

**Integrated Sensors for Real-Time Monitoring
of Filtration Performance during Membrane-Based
Liquid Separations**

By

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The final copy of this thesis has been examined by the signators, and we find
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Integrated Sensors for Real-Time Monitoring of Filtration Performance during Membrane-Based Liquid Separations

Dissertation directed by Victor M. Bright and Alan R. Greenberg

In many regions of the world, inorganic fouling (scaling) caused by sparingly soluble salts prevents the exploitation of underutilized brackish groundwater and municipal wastewater resources that require desalination. If such resources could be effectively utilized, pressure on existing scarce water supplies would be reduced. Scaling formation is of immense practical importance since it significantly degrades membrane performance.

Knowledge of scaling induction time allows for optimized operation of the desalination unit as well as execution of remediation measures. The presence of scaling is usually indicated by ex-situ measurements such as volumetric flux rate. These measurements, however, indicate the presence of scaling only after significant growth has already occurred. Remediation measures often require the use of expensive anti-scaling agents or back-flushing of the system. Both cases necessitate operational downtime, reducing system efficiency and increasing cost. Additionally, overuse of anti-scaling agents can cause significant reductions in membrane lifetime.

The availability of real-time, in-situ monitoring of the membrane condition would provide sensing capabilities for determining optimum timing of scaling remediation measures. Such sensors could be incorporated as control elements in smart membrane/module systems, greatly improving the efficiency of large-scale desalination processes. The work described in this thesis demonstrates the use of integrated electrolytic and ultrasonic sensors installed within a cross flow desalination module. Concentration polarization (CP) of the rejected species near the membrane surface is the precursor to scaling deposition and growth, presenting coupled phenomena that should be investigated in tandem.

Thin, flexible electrolytic sensors were manufactured using MEMS (Micro-Electro-Mechanical Systems) fabrication techniques, and were installed on the membrane surface to measure concentration within the concentration polarization boundary layer (CPBL), as well as early-stage scaling. The sensors were mounted at three positions along the length of the flow channel in a flat-sheet module, and experimentally demonstrated the expected concentration dependence on axial position as well as cross flow velocity. Scaling was also detected by these sensors as salt precipitated.

Ultrasonic transducers present a more simple systems integration problem, and thus demonstrate more immediate potential in commercial situations at the current time. Transducers were installed at three positions within the filtration module, in direct contact with the back-side of the membrane. Several studies in the literature report the use of externally mounted ultrasonic sensors to detect the presence of membrane fouling. However, significant acoustic energy losses can occur in the use of externally mounted transducers, due to unwanted reflections, scattering and beam spread. This thesis compares data from internally mounted transducers with simultaneous data from externally mounted transducers to evaluate the relative efficacy of both configurations.

It should be noted that the real-time monitoring techniques could be applied in many filtrations processes beyond desalination. This thesis serves as a case study to provide a basis for additional research in developing smart membranes/modules for municipal and agricultural wastewater treatment, as well as the processing of pharmaceutical and chemical products that rely upon membrane-based liquid separations.

Dedication

To my parents, Jerry and LeAnn, and my lovely Katie.

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Contents

1. Introduction	1
1.1. Membrane Processes	1
1.2. Concentration Polarization and Fouling	4
1.3. Practical Implications of Fouling and Fouling Control	5
1.4. Focus of this Research.....	8
1.5. Organization of Thesis.....	11
2. Literature Review	12
2.1. Overview	13
2.2. Modeling of Concentration Polarization.....	13
2.2.1. Fundamentals of Mass Transport in Filtration Systems	13
2.2.2. Unstirred Batch Cell	16
2.2.3. Laminar Cross Flow	21
2.2.4. Turbulent Cross-Flow	31
2.3. Modeling of Fouling.....	34
2.3.1. Fundamentals of Fouling	34
2.3.2. Micro- and Ultrafiltration	35
2.3.2.1. Standard Blocking Model.....	35
2.3.2.2. Intermediate and Complete Blocking Models	36
2.3.2.3. Cake Filtration Model	38
2.3.2.4. Gel Polarization Model	39
2.3.2.5. Combined Models.....	43
2.3.3. Reverse Osmosis and Nanofiltration: Inorganic Scaling	44
2.4. Non-Destructive Monitoring of Concentration Polarization and Fouling	53
2.4.1. Optical Methods	54
2.4.2. Ultrasonic Methods	59
2.4.3. Electrolytic Methods	63
2.5. Critique of the Literature	67
3. Integrated Electrolytic Sensors for Monitoring of Concentration Polarization.....	73
3.1. Motivation and Sensor Design Guidelines	73
3.2. Fundamentals of Electrolytic Conductivity Measurements	74
3.3. Electrolytic Conductivity Concepts.....	77
3.4. Double Layer Concepts in Electrolytic Solutions	79
3.5. Design and Fabrication of Integrated Electrolytic Sensors.....	88
3.5.1. Design Concepts.....	88
3.5.2. Fabrication Process.....	90
3.5.3. Electrode Design	91
3.6. Systems Integration	92
3.6.1. Filtration System	92
3.6.2. Electronic Control and Data Acquisition.....	93
3.6.3. Sensor Integration	96
3.7. Multiple Integrated Sensors: Experimental Design.....	100

3.7.1. Concentration Polarization Model.....	100
3.7.2. Experimental Protocol	102
3.7.3. Data Analysis Protocol	106
3.8. Results and Discussion	108
3.8.1. System Development – Prototype Module	108
3.8.2. System Performance – Multiple Integrated Sensors.....	117
3.8.3. Axial Dependence of Concentration Polarization	121
3.8.4. Analysis of Capacitance Responses	129
3.8.5. Analysis of Conductance Responses	132
3.8.6. Scaling Monitoring.....	139
3.9. Significance.....	141
4. Integrated Ultrasonic Sensors for Monitoring of Early-Stage Inorganic Scaling	143
4.1. Motivation and Components of Work	143
4.2. Acoustic Wave Propagation in Media and at Interfaces	144
4.3. Ultrasonic Transducers: Design Concepts	150
4.3.1. Plane Wave Transducer	150
4.3.2. Pulse-Echo and Pitch-Catch Ultrasonic NDT	152
4.3.3. Piezoelectricity	153
4.3.4. The KLM Equivalent Circuit and Acoustic Impedance Matching.....	154
4.4. Ultrasonic Signal Processing	157
4.4.1. Review: Membrane Monitoring and Thin Films.....	157
4.4.2. Wavelet Decomposition.....	163
4.4.3. Total Reflected Power	164
4.4.4. Cross-Correlation	165
4.5. Systems Integration	165
4.5.1. Initial Work: In-House Fabricated Transducers	165
4.5.2. Ultrasonic Transducer Integration.....	166
4.5.3. Electronic Control and Data Acquisition.....	168
4.6. Multiple Integrated Transducers: Experimental Design	170
4.6.1. Experimental Design and Protocol.....	170
4.6.2. Concentration Polarization Model.....	171
4.6.3. Ultrasonic Signal Processing and Interpretation	172
4.6.4. Model of Acoustic Reflection from Layered Media.....	175
4.7. Results and Discussion	182
4.7.1. Fabrication and Test of Miniature Ultrasonic Transducers.....	182
4.7.2. Analysis of Ultrasonic Signal Threshold	186
4.7.3. Extended Scaling Experiments.....	191
4.7.3.1. Ultrasonic Results: Extended Scaling Experiments.....	191
4.7.3.2. Post-Mortem Results: Extended Scaling Experiments.....	192
4.7.4. Interval Experiments	198
4.7.4.1. Ultrasonic Results: Interval Experiments.....	198
4.7.4.2. Post-Mortem Results: Interval Experiments.....	202
4.7.5. SEM Imaging and EDS Spectrum.....	203

