTR)= RHOBAR
      AMUBAR(CNTR)= MUBAR
      AFLXBR(CNTR)= FLXBAR
      AREJN(CNTR)= REJN
      AXPCUM(CNTR)= XPCUM
      APIN(CNTR+1)= POUT
      AVIN(CNTR+1)= VOUT
      AXFIN(CNTR+1)= XFOUT
C     SAVE THE LOWEST REYNOLD'S NO. AND LARGEST PRODUCT SALT CONCENTRATION
C     FOR ANY MODULE TO USE IN INEQUALITY CONSTRAINTS.
      REMIN= DMIN1(REMIN,REBAR)
      XPMAX= DMAX1(XPMAX,XPCUM)
      PMIN= DMIN1(PMIN,PBAR)
      IF(LIST1 .EQ. 0) WRITE(6,168) XFONE,XFOUT,POUT,VOUT,LIST6
168   FORMAT(1H0,' CHECK POINT 3',4D12.6,I4)
      IF(XFOUT/XFORIG .GE. CR) GO TO 1200
      IF(VOUT .LE. VLIM) GO TO 1200
C
C     INITIALIZATION OF VARIABLES TO BEGIN A NEW MODULE.
      VIN= VOUT
      PIN= POUT
      XFIN= XFOUT
C
170   IF(IOUT .EQ. 0) GO TO 180
      WRITE(6,6003) CNTR,APIN(CNTR),AXFIN(CNTR),AXWBAR(CNTR),
     1 AXPBAR(CNTR),AREBAR(CNTR),ARHOBR(CNTR),AMUBAR(CNTR),AFLXBR(CNTR),
     2 AREJN(CNTR)
6003  FORMAT(1H ,I4,5X,F9.3,2X,D12.6,2X,D12.6,2X,D12.6,F9.0,F9.2,2X,
     1 D12.6,F9.3,F9.4)
C
C     CHECK FOR SOLUBILITY AT WALL.
180   IF(XWBAR .GT. SOLIM) GO TO 8400
C
190   GO TO 800
C
C     ******************************************************************
C     END OF LOOP WHICH ADDS MODULES TO SECTION. SECTION HAS BEEN
C     COMPLETED WITH NO. OF MODULES IN SERIES = CNTR.
C     ******************************************************************
C
C     NOW STORE AVERAGE OPERATING CONDITIONS FOR LAST MODULE AT THE
C     BANK OUTLET.
1200  CNTR= CNTR+1
 1300 APBAR(CNTR)= APBAR(CNTR-1)
      AXWBAR(CNTR)= AXWBAR(CNTR-1)
      AXPBAR(CNTR)= AXPBAR(CNTR-1)
      AREBAR(CNTR)= AREBAR(CNTR-1)
      ARHOBR(CNTR)= ARHOBR(CNTR-1)
      AMUBAR(CNTR)= AMUBAR(CNTR-1)
      DIFPR= PMIN-PRLIM
      DIFXP= XPLIM-XPMAX
      DIFRE= REMIN-RELIM
CC    DIFCPE= XFEED-XPCUM
C     CHECK TO SEE IF MATERIAL BALANCE OVER SECTION CLOSES.
C     FIRST CALCULATE AVERAGE PERMEATE MOLE FRACTION FOR SERIES OF
```

```
C       MODULES IN SECTION.
        CNTR= CNTR-1
        XPAVE= SALT/SUMFLX
C       WATER BALANCE
        H2OIN= AX*VCNE
        H2OOUT= AX*VOUT+SUMFLX/646315.2D0
C
C       SALT BALANCE.
        SLTIN= AX*VCNE*XFCNE
        SLTOUT= AX*VOUT*XFOUT+(SUMFLX/646315.2D0)*XPAVE
        IF(DABS(SLTIN-SLTOUT) .LT. 1.0D-4 .OR. DABS(H2OIN-H2OOUT) .LT.
       1 0.01D0) GO TO 209
        WRITE(6,6006)
6006    FORMAT(1H0,'**MATERIAL BALANCE NOT SATISIFIED**')
        LINES= LINES+2
209     IF(IOUT .EQ. 0) GO TO 211
        WRITE(6,6003) CNTR,APIN(CNTR),AXFIN(CNTR),AXWBAR(CNTR),
       1 AXPBAR(CNTR),AREBAR(CNTR),ARHOBR(CNTR),AMUBAR(CNTR),
       2 AFLXBR(CNTR),AREJN(CNTR)
C
C       CALL ECON TO GET TOTAL COST AND LIST.
211     CALL ECON
C
        RETURN
C
C       ******************************************************************
C       SECTION TO HANDLE ERRORS. PROGRAM NOT TERMINATED...LINCON HANDLES
C       SITUATION.
C       ******************************************************************
8400    NFLAG= 6
        IF(LIST6 .EQ. 0) WRITE(6,6009)
6009    FORMAT('0SOLUBILITY LIMIT EXCEEDED.')
        LINES= LINES+2
        COST= 1.0D5*CR
        GO TO 925
C
8000    IF(LIST6 .EQ. 0) WRITE(6,1900)
1900    FORMAT('0 CR .LE. 1.0')
        NFLAG= 2
        GO TO 920
C
8100    IF(LIST6 .EQ. 0) WRITE(6,1901)
1901    FORMAT('0 NUMBER OF AVERAGES EXCEEDS 50.')
        NFLAG= 3
        GO TO 920
C
8200    IF(LIST6 .EQ. 0) WRITE(6,1902)
1902    FORMAT('0 NUMBER OF MODEL ITERATIONS EXCEEDS 50.')
        NFLAG= 4
        GO TO 920
C
8300    IF(LIST6 .EQ. 0) WRITE(6,1903)
1903    FORMAT('0 ABNORMAL SHAPE OF FUNCTION.')
        NFLAG= 5
        GO TO 920
C
8500    IF(LIST6 .EQ. 0) WRITE(6,1904)
1904    FORMAT('0 PRESSURE LESS THAN SPECIFIED LOWER LIMIT.')
        NFLAG= 7
```