4.8. Significance	205
5. Conclusions and Recommendations	206
5.1. Electrolytic Monitoring of Concentration Polarization and Scaling	206
5.2. Ultrasonic Monitoring of Early-Stage Scaling	211
5.3. Conclusions	214
References	216
Appendix A: Fabrication Process: Integrated Electrolytic Sensors	226
Appendix B: Engineering Drawings of Flat-Sheet Flow Cell Module	227
Appendix C: Schematic of full Hydraulic and Data Acquisition System: Electrolytic Tests	229
Appendix D: LabView Code for Real-Time Acquisition of Electrolytic Data	230
Appendix E: Matlab Code for Real-Time Plotting of Electrolytic Data	239
Appendix F: LabView Code for Real-Time Acquisition of Ultrasonic Waveforms	246
Appendix G: Matlab Code for Analyzing Ultrasonic Waveforms	248
Appendix H: Fabrication Process: In-House Ultrasonic Sensors	256

Tables

3.1. CP vertical profile calculations	129
3.2. Input uncertainty values in double layer capacitance model.....	131
3.3. Concentration vs. capacitance data, integrated sensors	132
4.1. Acoustic impedance of common materials	145
4.2. Input parameters for multi-layer reflection model, external transducers	179
4.3. Input parameters for multi-layer reflection model, internal transducers.....	179
4.4. TRP responses for in-house fabricated transducers	186
4.5. Ultrasonic signal threshold analysis, internal transducers.....	188
4.6. Ultrasonic signal threshold analysis, external transducers	188
4.7. Analysis of false-negative ultrasonic responses, internal transducers	189
4.8. Analysis of false-negative ultrasonic responses, external transducers.....	189
4.9. Ultrasonic and post-mortem results from extended scaling experiments.....	195
4.10. Ultrasonic and post-mortem results from interval experiments.....	200

Figures

1.1. Schematic of flat-sheet cross flow filtration module	3
1.2. Schematic of spiral-wound filtration module	4
1.3. Schematic of flow-reversal desalination system.....	7
2.1. Schematic of unstirred batch filtration cell	17
2.2. Flat-sheet laminar cross flow model configuration [Dresner 1964, Sherwood 1965]	24
2.3. Flat-sheet laminar cross flow model configuration [Srinivasan 1967]	28
2.4. Schematic demonstrating CP and pore transport coupling [Bhattacharjee 2001]	29
2.5. Flat-sheet turbulent cross flow model configuration.	32
2.6. Standard blocking model of membrane fouling	36
2.7. Complete/intermediate blocking model of membrane fouling [Bolton 2006]	38
2.8. Cake filtration model of membrane fouling [Bolton 2006].....	39
2.9. Gel layer model of membrane fouling	40
2.10. Cake filtration and surface blocking model of membrane scaling [Gilron 1987].....	47
2.11. SEM micrograph of CaSO_4 rosette scaling [Gilron 1987]	47
2.12. Combined cake filtration/surface blockage model of membrane scaling [Lee 1999].....	50
2.13. FEM model of membrane scaling [Lyster 2009].....	52
2.14. FEM model of flat-sheet module flow field [Lyster 2009].	53
2.15. Schematic of shadowgraphic monitoring of CP [Vilker 1981]	55
2.16. Direct visual observation of CaSO_4 scaling growth [Uchymiak 2007].....	58
2.17. Schematic of scaling monitoring by UTDR [Mairal 1999].....	60
2.18. Schematic of conductivity monitoring of CP in a dead-end cell [Liu 1970].....	64
2.19. Schematic of MEMS microcapacitors for monitoring of cross-flow CP [Zhang 2006]	65
2.20. Representative capacitance data from cross-flow CP monitoring [Zhang 2006]	67
3.1. Equivalent circuit for electrolytic conductivity measurement.....	75
3.2. Schematic of parallel plate conductivity probe	76
3.3. Schematic of electrolytic capacitor with ionic double-layers.....	80
3.4. Gaussian box used in solution of double-layer capacitance	84
3.5. Schematic of Stern-Gouy-Chapman double layer model.....	86
3.6. Schematic of Grahame double layer model	87
3.7. Interdigitated sensor design.....	91

3.8. Monolithic sensor design	92
3.9. Flow chart of LabView algorithm for data acquisition and control.....	95
3.10. Plan schematic of sensor placement on membrane and top of flow channel	97
3.11. Cross-sectional schematic of sensor placement.....	97
3.12. Schematic of electronic feed-through configuration 1	99
3.13. Schematic of electronic feed-through configuration 2.....	99
3.14. CP modeling: variable concentration.....	103
3.15. CP modeling: variable cross-flow rate.....	104
3.16. Physical configuration and equivalent circuit with monolithic electrodes	107
3.17. First early prototype electronic feed-through configuration	110
3.18. Second early prototype electronic feed-through configuration	112
3.19. Third early prototype electronic feed-through configuration	113
3.20. Inlet/outlet design of prototype flat sheet module	114
3.21. Photograph of interdigitated sensor	115
3.22. Capacitive demonstration of CP in prototype module	116
3.23. Feed and permeate conductivity measurement.....	118
3.24. Integrated sensor capacitance measurement: no electrodes	118
3.25. Capacitive demonstration of CP: multiple integrated sensors.....	119
3.26. Photograph of monolithic sensor	120
3.27. Calibration curves for CP monitoring	122
3.28. Concentration and CP: capacitance calibrated results.	124
3.29. Concentration and CP: impedance calibrated results.....	125
3.30. CP results: variable cross flow velocity	127
3.31. Schematic of CP vertical profile.....	128
3.32. Experimental and modeling capacitance results: integrated sensors	131
3.33. Conductance vs. concentration results: integrated sensors.....	133
3.34. Cell constant results: integrated sensors	136
3.35. Ionic relaxation time in conductivity measurement.....	137
3.36. Onsager model and experimental conductivity data: integrated sensors.....	138
3.37. Conductance data during scaling test.....	140
3.38. Post-mortem photographs of membrane after scaling test	141

4.1. Transmission and reflection coefficients as a function of Z_1/Z_2	147
4.2. Schematic of plane wave ultrasonic transducer.....	151
4.3. Pulse-echo and pitch-catch ultrasonic NDT configurations.....	152
4.4. KLM equivalent circuit of ultrasonic transducer.....	154
4.5. Wave generation and propagation through an acoustic matching layer.....	156
4.6. Schematic of acoustic paths and waveforms in membrane monitoring with external transducers....	159
4.7. Superposition of waveforms with internally mounted transducers.....	160
4.8. Schematic of spiral-wound module and corresponding ultrasonic waveform [Zhang 2003].....	161
4.9. TRP distribution from ultrasonic characterization of membrane biofouling [Kujundzic 2008].....	162
4.10. Schematic of wavelet decomposition methodology [Mathworks 2007].....	163
4.11. Photograph of Olympus M203-SM ultrasonic transducer	166
4.12. Schematic of internal transducer integration.....	167
4.13. Schematic of flow and electronic systems used in experiments.....	169
4.14. CP modeling for experiments.....	174
4.15. Idealized ultrasonic and permeate flux induction times.....	175
4.16. Schematic of acoustic reflection from a thin film.....	177
4.17. Schematic of acoustic reflection from stacked media.....	178
4.18. Plot of reflection coefficient from stack for variable membrane thickness	180
4.19. Test of cross-correlation analysis protocol for waveforms of differing magnitude.....	181
4.20. Photograph of in-house fabricated ultrasonic transducer	183
4.21. Demonstration of differing backing media on bang signal of in-house transducer	184
4.22. Delay-line reflection from in-house transducer.....	185
4.23. Reflection from microscope slide, in-house transducer.....	185
4.24. Photograph of in-house transducer installed in dead-end cell.....	186
4.25. Ultrasonic results from extended scaling test (internal transducers).....	193
4.26. Ultrasonic results from extended scaling test (external transducers).....	194
4.27. Post-mortem optical micrographs of membrane after extended scaling test ($v = 0.9$ cm/s).....	196
4.28. Post-mortem optical micrographs of membrane after extended scaling test ($v = 8.2$ cm/s).....	196
4.29. Data demonstrating permeate and ultrasonic induction times	199
4.30. Ultrasonic data from interval tests	201
4.31. Post-mortem optical micrographs of membrane after interval tests	203
4.32. SEM micrograph of CaSO_4 rosette clusters	204
4.33. EDS spectrum of CaSO_4 scaling.....	204

5.1. Schematic of electrolytic sensor fabricated directly on membrane	210
5.2. Photograph of Ashkelon Seawater Reverse Osmosis Plant, Israel	213

Chapter 1

Introduction

1.1 Membrane Processes

Micro- and nanoporous membranes are used in wide variety of liquid separation processes, such as filtration of municipal drinking water, desalination, manufacture of foodstuffs, as well as processing of pharmaceutical and chemical products [Osada 1992, USEPA 2003, Dow Water Solutions 2007]. Correspondingly, a wide variety of membranes and associated filtration systems are used to carry out these varied separation functions. Micro- and ultrafiltration (MF/UF) membranes utilize appropriately sized pores which serve as a sieve for removing biological agents (algae, bacteria, viruses...), colloidal particulates, and large molecules. Microfiltration membranes typically contain pores ranging from 0.1 μm to 10 μm , and operate at low pressures (50 kPa -150 kPa/7 psi – 22 psi). Ultrafiltration membranes also are used as a sieve, but they have smaller pores (1 nm to 100 nm) for separating smaller colloidal particles and macromolecules, and are used at slightly higher pressures (100 kPa – 300 kPa/15 psi – 44 psi) [Osada 1992].

Reverse osmosis (RO) and nanofiltration (NF) membranes are typically used to remove ions dissolved in solution, such as during desalination of seawater. These membranes consist of a very thin dense layer (~200 nm) which is supported by porous backing layer which provides mechanical support. The dense layer performs the filtration, and the most common variants used in desalination are composed of cellulose acetate or polyamide, with a polysulfone backing layer. Diffusion is the primary mechanism for fluid transport through these membranes, as opposed to convection in MF/UF. In addition to molecular sieving/steric effects, RO and NF membranes employ surface electrostatic functionalization to perform the filtering functions [Bhattacharjee 2001]. Several variations on NF/RO surface chemistry have been developed to impart desired filtering capabilities for specialized applications [Osada 1992,

Bhattacharjee 2001, Dow Water Solutions 2007]. Reverse osmosis membranes demonstrate greater solute rejection than nanofiltration membranes, thus requiring greater feed pressure and using more energy. RO membranes provide excellent rejection of both mono- and divalent ions, while NF membranes provide good rejection of monovalent ions and excellent rejection of divalent ions [Dow Water Solutions 2007]. Significantly greater operating pressures are required for NF/RO filtration (500 kPa – 12000 kPa/73 psi – 1740 psi) [Dow Water Solutions 2007, Osada 1992].

Several varieties of filtration module configurations are available, depending on the required applications. One of the most common, used in laboratory experiments and low-throughput processes, is the flat-sheet cross flow module. This type of module is commonly found in research settings due to its simple geometry and ease of use. A semi-permeable membrane is placed on a porous support plate, and is sealed between thick top and bottom module plates which are held together by bolts. A cavity in one of the plates forms the flow channel through which the feed solution flows. The bulk feed flows longitudinally over the membrane surface while solution permeates through the membrane, driven by the pressure in the flow channel; the filtered product stream is known as the permeate. The rejected species are retained in the flow channel and pass out of the cell through an exit port with the cross flow; this stream is known as the retentate (Figure 1.1). The use of cross-flow filtration, as opposed to dead-end filtration, significantly reduces osmotic resistance to permeation caused by the buildup of rejected species at the membrane surface resulting from convective mass transport. This increase in concentration at the membrane surface is known as concentration polarization (CP).

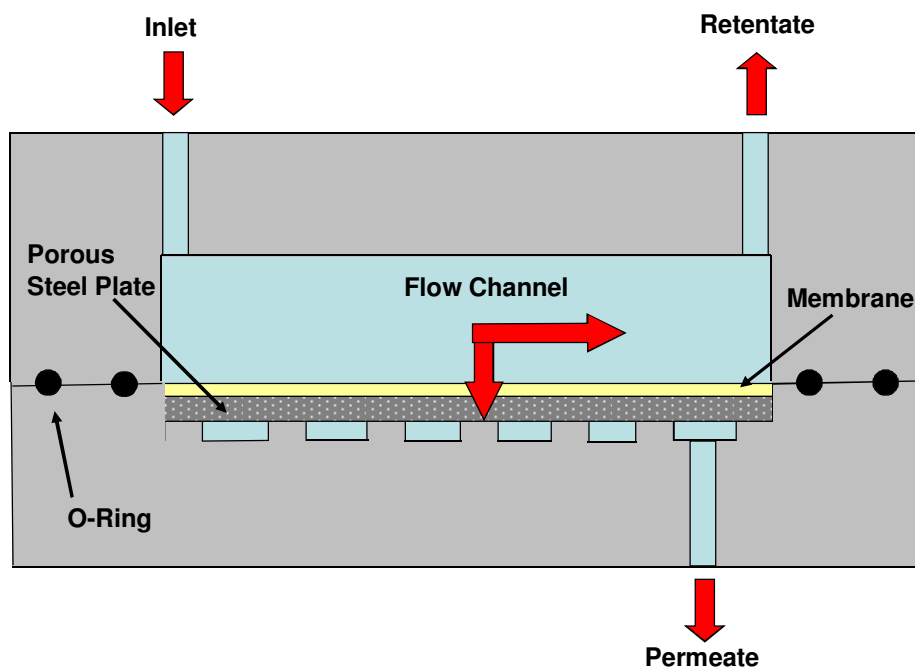


Figure 1.1: Schematic of flat-sheet cross flow filtration system.

Spiral-wound cross flow modules are generally considered the ‘work-horses’ of industrial applications such as municipal water filtration and desalination. A spiral-wound module consists of ‘envelopes’ made from the semi-permeable membrane material. Mesh spacer layers are placed inside and between the envelopes (Figure 1.2). The membrane/mesh envelopes are wrapped around a hollow product tube that collects the permeate product. The spiral-wound membrane and product tube are then placed inside a cylindrical casing, which can then be pressurized. Feed solution enters the casing and flows longitudinally along the wound membrane envelope. Pressure drives the liquid through the membrane and into the mesh spacer layer. The permeate then spirals inward and enters the product tube, where it is recovered. This membrane configuration is used in large-scale industrial applications because very high product throughput can be achieved due to the large ratio of permeable area to module volume.