```
      GO TO 920
CC    IF(LIST6 .EQ. 0) WRITE(6,1905)
1905  FORMAT('0 VELOCITY LESS THAN SPECIFIED LOWER LIMIT.')
CC    NFLAG= 8
C
920   IF(NFLAG .EQ. 1) NFLAG=2
      LINES= LINES+2
C     IN CASE OF ERROR SET COST = LARGE NO. FOR OPTIMUM ROUTINE.
C
      COST= 1.01D5
925   RETURN
C
C     ******************************************************************
C     ENTRY SETUP-SEPARATE SECTION CALLED ONLY BY MAIN PROGRAM OPT TO
C     INITIALIZE VARIABLES USED BY MODULE BEFORE EACH CASE.
C     ******************************************************************
C
      ENTRY SETUP
C     ZERO ALL SUBSCRIPTED VARIABLE STORAGE ARRAYS. MAX. 20 MODULES.
C
      DO 35 I=1,20
      AXFIN(I)= 0.0D0
      APIN(I)= 0.0D0
      AVIN(I)= 0.0D0
      AXWBAR(I)= 0.0D0
      AXPBAR(I)= 0.0D0
      AREBAR(I)=0.0D0
      ARHOBR(I)= 0.0D0
      AMUBAR(I)= 0.0D0
      AFLXBR(I)= 0.0D0
      APBAR(I)= 0.0D0
35    AREJN(I)= 0.0D0
      DO 36 I=1,2
      AXPSAV(I) = 0.0D0
      AVLSAV(I) = 0.0D0
      XPBLND(I) = 0.0D0
36    BLNDRT(I) = 0.0D0
C
      PI= 3.1415926535897 9D0
      GC= 32.2D0
C     SALT SOLUBILITY LIMIT AT MEMBRANE (MOLE FRACTION).
      SOLIM= 0.097752D0
C     T IS EQUIVILENT TO TEMP.
      T2=T*T
      LOG10T=DLOG10(T)
      LOGT2=LOG10T**2
C
C     TEMP DEPENDENT COEFFICIENTS FOR FIT OF SCHMIDT NO.**0.667, SC667.
      AA=5.63738D0-2.0455 09D-2*T+0.29927225D-4*T2
      BB=0.8673596D0-0.7184158D-3*T+0.8589322D-5*T2
C
C     SET TEMP DEPENDENT COEFF'S FOR KELLOGG DENSITY FIT, RHOF.
      A1=62.717753D0-0.32152986D-2*T-0.48932777D-4*T2
      B1=44.3150006D0-0.11647394D-1*T + 0.34231326D-5*T2
      C1=16.449945D0 + 0.13761984D-1*T - 0.92275301D-4*T2
      TWCC1=2.0D0*C1
C     DEN77 IS RHOF DENSITY FIT FOR H2O AT 77 F AND ZERO NACL CONC.
C     FOR USE IN CTAB, BETAF.
      DEN77=62.1800527D0
```

```
C
C       CTAB (ATM G SOLVENT/GMOLE NACL) FOR USE IN BETAF, OSMOTIC
C       PRESSURE FIT FOR LOW NACL CONC. 2*24.4 AT 77 F, H20.
        CTAB=48.8D0*(TEMP+460.0D0)/537.0D0*RHOF(0.0D0)/DEN77
C
C       TEMPERATURE DEPENDENT COEFFICIENTS FOR KELLOGG VISCOSITY FIT
C       MUF.
        A2=( 22.216306D0- 16.460588D0*LOG10T+ 3.0949585D0*LOGT2)/3600.0D0
        B2=(-14.161033D0+ 16.430566D0*LOG10T- 4.205263 D0*LOGT2)/3600.0D0
        C2=(284.84684 D0-219.40291 D0*LOG10T+42.287729 D0*LOGT2)/3600.0D0
C
C       UNUSED COEFFICIENTS FOR OSMOTIC PRESSURE FIT, BETAF, FOR SEA WATER
CC      A0=0.602699E+3+0.135850E+1*T-0.145757E-2*T2
CC      B0=0.272902E+3+0.714610E+1*T-0.196794E-1*T2
CC      C0=0.186395E+4+0.319417E+2*T-0.460908E-1*T2
CC      D0=0.176486E+5-0.133310E+3*T+0.249592E+0*T2
C       UNUSED ARITHMETIC STATMENT FUNCTION FOR SEA WATER FOR BETAF,DBETA.
CC      BETAF(Z)=(((D0*Z+C0)*ZB0)*Z+A0)*Z
CC      DBETA(Z)=(((W4*Z+W3)*Z+W2)*Z+W1)
C
        RETURN
C
C       ****************************************************************
C       ENTRY ADJUST ADJUSTS PRESSURE,VELOCITY TO ACCEPTABLE STARTING
C       VALUES.
C       ****************************************************************
C
        ENTRY ADJUST(XBA)
C
        NN = CNTR
C       CHECK PRESSURE AND ALLOW NO VIOLATIONS.
        DO 660 I=1,NN
        M= NN-I+1
        IF(APBAR(M) .GE. PRLIM) GO TO 680
660     CONTINUE
        IGOOD = 1
        GO TO 700
680     IGOOD= M
C       ADJUST STARTING PRESSURE.
700     XBA(1) = (DFLOAT(CNTR)/DFLOAT(IGOOD))*XBA(1)
        IF(XBA(1) .LT. 2.0D0*PRLIM) XBA(1) = 4.0D0*PRLIM
        WRITE(6,701) IGOOD,XBA(1)
701     FORMAT('0','NO. OF GOOD MODULES = ',I4,2X,'PRESSURE HAS BEEN CHANG
       1ED TO = ',D12.6)
C       CHECK REYNOLD'S NO. AND ALLOW NO VIOLATIONS#
        DO 620 I=1,NN
        L= NN-I+1
        IF(AREBAR(L) .GE. RELIM) GO TO 640
620     CONTINUE
        IGOOD = 1
        GO TO 793
640     IGOOD= L
C       ADJUST STARTING VELOCITY.
793     XBA(2) = (DFLOAT(CNTR)/DFLOAT(IGOOD))*XBA(2)
        IF(XBA(2) .LT. 4.0D0*VLIM) XBA(2) = 10.0D0*VLIM
        WRITE(6,801) IGOOD,XBA(2)
801     FORMAT('0','NO. OF GOOD MODULES = ',I4,2X,'VELOCITY HAS BEEN CHANG
       1ED TO = ',D12.6)
        LINES= LINES+32
```

```
      RETURN
C
C     ******************************************************************
C     ENTRY ACCUM- ACCUMULATES PRODUCT WATER MEETING SPECIFICATION.
C     ******************************************************************
C
      ENTRY ACCUM
      J = STGNUM
      IF(J .EQ. 2) GO TO 400
      VOLSAV = 0.0D0
      XPSAV = 0.0D0
      NACCUM = 1
C
400   DO 500 I=1,BNKNUM
      NBLEND = NACCUM+1
      AXPSAV(J) = XPBLND(J)
      AVLSAV(J) = BLNDRT(J)
      XPBLND(J) = (XPBLND(J)*BLNDRT(J)+AXPAVE(J,I)*ASMFLX(J,I))/
     1 (BLNDRT(J)+ASMFLX(J,I))
      BLNDRT(J) = BLNDRT(J)+ASMFLX(J,I)
      IF(XPBLND(J) .GT. XPRMIT) GO TO 101
      NACCUM = NACCUM+I
500   CONTINUE
101   XPSAV = XPSAV+AXPSAV(J)
      VOLSAV = VOLSAV+AVLSAV(J)
      GO TO (11,12),J
11    FEEDIN = ASMFLX(J,I)
      WRITE(6,1483) J,I,ASMFLX(J,I)
1483  FORMAT('0',I4,I4,D12.6)
      XFONE = AXPAVE(J,I)
      RCYLRT = 0.0D0
      RCYLXF = 0.0D0
      GO TO 13
12    RCYLRT = FDOUT
      RCYLXF = XFOUT
      FEEDIN = 0.0D0
      XFONE = 0.0D0
13    FDONE = FDORIG-RCYLRT
C     WRITE RESULTS FOUND IN -ENTRY ACCUM-FOR EACH STAGE.
      WRITE(6,14)STGNUM,XPSAV,VOLSAV,FEEDIN,XFONE,RCYLRT,RCYLXF,FDONE
14    FORMAT('0 RESULTS FOUND IN -ENTRY ACCUM-FOR STAGE NO.',I4/
     151H CUMULATIVE MOLE FRACTION OF PERMEATE MEETING SPEC.,E14.7/
     151H CUMULATIVE GAL/DAY OF PERMEATE MEETING SPEC.       ,D12.6/
     151H FEEDRATE GAL/DAY OF FIRST STG PROD. TO SECOND STG ,D12.6/
     151H MOLE FRACTION OF FIRST STG PROD. TO SECOND STG.   ,E14.7/
     151H RECYCLED FEED FROM SECOND STG TO FIRST STG INLET  ,D12.6/
     151H RECYCLED MOLE FRAC FROM SECOND STG TO FIRST STG   ,E14.7/
     151H FEEDRATE PUMPED TO PLANT                          ,D12.6)
      RETURN
C
C     ******************************************************************
C     ENTRY BLEND-INJECTS PERMEATE FROM FIRST STAGE INTO APPROPRIATE
C     LOCATIONS IN SECOND STAGE.
C
      ENTRY BLEND
20    CONTINUE
      I = NBLEND
      IF(I .GT. NBANKS) GO TO 40
      IF(AXPAVE(1,I) .LT. XFOUT) GO TO 25
```

```
      GO TO 40
25    WRITE(6,23) NBLEND,I,AXPAVE(1,I),ASMFLX(1,I),XFONE,FEEDIN
23    FORMAT('0',I4,I4,2X,D12.6,2X,D12.6,2X,D12.6,2X,D12.6)
      XFONE =(XFONE*FEEDIN+AXPAVE(1,I)*ASMFLX(1,I))/(ASMFLX(1,I)+FEEDIN)
      FEEDIN = FEEDIN+ASMFLX(1,I)
      NBLEND = I+1
      GO TO 20
40    CONTINUE
      RETURN
      END
```

```
C
      SUBROUTINE NONOPT
C
C     SUBROUTINE NONOPT IS USED IN LIEU OF THE OPTIMIZATION PROCEDURE
C     TO DETERMINE NON-OPTIMUM COSTS AND PLANT GEOMETRY FOR FIXED
C     OPERATING CONDITIONS.
C     ******************************************************************
C
      IMPLICIT REAL*8(A-H,O-Z)
C
      DIMENSION XBNOPT(20)
C
      COMMON / CMOBON /FEEDIN,XFONE,XFORIG,FDORIG,XFDIS,FDOUT,VOUT,POUT,
     1XFOUT,VLAST,PLAST,XPRMIT,CA,CE,EP,ET,AXPAVE,ASMFLX,STGNUM,BNKNUM,
     2NBANKS
C
C     INITIALIZE OPERATING CONDITIONS-FIRST MODULE BANK.
C
      FEEDIN = 1.0D6
      XFONE = 1.0677D-2
      XFORIG = 1.0677D-2
      FDORIG = FEEDIN
      XFDIS = 2.1354D-2
      RETURN
C
      ENTRY STGADR(XBNOPT,PNWT,VNWT,CRNWT,DIANWT)
C
C     SET XB INITIAL VALUES FOR NON-OPTIMUM CASE.
C
      READ(5,1) (XBNOPT(I),I=1,4)
1     FORMAT(4D10.0)
      PNWT = 0.0D0
      VNWT = 0.0D0
      CRNWT = 0.0D0
      DIANWT = 0.0D0
      XFORIG = XFONE
      PLAST = 0.0D0
      VLAST = 0.0D0
      XFOUT = XFORIG
C
      RETURN
C
      ENTRY BNKADR(XBNOPT,PNWT,VNWT,CRNWT,DIANWT)
C
C     SET OPERATING VARIABLES FOR NEXT NON-OPTIMUM MODULE BANK.
C
      READ(5,1) (XBNOPT(I),I=1,4)
      PNWT = 0.0D0
      VNWT = 0.0D0
      CRNWT = 0.0D0
      DIANWT = 0.0D0
C
      XFONE = XFOUT
      FEEDIN = FDOUT
      VLAST = VOUT
      PLAST = POUT
C
      RETURN
      END
```