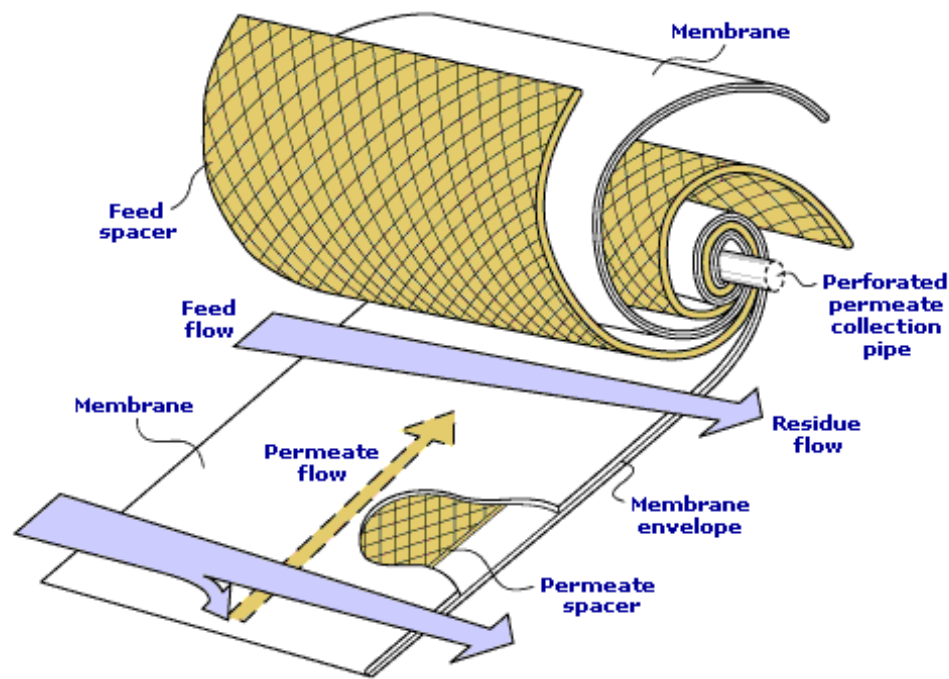


Figure 1.2: Schematic of spiral-wound membrane [Membrane Technology & Research 2007].

1.2 Concentration Polarization and Fouling

During cross-flow liquid separations, a concentration polarization boundary layer (CPBL) forms near the membrane surface. A gradient in the concentration of the rejected species develops between the membrane surface (higher concentration) and the bulk flow (lower bulk feed concentration). As the feed solution flows from upstream to downstream, water at the membrane surface is lost to permeation while the rejected species is retained. This results in an axial variation in the surface solute concentration along the flow direction, with the concentration increasing from upstream to downstream. In many cases, the concentration of the solute will exceed the solubility limit resulting in precipitation and crystal growth on the membrane surface, forming a solid fouling layer on the membrane surface. Left unchecked, such fouling layers can be difficult and expensive to clean [Pomerantz 2006].

Fouling of membranes presents one of the most common and challenging difficulties encountered in filtration processes. Biofouling is the irreversible growth of a biofilm on a membrane, and can be caused by deposition of proteins or growth of algal or bacterial colonies [Kujundzic 2008]. Scaling is the deposition and growth of salt crystals when ions precipitate out of solution during reverse osmosis or nanofiltration desalination [Gilron 1986]. These forms of fouling not only alter the functional properties of the membrane, such as selectivity and efficiency, but can also serve as sources of contamination. In the current thesis, we are concerned with concentration polarization and scaling of sparingly soluble salts during desalination.

These phenomena represent a continuum in desalination processes; i.e., scaling does not occur without the necessary CP first being present. Moreover, depending on operating conditions, scaling may take days or weeks to form a noticeable layer. Indeed, as scaling forms on the membrane surface, the local properties of concentration polarization will change as well because of the change in permeation conditions [Gilron 1987, Lyster 2009]. Clearly CP and fouling are interrelated processes, and thus warrant study as combined phenomena for improved understanding of filtration processes.

1.3 Practical Implications of Fouling and Challenges in Fouling Control

Fouling represents one of the most common and challenging problems in NF/RO desalination processes. As available fresh water supplies become increasingly scarce, membrane based filtration becomes ever more important to supplying the growing need for both drinking and agricultural use. When salt precipitates and crystals grow on the membrane surface forming a scaling layer, permeate flux becomes locally blocked. This reduced the efficiency of the overall filtration process. Currently, the presence of scaling is observed by external volumetric flux measurements. These measurements, however, are based on average flux over the entire membrane surface area. Therefore, a significant portion of the membrane surface area must already be covered by scaling before a drop in permeate flux becomes detectable. This fact can have a significant impact in large desalination plants where arrays of

spiral-wound modules are in use. Scaling can significantly reduce the overall efficiency of large-scale desalination processes, making the exploitation of certain brackish water resources economically infeasible.

Remediation measures typically involve back-flushing the system with pure water or cleaning with chemical anti-scalants [USEPA 2003, Pomerantz 2006]. Both of these measures require operational downtime of the affected modules, further reducing process efficiency. Chemical cleaning agents also reduce the lifetime of the membranes, necessitating more frequent membrane replacement. These remediation measures incur significant costs when operating on a large scale, in terms of materials as well as operational efficiency. Early detection of the onset of scaling could significantly improve process efficiency by allowing for remediation measures to be carried out in a more targeted and refined manner. Quantities of anti-scalant chemicals could be reduced to remove less extensive scaling layers, thereby minimizing membrane damage and increasing lifetime. Similarly, back-flushing procedures could be performed in shorter times, reducing the operational downtime of the affected modules.

An intriguing remediation measure for scaling control during desalination has been presented by the desalination research group under the guidance of Dr. Jack Gilron at Ben Gurion University (Beersheva, Israel) [Pomerantz 2006]. This measure involves a process for periodically replacing the supersaturated end-brine in contact with the reverse osmosis (RO) membrane with an undersaturated feed brine. This substitution works when the solution replacement is made prior to or shortly after the initiation of scaling via salt crystallization, and makes use of the fact that there is an induction time between reaching supersaturation and the start of scaling. By replacing the end-brine, the induction clock is effectively re-zeroed. Solution replacement can be accomplished without stopping the RO desalination process by simply reversing the flow so that RO feed now enters into the original concentrate (downstream) end of the RO train and the RO concentrate leaves from the original feed (upstream) end of

the RO train. A critical aspect of successfully implementing this process is knowledge of the induction time so that the flow-reversal step can be initiated at exactly the optimum point.

A diagram of the prototype flow-reversal system developed by Pomerantz et al. [2006] is shown in Figure 1.3. The feed flow initially enters the left side of pressure vessel PV1 and the concentrate exits the right side of pressure vessel PV3. Valve V-4 is closed and the three-way valves V-1 and V-2 are in the up position (flow permitted in the down direction, blocked in the up direction). All permeate and concentrate flows are recycled to the feed. When the flow is reversed, it enters PV3 from the right and the concentrate exits PV1 from the left. This is achieved by opening valve V-4, followed by moving valve V-2 to the down position and then moving valve V-1 to the down position. This sequence of events is performed so that there are no sudden pressure changes that could damage the membranes in the pressure vessels, i.e., the “water hammer” effect.