```
C
      SUBROUTINE ECON
C     SUBROUTINE ECON CALLED BY SECTION TO CALCULATE ECONOMIC PARAMETERS
C     FOR GIVEN OPERATING CONDITIONS.
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 MODPAR,MODSRS,MODTOT,NP
      DIMENSION ARHOBR(50),AXPAVE(2,10),ASMFLX(2,10)
      INTEGER CNTR,STGNUM,BNKNUM
C
C     NAME OF COMMON TELLS WHICH ROUTINES USE IT...O=OPT,L=LINCON,
C     E=EVAL,B=BANK,C=ECON
      COMMON / CMOLBC /STEP,XPLIM,RELIM,PRLIM,VLIM,LIST1,LIST6,LINES
      COMMON / CMOBCN /FEEDIN,XFONE,XFORIG,FDORIG,XFDIS,FDOUT,VOUT,POUT,
     1XFOUT,VLAST,PLAST,XPRMIT,CA,CE,EP,ET,AXPAVE,ASMFLX,STGNUM,BNKNUM,
     2NBANKS
      COMMON / COMEBC /PONE,VONE,CR,DIA,COST,REMIN,XPMAX,PMIN,NFLAG,IOUT
      COMMON / COMBC /PI,SUMFLX,SALT,ARHOBR,DIFXP,DIFRE,DIFPR,CNTR
C
C     ***************************************************************
C
C     CALCULATE THE NUMBER OF MODULES IN PARALLEL,SERIES,TOTAL.
C     FT/SEC= 1.0D6/7.4805*86400*(PI*DIA**2/4.0D0*144.0D0)
      MODPAR=FEEDIN*4.0D0*144.0D0/(7.4805D0*86400.0D0*PI*DIA**2.0D0
     1 *VONE)
      MODSRS= CNTR
      MODTOT= CNTR*MODPAR
C     CALCULATE TOTAL WATER PRODUCTION RATE (GPD).
      PRODRT= SUMFLX*MODPAR
      ASMFLX(STGNUM,BNKNUM) = PRODRT
      WRITE(6,1481) STGNUM,BNKNUM,ASMFLX(STGNUM,BNKNUM)
1481  FORMAT('0',I4,I4,D12.6)
C     CALCULATE TOTAL WATER QUALITY (MOLE FRACTION).
      XPAVE= SALT/SUMFLX
      AXPAVE(STGNUM,BNKNUM) = XPAVE
C     CALCULATE PUMP POWER.
C     0.746*14.7*144/550=2.8711
C     0.746/(2.0*32.2*550)= 2.11E-5
C     LB/SEC= 1.0D6*8.3422/86400= 96.5532
      PDIF = DABS(PONE-PLAST)
      VDIF = DABS(VONE-VLAST)
      PP= (FEEDIN*9.65532D-5)*(PDIF*2.8711/ARHOBR(1)+VDIF**2*2.11E-5)/EP
C     CALCULATE TURBINE POWER (KW).
      VOLRT= VOUT*MODPAR*((PI*DIA**2/4.0D0)/144.0D0)
      FDOUT= VOLRT*7.48C0*864C0.0D0
      GOUT= VOLRT*ARHOBR(CNTR)
      TP= GOUT*(POUT/ARHOBR(CNTR)*2.8711+VOUT**2*2.11E-5)*ET
C     CALCULATE NET POWER.
      NP=PP-TP
C     CALCULATE NET POWER PER KGAL.
      UNP=NP/PRODRT*24C00.0C0
C     CALCULATE  AREA (FT**2).
      A= 9.5D0*MODTOT
C     CALCULATE AVERAGE FLUX FOR SECTION (GAL/FT**2 DAY).
      COPT= PRODRT/A
C     CALCULATE PERCENT WATER RECOVERY.
      PERCNT= (PRODRT/FEEDIN)*100.0D0
C
C     CALCULATE AREA COST (CENTS/KGAL).
```

```
      C1= CA*A/PRODRT*1000.0D0
C     CALCULATE POWER COST (CENTS/KGAL).
      C2= CE*UNP
C     CALCULATE TOTAL UNIT COST (CENTS/KGAL).
      CT=C1+C2
      COST=CT
C
      IF(IOUT .EQ. 0) GO TO 5
C     WRITE ECONOMIC RESULTS ONCE FOR OPTIMUM. (IOUT=1)
      WRITE(6,1) MODPAR,MODSRS,MODTOT,PRODRT,XPAVE,NP,UNP,A,QOPT,PERCNT,
     1 C1,C2
1     FORMAT( 1H0/ 1H ,'ECONOMIC RESULTS'/
     140H NUMBER OF MODULES IN PARALLEL          ,F12.6/
     240H NUMBER OF MODULES IN SERIES            ,F12.6/
     340H NUMBER OF MODULES IN SECTION           ,F12.6/
     440H PRODUCT RATE (GPD)                     ,D12.6/
     540H AVERAGE PRODUCT MOLE FRACTION          ,E14.7/
     640H NET POWER USED (KW)                    ,E14.7/
     740H UNIT POWER USED (KWH/KGAL)             ,E14.7/
     840H TOTAL AREA IN SECTION (SQFT)           ,E14.7/
     940H AVERAGE FLUX FOR SECTION (GFD)         ,E14.7/
     X40H PERCENT WATER RECOVERY                 ,E14.7/
     140H AREA COST (CENTS/KGAL)                 ,E14.7/
     240H POWER COST (CENTS/KGAL)                ,E14.7)
C
      GO TO 3
C
5     IF(LIST6 .NE. 0) GO TO 3
      IF(LINES .LT. 50) GO TO 10
C     PRINT ONE LINE PER CALL FROM OPT OR LINCON (SEARCHING, IOUT=0).
      WRITE(6,6001)
6001  FORMAT(1H1/1H ,41X,  'RESULTS CALCULATED WHILE SEARCHING FOR OPTIM
     1UM' / 1H0,' STEP  PONE  VONE  CR  DIA  QOPT  PERCNT  DIFXP  DIFRE
     2 C1  C2  COST' /1H )
      LINES=0
10    WRITE(6,6002) STEP,PONE,VONE,CR,DIA,QOPT,PERCNT,DIFXP,DIFRE,C1,C2,
     1 COST
6002  FORMAT(1H ,A1,F9.3,F8.3,F7.3,F8.4,F9.5,D12.6,D12.6,D12.6,3F10.4)
      LINES= LINES+1
C
3     RETURN
      END
```

Marquardt's Nonlinear Least Squares Code

```
C     <*************************************************************>
C
C     THIS PROGRAM FINDS THE SOLUTION TO A SET OF NONLINEAR EQUATIONS BY
C     MARQUARDT'S METHOD.
C     PURPOSE- THIS ROUTINE MAY BE USED TO SOLVE N NONLINEAR EQUATIONS
C     IN M UNKNOWNS IN A LEAST-SQUARES SENSE WHERE N>M.
C     <*************************************************************>
C     KK        = NUMBER OF UNKNOWNS                          -INPUT
C     B(I)      = VECTOR OF UNKNOWNS (KK LONG)
C                 ON FIRST ENTRY INITIAL GUESSES
C                 ON FINAL EXIT ARE ANSWERS
C     NN        = NUMBER OF EQUATIONS - MUST BE .GE. KK
C     Z(I)      = VECTOR OF COMPUTED VALUES (NN LONG)         -INPUT
C                 WANT Z(I) = Y(I)
C     Y(I)      = VECTOR OF GIVEN VALUES (NN LONG)            -INPUT
C     PH        = FUNCTION VALUE (SUM OF Z(I)-Y(I)**2)        -INPUT
C     FNU       = NU FACTOR (SET TO 10.0 IF 0.0)              -INPUT
C     FLA       = LAMBDA FACTOR  (SET TO 0.01 IF 0.0)         -INPUT
C     TAU       = TAU FACTOR  (SET TO 0.001 IF 0.0)           -INPUT
C     EPS       = EPS FACTOR  (SET TO 0.00002 IF 0.0)         -INPUT
C     PHMIN     = CUT OFF POINT FOR RECALCULATING JACOBIAN MATRIX
C                 USUALLY MAY BE SET TO 0.0
C     I         = ITERATION COUNTER - INITIALLY MUST BE ZERO
C     ICON      = NUMBER OF UNKNOWNS NOT SATISFYING THE CONVERGENCE
C                 REQUIREMENT DEFINED AS
C     ABS(DELTA B(I))/((ABS(DELTA B(I))+TAU) .LE. EPS
C               = 0 ANSWERS FOUND
C               = -1 IF NO FUNCTION IMPROVEMENT POSSIBLE
C               = -2 IF MORE UNKNOWNS THAN FUNCTIONS
C               = -3 IF TOTAL VARIABLES ARE ZERO
C               = -4 IF CORRECTIONS SATISFY CONVERGENCE REQUIREMENTS
C                 BUT FLA IS STILL LARGE
C     FV        = DUMMY VARIABLE VECTOR PASSED ON TO FUNC AND DERIV
C     OV        = DUMMY VARIABLE VECTOR PASSED ON TO DERIV
C     BV(I)     = CODE FOR VARIABLE TYPE (KK LONG)            -INPUT
C               = 0.0 IF B(I) IS NOT VARIABLE                 -INPUT
C               = 1.0 IF B(I) IS VARIABLE AND NUMERICAL DERIVATIVES
C                 ARE TO BE USED
C               = -1.0 IF B(I) IS A VARIABLE AND ANALYTIC DERIVATIVES
C                 ARE TO BE USED - SUBROUTINE DERIV REQUIRED
C     BMIN(I)   = MINIMUM VALUES OF B(I) (KK LONG)            -INPUT
C     BMAX(I)   = MAXIMUM VALUES OF B(I) (KK LONG)            -INPUT
C     P(I)      = JACOBIAN VECTOR ARRANGED COLUMNWISE NN BY KK
C                 VECTOR IS NN*KK LONG
C                 P(L) = DZ(I)/DB(J) WITH L=I + (J-1)*NN
C                 TOTAL VECTOR LENGTH IS KK*(NN+2) + NN
C                 LOCATIONS STARTING WITH NN*KK+1 USED FOR SCRATCH
C                 NOTE THAT THIS VECTOR IS CALCULATED BY DERIV IF ANY
C                 BV(I) = -1.0
C
C     <*************************************************************>
C
C     FUNC      = NAME OF FUNCTION SUBPROGRAM TO BE WRITTEN BY USER-
C                 NAME MUST APPEAR IN EXTERNAL STATEMENT IN MAIN PROGRAM-
C                 THIS ROUTINE MUST ALWAYS BE SUPPLIED
C                 CALL FUNC(KK,B,NN,Z,FV)
C                   KK   = NUMBER OF UNKNOWNS        -INPUT
C                   B(I) = VECTOR OF UNKNOWNS (KK LONG)   -INPUT
C                   NN   = NUMBER OF EQUATIONS            -INPUT
```