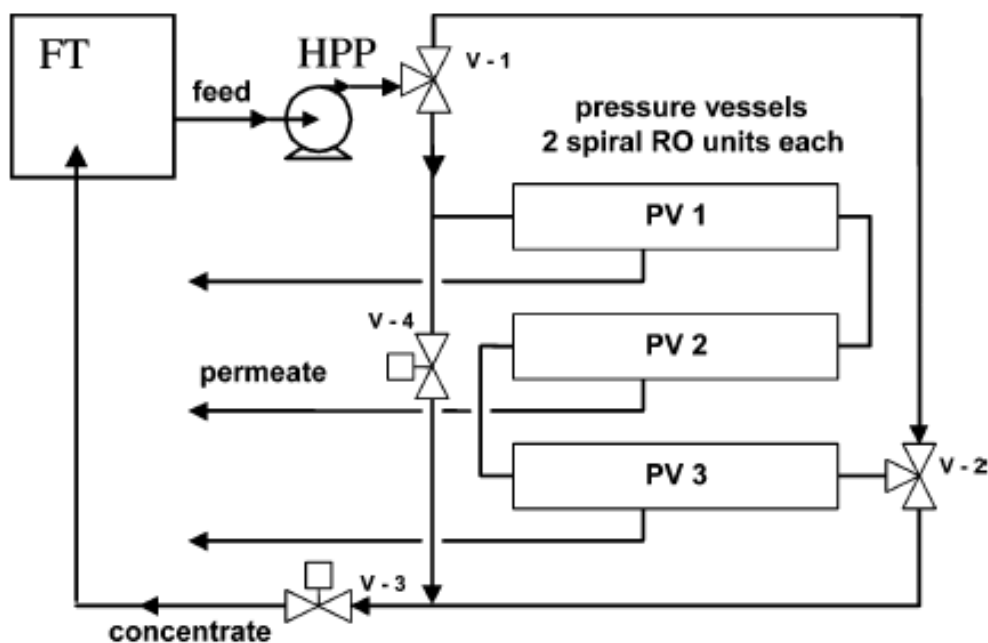


Figure 1.3: Schematic of flow-reversal desalination system for remediation of membrane scaling [Pomerantz 2006].

The availability of in-situ monitors for use in the membrane modules would provide reliable real-time sensing capability for determining exactly when to initiate the flow-reversal. The work presented in this thesis is focused on development of integrated electrolytic sensors for monitoring of concentration polarization, and integration of ultrasonic sensors for monitoring of early-stage scaling. These sensors could be employed as control elements within the flow-reversal scaling mitigation scheme. Although this thesis does not focus specifically on the flow-reversal process itself, aspects of the work were performed in collaboration with Dr. Gilron's group at Ben Gurion University, and are intended to serve as a tool for future implementation of the flow-reversal scheme.

1.4 Focus of This Research

The work presented in this thesis addresses the continuing need for improvements in real-time monitoring of concentration polarization and membrane condition during filtration processes. We investigate the use of two different monitoring schemes for making real-time observations of CP and early-stage scaling during nanofiltration of sparingly soluble salts. Dissolved calcium sulfate, which is commonly found in real-world desalination processes, was used as the model salt in the feed stream for all experiments described in this thesis. Integrated flexible MEMS electrolytic sensors were designed, fabricated and tested for characterization of the concentration polarization boundary layer near the membrane surface. Integrated ultrasonic transducers were used to detect early-stage scaling.

Industrial-scale desalination is an important application where real-time knowledge of scaling and feed concentration profile may have a significant impact on the overall process efficiency. In such applications, if these conditions can be monitored without interrupting the process, remediation measures can be carried out in a more timely fashion, resulting in the improvements in efficiency and corresponding economic savings. This, in turn, may open up many brackish water sources worldwide that are currently underutilized for economic and environmental reasons. This thesis demonstrates novel applications of two different classes of sensors for monitoring CP and scaling phenomena during

nanofiltration. Ultrasonic transducers were mounted internally into a flat sheet cross-flow module for the first time and responses were analyzed with a signal processing protocol that attempts to improve upon those reported in prior literature. One of the key goals of the work involving the ultrasonic transducers is to provide a reliable means to characterize the induction time between the introduction of the salt feed solution and the subsequent growth of scaling deposits on the membrane. The signal processing protocol was assessed to minimize the occurrence of false-positive or false-negative responses by correlation with appropriate post-mortem metrics (scaling area coverage, gravimetric measurement).

Previous studies have reported electrolytic monitoring of concentration polarization for separation of ions in aqueous feed solutions [Liu 1970, Zhang 2006]. These works, however, were performed in systems not representative of real desalination plants; they employed modules with tall flow channels under conditions where very thick, strong concentration polarization boundary layers would form (millimeters). The study with integrated flexible electrolytic sensors reported in this thesis attempts to build upon the previous works, but under more industrially realistic conditions. Although the work presented here was performed in a flat-sheet cross flow module, the sensors demonstrate strong potential for future testing within a spiral-wound module. The sensor must be thin to fit within a thinner flow channel with a thinner CPBL, and must be flexible so that it can be applied to other filtration module geometries, such as spiral-wound. These sensors could provide insights into the development of the concentration profile and serve as a trigger for remediation measures prior to the onset of scaling, by indicating locations of high supersaturation where precipitation is imminent. Additionally, electrolytic sensors could provide corollary information to complement the ultrasonic data, allowing for a more complete description of filtration phenomena.

As mentioned previously, concentration polarization and scaling represent a continuum in desalination processing. Significant work with ultrasonic transducers has been reported in the literature, but such ultrasonic methodology is not capable of detecting CP because of a lack of acoustic contrast and

resolution [Chai 2003]. This provides the motivation for using electrolytic sensors to monitor CP. These novel sensor applications and analysis methods can be applied as active control components in filtration systems, for indicating the optimal time to carry out remediation measures, such as that presented by Pomerantz et al. [2006]. However, in addition to serving as an engineering tool to be applied to industrial applications, these sensors can be used as tools in fundamental research on the development of concentration profiles and growth model of fouling layers. While there are many models explaining these phenomena, many fundamental details are still unclear [Kujundzic 2008]. These tools can be used to provide further experimental data to support or develop new or more detailed explanations on the mechanisms of CPBL and fouling growth. This work builds upon previous literature in the area of non-destructive monitoring of membrane separations and brings the technology another significant step closer to commercial application. The following points outline specific objectives of work conducted for this thesis:

- Implement a scheme for integrating miniature ultrasonic transducers internally into a working filtration module for monitoring of the onset of membrane fouling with greater sensitivity than the currently existing methods using externally mounted transducers.
- Develop an improved data acquisition and signal processing protocol for analysis of ultrasonic echo waveforms to improve detection capabilities.
- Fabricate thin flexible MEMS electrolytic sensors to characterize concentration polarization at the membrane surface during filtration of sparingly soluble inorganic dissolved salts.
- Develop an integration scheme for MEMS electrolytic sensors for operation in a working filtration module.
- Assess the degree to which the presence of the internally integrated sensors influence local filtration conditions, as determined by correlation of ultrasonic/electrolytic data with post-mortem metrics.
- Demonstrate suitability of real-time data from ultrasonic and electrolytic sensors for future use as active control elements in executing scaling remediation measures with optimal efficiency.

1.5 Organization of This Thesis

In Chapter 2 we review the literature on topics related to this thesis, including experimental and theoretical investigations into concentration polarization and fouling growth in filtration processes, as well as studies on non-destructive real-time monitoring of CP and fouling. Chapter 3 reports methodology and experimental results for work performed in this thesis involving integrated electrolytic sensors for monitoring concentration polarization very close to the membrane surface. In Chapter 4 we discuss the integrated ultrasonic sensor systems used to monitor early-stage growth of inorganic scaling on the membrane surface due to sparingly soluble salts. This includes presentation of the experimental methodology and discussion of results. Chapter 5 reviews the work presented in this thesis with analysis and discussion of important insights, and recommendations for future research in these areas are made. Additional software code and schematics not presented within the chapters can be found in the appendices.

Chapter 2

Literature Review

2.1. Overview

This thesis is focused on the development of integrated sensors for monitoring concentration polarization and scaling of sparingly soluble salts during membrane-based desalination. The goal of developing nondestructive methods for monitoring membrane filtration performance is to provide a tool that can be used to indicate when a system operator needs carry out scaling remediation measures. Optimization of the timing of such measures could result in significant improvements in overall system efficiency, thereby resulting in reduced operational costs. In fundamental scientific investigations, integrated sensors can be used to provide experimental evidence supporting or refuting various theories on CP and fouling phenomena. Such experimental information is important to further understanding these extremely complex processes.

This chapter presents a review of prior studies that have attempted to explain concentration polarization and membrane fouling phenomena under a variety of configurations. These configurations include dead-end and cross flow filtration, turbulent and laminar flow, as well as filtration of biological and inorganic components. In order to develop appropriate sensor systems for real-time monitoring of CP and fouling, an understanding of the fundamental principles is essential. After the discussion of theoretical principles behind CP and fouling, we review previous studies that have been conducted for real-time non-destructive observation. A review of these studies demonstrates the necessity of developing further sophisticated techniques which can be utilized in large-scale industrial filtration processes.

2.2. Modeling of Concentration Polarization

A review of the literature on concentration polarization (CP) is thus warranted as one component in developing integrated sensor systems for monitoring membrane-based filtrations. The development of CP is the precursor to the onset of fouling, and CP itself has a significant impact on the performance of membrane-based filtration systems. Mass transport in such separation systems is very complex, and many theoretical works have been presented to explain experimentally observed behavior. Models have been developed to describe systems with a wide variety of feed solution compositions (dissolved salts, colloidal particles, biological agents), under varying flow conditions (dead-end, laminar cross flow, turbulent cross flow), and in modules of differing geometry (dead-end batch cell, flat-sheet, hollow-fiber and spiral-wound modules). The goal of this section is to highlight major theoretical and modeling approaches that have been used to describe concentration polarization phenomena.

2.2.1. Fundamentals of Mass Transport in Filtration Systems

An analytical description of concentration polarization, under any flow conditions or in any given geometry, is based on the solution of the following system of coupled nonlinear equations: the continuity equation (conservation of mass, equation 2.1), The Navier-Stokes equation (equation of motion, 2.2), and the convection-diffusion equation (solute transport, equation 2.3).

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad (2.1)$$

$$\rho \left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) = -\nabla P + \mu \nabla^2 \vec{v} + \vec{F} \quad (2.2)$$

$$\frac{\partial C}{\partial t} = D_s \nabla^2 C - \vec{v} \cdot \nabla C \quad (2.3)$$

The continuity equation must be satisfied in order to ensure conservation of mass in the fluid flow. Here, ρ is the density of the fluid, t is time, and $\mathbf{v}$ is the velocity of the fluid. The Navier-Stokes equation is the equation of motion for fluid flow, enforcing conservation of momentum. Here, P is the pressure, μ is the dynamic viscosity, and $\mathbf{F}$ refers to body forces acting on the fluid, such as gravity or electromagnetic forces. The form of the Navier-Stokes equation given above is for incompressible flow, which is an acceptable approximation for the aqueous solutions considered in this thesis. The equation may be generalized for compressible flows, in which case the analysis and solution are more complicated. The convection-diffusion equation describes the transport of dissolved or suspended species in a fluid flow. Here, C is the concentration of the dissolved or suspended species and D_s is the diffusion coefficient of the given solute. The form of the equation above omits any sources or sinks in the control volume. All three of these equations must be solved simultaneously, presenting a challenging mathematical problem. In most realistic situations it is not possible to solve these equations in a simple closed form, and recourse must be made to simplifying approximations and numerical methods.

In describing the concentration polarization boundary layer (CPBL), the main work lies in setting the appropriate boundary conditions, making appropriate approximations and simultaneously solving these three coupled equations. The boundary conditions are dependent on the physical system geometry, which include assumed inlet and outlet flow conditions and solute/fluid conservation equations at physical boundaries. In this section we will consider some of the classical works that have yielded analytical and quasi-analytical solutions to the concentration polarization problem. These solutions apply for dead-end flow in an unstirred batch cell as well as for laminar and turbulent cross flow between semi-permeable parallel plates. Many of the fundamental concepts in the mathematical treatment of CP apply to reverse osmosis (RO) as well as ultra- and microfiltration (UF, MF). Several additional good reviews are available that outline developments in mathematical solutions to the concentration polarization

problem. See [Matthiasson 1980, Bruin 1980, Potts 1981, Belfort 1983, Fane 1987, Barger 1991, Vassilief 1992, Belfort 1994, Bowen 1995].

The flux through a membrane during desalination depends on the pressure difference across the membrane. When a solute concentration gradient develops near the membrane surface, osmotic pressure develops. This increases back-diffusion of the solute into the bulk feed solution. The back diffusion follows from Fick's Law of Diffusion, and the resulting reduction in net driving pressure correspondingly reduces permeate flux, according to equation 2.4.

$$J_v = A(\Delta P - \Delta \pi_w) \quad (2.4)$$

Where J_v is the fluid flux through the membrane, which is also often referred to as the wall velocity, v_w , A is the membrane permeability constant; in many cases, the pure water membrane permeability, L_p , is used interchangeably. ΔP is the driving pressure across the membrane, and $\Delta \pi_w$ is the osmotic pressure difference across the membrane, i.e. the difference between the osmotic pressure at the membrane surface (feed side) and that on the permeate side.

The following equations (2.5, 2.6) describe the rejection of salts by the membrane. No membrane perfectly rejects all salt ions; however, many types of nanofiltration (NF) and reverse osmosis (RO) membranes demonstrate rejections of ~99% or higher [Dow Water Solutions 2007]. This makes the assumption of perfect salt rejection acceptable in many models.

$$R_{true} = 1 - \frac{C_p}{C_w} \quad (2.5)$$

$$R_{obs} = 1 - \frac{C_p}{C_b} \quad (2.6)$$

Where R_{true} is the true solute rejection coefficient with respect to the local wall concentration, C_w (membrane surface), R_{obs} is the observed solute rejection coefficient with respect to the bulk feed concentration, C_b . C_p is solute concentration in the permeate solution. It is very simple to calculate the observed rejection from experimental data. However, most models describing the CP phenomena aim to describe the true behavior at the membrane surface, where making direct observations is much more difficult.

Using the preceding equations, a solution of the convection-diffusion equation gives the following solution for concentration polarization, where CP is the concentration polarization factor, $\Delta\pi_m$ is the osmotic pressure at the membrane surface, $\Delta\pi_b$ is the osmotic pressure in the bulk feed and k_d is the mass transport coefficient:

$$CP = \frac{\Delta\pi_m}{\Delta\pi_b} = (1 - R_{obs}) + R_{obs} \cdot \exp\left(\frac{J_v}{k_d}\right) \quad (2.7)$$

2.2.2. Unstirred Batch Cell

The simplest geometry to consider is the unstirred batch cell. Fluid fills a chamber and is pressurized either by a piston or a pump, where fluid is forced through the membrane. This configuration is also often called a dead-end cell. A schematic of such a cell is shown in Figure 2.1.