```
C                 Z(I) = VECTOR (NN LONG) OF VALUES CALCULATED BY FUNC
C                 FV   = A DUMMY VECTOR TRANSMITTED TO FUNC BY BSOLVE
C                 TO BE USED AS DESIRED
C
C
C     <*****************************************************************>
C
C     DERIV   = NAME OF SUBPROGRAM USED TO EVALUATE DERIVATIVES IF
C               INDICATED BY BV(I). IT IS CALLED ONLY FOR THOSE
C               VARIABLES FOR WHICH BV(I) = -1.0. THE NAME OF THE
C               SUBPROGRAM MUST APPEAR IN THE CALLING PROGRAM
C               AS AN EXTERNAL STATEMENT
C               CALL DERIV(KK,B,NN,Z,PJ,FV,DV,J,JTEST)
C                 KK   = NUMBER OF UNKNOWNS        -INPUT
C                 B(I) = VECTOR OF UNKNOWNS (KK LONG)    -INPUT
C                 NN   = NUMBER OF EQUATIONS               -INPUT
C                 Z(I) = VECTOR (NN LONG) OF VALUES CALCULATED BY FUNC
C                 NEED NOT BE CALCULATED UNLESS JTEST=-1 IS RETURNED
C                 FV = A DUMMY VECTOR TRANSMITTED TO DERIV BY BSOLVE
C                 DV = A DUMMY VECTOR TRANSMITTED TO DERIV BY BSOLVE
C                 J    = THE INDEX OF THE VARIABLE FOR WHICH DERIVATIVES
C                 ARE TO BE CALCULATED BY DERIV
C                 JTEST= IF THE DERIVATIVES HAVE BEEN CALCULATED SET
C                 JTEST TO ZERO. IF A VALUE OF -1 IS RETURNED BSOLVE
C                 WILL ATTEMPT TO TAKE NUMERICAL DERIVATIVES BASED ON
C                 THE Z VECTOR RETURNED.
C
C
C
C
C     MAIN LINE PROGRAM FOR SUBROUTINE BSOLVE
      DIMENSION P(1500),A(25,25),AC(25,25),X1(100),X2(100),X3(100)
      DIMENSION B(25),Z(100),Y(100),BV(25),BMIN(25),BMAX(25)
      EXTERNAL FUNC,DERIV
      COMMON X1,X2,X3
C
      NI = 5
      NO = 6
C
C     READ IN NUMBER OF DATA POINTS, UNKNOWNS.
C
      READ(NI,011) NN,KK
011   FORMAT(8I10)
C
C     READ IN INITIAL GUESSES.
C
      READ(NI,013) (B(J), J=1,KK)
013   FORMAT(10E8.4)
C
C     READ IN LIMITS ON VARIABLES.
C
      READ(NI,013) (BMIN(J),J=1,KK)
      READ(NI,013) (BMAX(J), J=1,KK)
C
C     READ IN INDEPENDENT VARIABLES.
C     READ IN DEPENDENT VARIABLES.
C
      READ(NI,012) (X1(I),I=1,NN)
012   FORMAT(8E10.4)
```

```
      READ(NI,012) (X2(I),I=1,NN)
      READ(NI,012) (X3(I),I=1,NN)
      READ(NI,012) ( Y(I),I=1,NN)
C
      FNU = 0.0
      FLA = 0.0
      TAU = 0.0
      EPS = 0.0
      PHMIN = 0.0
      I = 0
      KD = KK
      FV = 0.0
      DO 100 J=1,KK
      EV(J) = 1
100   CONTINUE
      ICON = KK
      ITER = 0
      WRITE(NO,015)
015   FORMAT(1H1,10X,27HBSOLVE REGRESSION ALGORITHM )
C
200   CALL BSOLVE(KK,B,NN,Z,Y,PH,FNU,FLA,TAU,EPS,PHMIN,I,ICON,FV,DV,BV,
     1EMIN,BMAX,P,FUNC,DERIV,KD,A,AC,GAMM)
C
      ITER = ITER+1
      WRITE(NO,001) ICON,PH,ITER
001   FORMAT(/,2X,6HICON = ,I3,4X, 5HPH = ,E15.8,4X, 16HITERATION NO. =
     1 ,I3)
      IF(ICON) 10,300,200
10    IF(ICON+1) 20,60,200
20    IF(ICON+2) 30,70,200
30    IF(ICON+3) 40,80,200
40    IF(ICON+4) 50,90,200
50    GO TO 95
60    WRITE(NO,004)
004   FORMAT(//,2X,32HNO FUNCTION IMPROVEMENT POSSIBLE )
      GO TO 300
70    WRITE(NO,005)
005   FORMAT(//,2X, 28HMORE UNKNOWNS THAN FUNCTIONS)
      GO TO 300
80    WRITE(NO,006)
006   FORMAT(//,2X, 24HTOTAL VARIABLES ARE ZERO)
      GO TO 300
90    WRITE(NO,007)
007   FORMAT (//,2X,79HCORRECTIONS SATISFY CONVERGENCE REQUIREMENTS BUT
     1LAMDA FACTOR (FLA) STILL LARGE          )
      GO TO 300
95    WRITE(NO,008)
008   FORMAT(//,2X, 20HTHIS IS NOT POSSIBLE)
      GO TO 300
300   WRITE(NO,002)
002   FORMAT(//,2X, 26HSOLUTIONS OF THE EQUATIONS)
      DO 400 J=1,KK
      WRITE(NO,003) J,B(J)
003   FORMAT(/,2X, 2HB(,I2,4H) = ,E16.8)
400   CONTINUE
      END
```