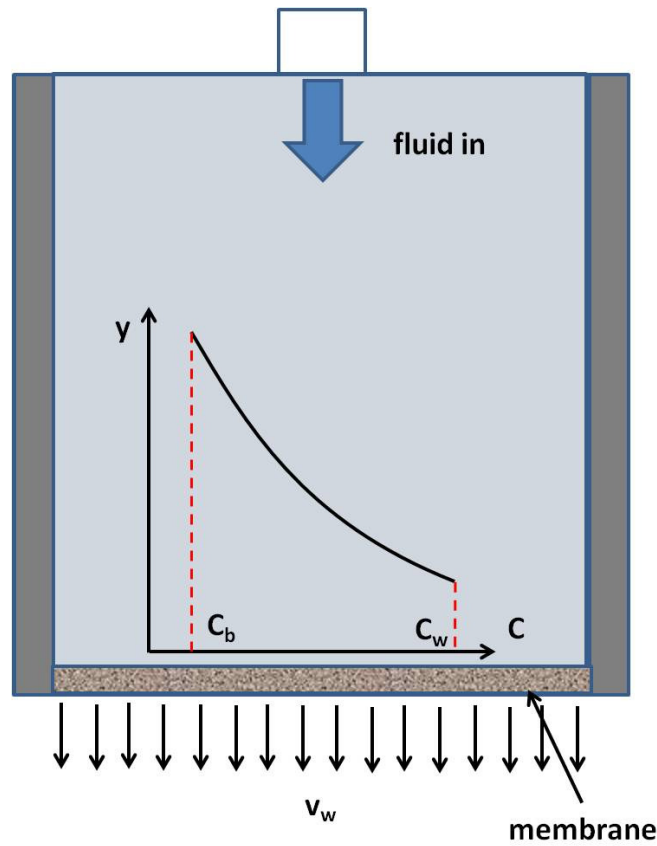


Figure 2.1: Schematic of an unstirred batch cell. C_b is the bulk solute concentration and C_w is the concentration at the membrane surface.

In the unstirred batch cell, it is generally assumed that there is no change in solute concentration far from the membrane surface; the concentration is that of the bulk solution and a concentration polarization boundary layer is clearly defined, yielding a semi-infinite system. Thus, the continuity of solute is expressed in the following one-dimensional form of the convection-diffusion equation:

$$\frac{\partial C}{\partial t} - v_w \frac{\partial C}{\partial y} = D_s \frac{\partial^2 C}{\partial y^2} \quad (2.8)$$

With the following boundary conditions:

$$C = C_b \text{ for } y \geq 0 \text{ at } t \leq 0 \quad (2.9)$$

$$C = C_b \text{ for all } t \text{ at } y \rightarrow \infty \quad (2.10)$$

$$v_w C_w + D \frac{\partial C_w}{\partial y} = (1 - R) v_w C_w \quad (2.11)$$

The term C in equation 2.8 is the concentration as a function of position, y , and time, t . v_w is the transverse fluid velocity at the membrane surface (also J_v , the permeate flux). Equation 2.9 states that the concentration is uniformly at the bulk level at the beginning of filtration. Equation 2.10 states that the concentration is that of the bulk far from the membrane at all times. Equation 2.11 represents the solute mass balance at the membrane surface.

Dresner was one of the first authors to present a thorough theoretical analysis of this type of system [1964]. Perfect rejection by the membrane was assumed, with constant permeate velocity, and the effect of osmotic pressure was neglected, i.e., $\Delta\pi_w = 0$. Laplace transformations of the governing convection-diffusion equation were used, yielding the following closed-form solution:

$$\frac{C_w}{C_b} - 1 = 1 - \left(1 + \frac{\tau}{2}\right) \operatorname{erfc}\left(\frac{\sqrt{\tau}}{2}\right) + \sqrt{\frac{\tau}{\pi}} e^{-\tau/4} + \tau \quad (2.12)$$

Where τ is a non-dimensionalized time parameter:

$$\tau = \frac{v_w^2 t}{D_s} \quad (2.13)$$

The error function is defined as:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (2.14)$$

And the complementary error function is defined as:

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) \quad (2.15)$$

Dresner's work was a first attempt at a closed-form analytical solution to the concentration polarization boundary layer problem, but the assumption of negligible osmotic pressure is clearly unrealistic in many practical situations. Although no membrane is perfect, the assumption of a perfect rejection coefficient, $R_{true} = 1$, significantly simplifies the solution and can be considered appropriate where rejections are very high. Later theoretical approaches built upon Dresner's work developed more sophisticated models accounting for both osmotic pressure effects and imperfect rejection.

Raridon et al. [1966] extended Dresner's analysis, again using a Laplace transform approach. In this work, though, non-ideal membrane rejection was accounted for through the solute continuity boundary condition at the membrane surface. Raridon's analysis assumed constant permeate velocity rather than constant applied pressure. Development of osmotic pressure would lead to a reduction of flux if constant applied pressure were assumed. Raridon showed that the calculated concentration polarization increased more quickly (in non-dimensionalized time) at lower values of R . The results matched well with experimental values, and with Dresner's calculated values at $R = 1$. The resulting solution is equation 2.16:

$$\begin{aligned} \frac{C_w}{C_b} - 1 = & \frac{1}{1 - R_{true}} \left[R_{true} - k(2R_{true} - 1)e^{tR_{true}(R_{true}-1)} \right] + \\ & \frac{1}{2(1 - R_{true})} \left[(2R_{true} - 1)e^{tR_{true}(R_{true}-1)} \operatorname{erfc}\left(\frac{\sqrt{t}}{2}(2R_{true} - 1)\right) - \operatorname{erfc}\left(\frac{\sqrt{t}}{2}\right) \right] \end{aligned} \quad (2.16)$$

Where $k = 1$ for $R_{true} \geq 0.5$ and $k = 0$ for $R_{true} < 0.5$.

Liu and Williams [1970] generated a solution that built upon those presented by Raridon et al. [1966] and Dresner [1964], using Laplace transform and integral methods. Both imperfect solute rejection and osmotic pressure were taken into account. In this theoretical development, the fluid in the filtration cell was considered to be under constant applied pressure, with the development of osmotic pressure and permeate flux rate being calculated as a function of time for various assumed membrane rejection values. It was demonstrated that the theory matched experimental values for short and asymptotic times, but at intermediate time ranges it did not match well (within 10%).

$$\begin{aligned} \frac{C}{C_0} = & 1 + \frac{R_{true}}{2(1-R_{true})} e^{-\eta'} \operatorname{erfc}\left(\frac{\eta'}{2\sqrt{\tau'}} - \frac{\sqrt{\tau'}}{2}\right) - \frac{1}{2} \operatorname{erfc}\left(\frac{\eta'}{2\sqrt{\tau'}} - \frac{\sqrt{\tau'}}{2}\right) - \\ & \frac{2R_{true}-1}{2(1-R_{true})} \exp(-R_{true}\eta' - R_{true}(1-R_{true})\tau') \operatorname{erfc}\left(\frac{\eta'}{2\sqrt{\tau'}} - (2R_{true}-1)\frac{\sqrt{\tau'}}{2}\right) \end{aligned} \quad (2.17)$$

Where:

$$\eta' = \frac{A(\Delta P)y}{D_s} \left(1 - R_{true} \frac{\pi_0}{\Delta P}\right) \quad \text{and} \quad (2.18)$$

$$\tau' = \frac{A^2(\Delta P)^2 t}{D_s} \left(1 - R_{true} \frac{\pi_0}{\Delta P}\right)^2 \quad (2.19)$$