```
C
      SUBROUTINE FUNC(KK,B,NN,Z,FV)
      DIMENSION X1(100),X2(100),X3(100),B(25),Z(100)
      COMMON X1,X2,X3
C
      FV = FV + 1
      DO 100 JJ=1,NN
      Z(JJ) = B(1)+B(2)*X1(JJ)+B(3)*X2(JJ)+B(4)*X3(JJ)+B(5)*X1(JJ)**2
     1 +B(6)*X1(JJ)*X2(JJ)+B(7)*X1(JJ)*X3(JJ)+B(8)*X2(JJ)**2+B(9)*X2(JJ)
     2 *X3(JJ)+B(10)*X3(JJ)**2
100   CONTINUE
      RETURN
      END
```

```
C
      SUBROUTINE DERIV(KK,B,NN,Z,PJ,FV,DV,J,JTEST)
      DIMENSION B(25),Z(100),PJ(1500),X1(100),X2(100),X3(100)
      COMMON X1,X2,X3
C
C
C
C
C
C
      JTEST = -1
      RETURN
      END
```

```
C
C
      SUBROUTINE BSOLVE(KK,B,NN,Z,Y,PH,FNU,FLA,TAU,EPS,PHMIN,I,ICON,FV,
     1DV,BV,BMIN,BMAX,P,FUNC,DERIV,KD,A,AC,GAMM)
      DIMENSION B(25),Z(100),Y(100),BV(25),BMIN(25),BMAX(25)
      DIMENSION P(1500),A(25,25),AC(25,25),X1(100),X2(100),X3(100)
C
      K = KK
      N = NN
      KP1 = K+1
      KP2 = KP1+1
      KBI1 = K*N
      KBI2 = KBI1+K
      KZI = KBI2+K
      IF(FNU .LE. 0.0) FNU=10.0
      IF(FLA .LE. 0.0) FLA=0.01
      IF(TAU .LE. 0.0) TAU=0.001
      IF(EPS .LE. 0.0) EPS= 0.00002
      IF(PHMIN .LE. 0.0) PHMIN=0.0
120   KE = 0
130   DO 160 I1=1,K
160   IF(BV(I1) .NE. 0.0) KE=KE+1
      IF(KE .GT. 0) GO TO 170
162   ICON = -3
163   GO TO 2120
170   IF(N .GE. KE) GO TO 500
180   ICON = -2
190   GO TO 2120
500   I1 = 1
530   IF(I .GT. 0) GO TO 1530
550   DO 560 J1=1,K
      J2 = KBI1 + J1
      P(J2) = B(J1)
      J3 = KBI2 + J1
560   P(J3) = ABS(B(J1)) + 1.0E-02
      GO TO 1030
590   IF(PHMIN .GT. PH .AND. I .GT. 1) GO TO 625
      DO 620 J1=1,K
      N1 = (J1-1)*N
      IF(BV(J1)) 601,620,605
601   CALL DERIV(K,B,N,Z,P(N1+1),FV,DV,J1,JTEST)
      IF(JTEST .NE. (-1)) GO TO 620
      BV(J1) = 1.0
605   DO 606 J2=1,K
      J3 = KBI1 +J2
606   P(J3) = B(J2)
      J3 = KBI1 + J1
      J4 = KBI2 + J1
      DEN = 0.001*AMAX1(P(J4),ABS(P(J3)))
      IF(P(J3) + DEN .LE. BMAX(J1)) GO TO 55
      P(J3) = P(J3) - DEN
      DEN = -DEN
      GO TO 56
55    P(J3) = P(J3) + DEN
56    CALL FUNC(K,P(KBI1+1),N,P(N1+1),FV)
      DO 610 J2=1,N
      J8 = J2 + N1
610   P(J8) = (P(J8) - Z(J2))/DEN
620   CONTINUE
```

```
C
C       SET UP CORRECTION EQUATIONS
C
625     DO 725 J1=1,K
        N1 = (J1-1)*N
        A(J1,KP1) = 0.0
        IF(BV(J1)) 630,692,630
630     DO 640 J2=1,N
        N2 = N1 + J2
640     A(J1,KP1) = A(J1,KP1) + P(N2)*(Y(J2)-Z(J2))
650     DO 680 J2=1,K
660     A(J1,J2) = 0.0
665     N2 = (J2-1)*N
670     DO 680 J3=1,N
672     N3 = N1 + J3
674     N4 = N2 + J3
680     A(J1,J2) = A(J1,J2) + P(N3)*P(N4)
        IF(A(J1,J1) .GT. 1.0E-20) GO TO 725
692     DO 694 J2=1,KP1
694     A(J1,J2) = 0.0
695     A(J1,J1) = 1.0
725     CONTINUE
        GN = 0.0
        DO 729 J1=1,K
729     GN = GN + A(J1,KP1)**2
C
C       SCALE CORRECTION EQUATIONS.
C
        DO 726 J1=1,K
726     A(J1,KP2) = SQRT(A(J1,J1))
        DO 727 J1=1,K
        A(J1,KP1) = A(J1,KP1)/A(J1,KP2)
        DO 727 J2=1,K
727     A(J1,J2) = A(J1,J2)/(A(J1,KP2)*A(J2,KP2))
730     FL = FLA/FNU
        GO TO 810
800     FL = FNU*FL
810     DO 840 J1=1,K
820     DO 830 J2=1,KP1
830     AC(J1,J2) = A(J1,J2)
840     AC(J1,J1) = AC(J1,J1) + FL
C
C       SOLVE CORRECTION EQUATIONS.
C
        DO 930 L1=1,K
        L2 = L1+1
        DO 910 L3=L2,KP1
910     AC(L1,L3) = AC(L1,L3)/AC(L1,L1)
        DO 930 L3=1,K
        IF(L1-L3) 920,930,920
920     DO 925 L4=L2,KP1
925     AC(L3,L4) = AC(L3,L4) - AC(L1,L4)*AC(L3,L1)
930     CONTINUE
C
        DN = 0.0
        DG = 0.0
        DO 1028 J1=1,K
        AC(J1,KP2) = AC(J1,KP1)/A(J1,KP2)
        J2 = KBII + J1
```

```
      P(J2) = AMAX1(BMIN(J1),AMIN1(BMAX(J1),B(J1)+AC(J1,KP2)))
      DG = DG + AC(J1,KP2)*A(J1,KP1)*A(J1,KP2)
      DN = DN + AC(J1,KP2)*AC(J1,KP2)
1028  AC(J1,KP2) = P(J2)-B(J1)
      COSG = DG/SQRT(DN*GN)
      JGAM = 0
      IF(COSG) 1100,1110,1110
1100  JGAM = 2
      COSG = -COSG
1110  CONTINUE
      COSG = AMIN1(COSG,1.0)
      GAMM = ARCOS(COSG)*180.0/(3.14159265)
      IF(JGAM .GT. 0) GAMM = 180.0 - GAMM
1030  CALL FUNC(K,P(KBI1+1),N,P(KZI+1),FV)
1500  PHI = 0.0
      DO 1520 J1=1,N
      J2 = KZI + J1
1520  PHI = PHI + (P(J2)-Y(J1))**2
      IF(PHI .LT. 1.0E-10) GO TO 3000
      IF(I .GT. 0) GO TO 1540
1521  ICON = K
      GO TO 2110
1540  IF(PHI .GE. PH) GO TO 1530
C
C     EPSILON TEST.
C
1200  ICON = 0
      DO 1220 J1=1,K
      J2 = KBI1 + J1
1220  IF(ABS(AC(J1,KP2))/(TAU + ABS(P(J2))).GT. EPS) ICON = ICON+1
      IF(ICON .EQ. 0) GO TO 1400
C
C     GAMMA LAMBDA TEST.
C
      IF(FL .GT. 1.0 .AND. GAMM .GT. 90.0) ICON = -1
      GO TO 2105
C
C     GAMMA EPSILON TEST.
C
1400  IF(FL .GT. 1.0 .AND. GAMM .LE. 45.0) ICON = -4
      GO TO 2105
C
1530  IF(I1-2) 1531,1531,2310
1531  I1 = I1 +1
      GO TO (530,590,800),I1
2310  IF(FL .LT. 1.0E+8) GO TO 800
1320  ICON = -1
C
2105  FLA = FL
      DO 2091 J2=1,K
      J3 = KBI1 + J2
2091  E(J2) = P(J3)
2110  DO 2050 J2=1,N
      J3 = KZI + J2
2050  Z(J2) = P(J3)
      PH = PHI
      I = I + 1
2120  RETURN
3000  ICON = 0
```

```
      GO TO 2105
C
      END
```

```
      FUNCTION ARCOS(Z)
C
      X = Z
      KEY = 0
      IF(X .LT. (-1.0)) X=-1.0
      IF(X .GT. 1.0) X=1.0
      IF(X .GE.  (-1.0) .AND. X .LT. 0.0) KEY=1
      IF(X .LT. 0.0) X=ABS(X)
      IF(X .EQ. 0.0) GO TO 10
      ARCOS = ATAN(SQRT(1.0-X*X)/X)
      IF(KEY .EQ. 1) ARCOS = 3.14159265 - ARCOS
      GO TO 999
10    ARCOS = 1.5707963
C
999   RETURN
      END
```

BSOLVE REGRESSION ALGORITHM

```
ICON = 10    FH =  0.45604616E 17    ITERATION NO. =   1
ICON =  5    FH =  0.23509775E 12    ITERATION NO. =   2
ICON =  9    FH =  0.42509580E 07    ITERATION NO. =   3
ICON = 10    FH =  0.10269629E 05    ITERATION NO. =   4
ICON = 10    FH =  0.81436055E 04    ITERATION NO. =   5
ICON = 10    FH =  0.71644180E 04    ITERATION NO. =   6
ICON =  9    FH =  0.71643750E 04    ITERATION NO. =   7
ICON =  9    FH =  0.71643633E 04    ITERATION NO. =   8
ICON =  6    FH =  0.71643594E 04    ITERATION NO. =   9
ICON =  0    FH =  0.71643555E 04    ITERATION NO. =  10
```

SOLUTIONS OF THE EQUATIONS

```
B( 1) =  -0.31911087E 02
B( 2) =   0.37052650E 01
B( 3) =  -0.34236652E-02
B( 4) =  -0.55646250E 04
B( 5) =  -0.82865730E-02
B( 6) =   0.85154388E-04
B( 7) =  -0.40184357E 02
B( 8) =  -0.47012617E-06
B( 9) =   0.22535348E 00
B(10) =   0.36614645E 05
```

APPENDIX V

Definitions of Toxicity and Solubility

Based on the ratings given in Clinical Toxicology of Commercial Products by Gleason et al (Baltimore, Williams and Wilkins Co., 1969), the toxicity of a specific compound is related to the probable lethal dose for humans as follows:

Toxicity	Rating	Probable Lethal Dose (Human), mg/Kg
6	Super	<5
5	Extremely	5-50
4	Very	5-500
3	Moderately	500 mg - 5 gr/Kg
2	Slightly	5-15 gr/Kg
1	non-	>15 gr/Kg

Also, remarks on "The Scale of Solubility" are made in the Handbook of Chemistry and Physics (48th Ed. The Chemical Rubber Co. 1967) as follows, "... As numerical data on this property scarcely appear in literature, and when they appear their degree of approximation is not great, it was preferred to rely on the intuitive meaning that the following scale has for the chemist (corresponding abbreviations in brackets): insoluble (i), slightly soluble (δ), soluble (s), very soluble (v), miscible (∞), decomposes (d). If no special remark is made about the temperature, the reference is to room temperature; otherwise, a superscript appears."