Bellucci and Pozzi [1975] took a similar approach, by converting the continuity and convection-diffusion equations into an integral form and using Laplace Transforms. Approximate numerical and analytical solutions were then calculated based on this integral form of the governing equation. Perfect rejection by the membrane was assumed; however permeate velocity and osmotic pressure were allowed to vary. The integral form of the governing equation could be expanded in series, in terms of the time variable, in order to obtain accurate numerical results for small times. The numerical solution was compared with the exact analytical solution for the case of no osmotic pressure, which can be solved in

closed form, and the match was good over all time values. Through this analysis, an approximate solution was developed, showing good matching between the solution for small values of y (vertical position), and the asymptotic solution for large values of y . The solution is given in equation 2.20:

$$\frac{C}{C_b} - 1 = \frac{1 - \frac{\pi_b}{\Delta P}}{\frac{\pi_b}{\Delta P}} \left[\operatorname{erfc} \left(\frac{y}{2\sqrt{\tau'}} \right) - \exp \left(\frac{\pi_b}{\Delta P} y + \left(\frac{\pi_b}{\Delta P} \right)^2 \tau' \right) \operatorname{erfc} \left(\frac{\pi_b}{\Delta P} \sqrt{\tau'} + \frac{y}{2\sqrt{\tau'}} \right) \right] \quad (2.20)$$

Where:

$$\tau' = [(\Delta P)A]^2 \frac{t}{D_s} \quad (2.21)$$

It is interesting to note that the term τ' , the non-dimensionalized time parameter, is similar to that used by Dresner [1964]. Here, however, it directly incorporates the applied pressure and the membrane constant terms. This distinction is important to note, since the solution here explicitly accounts for a variable permeate flux velocity, as opposed to Dresner's solution that assumed constant flux.

2.2.3. Laminar Cross Flow

The solution to the concentration polarization problem is much more complicated when a tangential cross flow over the semi-permeable membrane is present. In this situation, the Navier-Stokes equation (equation of motion, equation 2.2) must now be solved in addition to the continuity and convection-diffusion equations. Several different approaches have been taken to theoretically describe the form of the concentration polarization boundary layer (CPBL) for the case of laminar cross flow. The simplest case to consider is that of flow between two semi-permeable plates.

In addition to his analysis of the concentration profile in an unstirred batch cell, Dresner [1964] performed theoretical calculations of the concentration profile with a laminar cross flow between two semi-permeable parallel plates. In this analysis, the rejection coefficient of the membranes was assumed to be unity, and the permeation velocity was assumed constant along the entire length of the membrane (Figure 2.2). A fully developed velocity profile was assumed to exist at the entrance of the flow channel. This velocity profile had been calculated by Berman [1953] for simple flow in a parallel plate channel with fluid passing through membranes of a given permeability (equations 2.22 and 2.23), and thus was used by Dresner as a boundary condition for the governing equations. Dresner's solution approach used Laplace transforms, in a similar fashion to the unstirred batch cell, but now accounting for the axial flow in the Navier-Stokes and convection-diffusion equations. Under most typical laminar cross flow conditions, the axial diffusion term can be neglected, being greatly outweighed by the convective term. This assumption helps simplify the problem so that a solution can be found, and is applied in all the works analyzing systems with cross flow.

$$u(x, y) = \frac{3}{2} \left[u_{avg}(0) - \frac{v_w x}{h} \right] \left(1 - \frac{y^2}{h^2} \right) \quad (2.22)$$

$$v(y) = \frac{v_w y}{2h} \left(3 - \frac{y^2}{h^2} \right) \quad (2.23)$$

Here, u is the axial velocity as a function of axial (x) and transverse (y) position. v is the transverse fluid velocity, assumed to be independent of axial position, and h is the flow channel half-height. In practical systems, the flow rate transverse to the membrane is very small compared to the axial flow, so this component can be neglected and still yield reasonably accurate results using the Poisseuille flow profile between two infinite plates [Dresner 1964]. This analysis yielded the following results for three axial regions within the flow channel (equations 2.23, 2.24, and 2.25, respectively). The defined ranges for the

non-dimensionalized length term, ξ , correspond to different axial regions within the rectangular flow channel.

$$\frac{C_w}{C_b} - 1 = 1.536\xi^{1/3} \quad \text{for } \xi \leq 0.02 \quad (2.24)$$

$$\frac{C_w}{C_b} - 1 = \xi + \left[1 - \exp\left(-\sqrt{\frac{\xi}{3}}\right) \right] \quad \text{for } \xi > 0.02 \quad (2.25)$$

$$\frac{C_w}{C_b} - 1 = \frac{v_w^2 h^2}{3D_s^2} \quad \text{for } \xi \rightarrow \infty \quad (2.26)$$

Where:

$$\xi = \frac{v_w^3 x h}{3u_{avg}(0)D_s^2} \quad (2.27)$$

Sherwood et al. [1965] also performed a theoretical analysis of the concentration profile for laminar flow between two semi-permeable membranes. Again, the inlet velocity profile was assumed to be fully developed [Berman 1953], where flow transverse to the membrane is much smaller than cross flow. The membrane was assumed to be impervious to salt ($R = 1$), with constant flux over the entire membrane length. Sherwood utilized a series expansion of the governing convection-diffusion equation, using the Berman velocity profile, and the results were calculated numerically. The numerical results were found to be in good agreement with the analytical results of Dresner [1964]. Sherwood's method represented an alternative numerical technique to solve the laminar flow CP problem with the same starting assumptions.

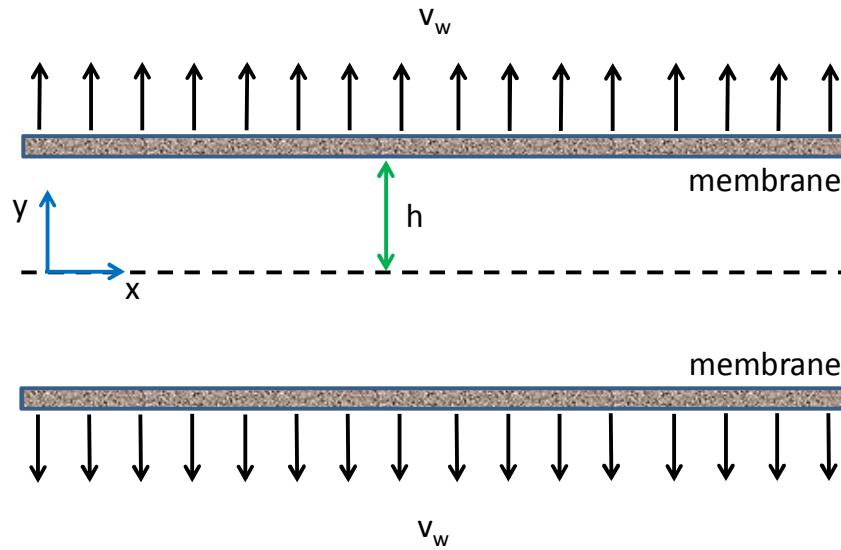


Figure 2.2: Schematic of flat-sheet filtration geometry and permeate velocity in analyses performed by Dresner [1964] and Sherwood et al. [1965].

Gill et al. [1965] were among the first to consider RO filtration between parallel semi-permeable plates with variable the permeate flux (v_w). The approach was similar to that employed in the analyses for unstirred batch cells where permeation velocity was not constant with time. A constant driving pressure was applied, and osmotic pressure was allowed to develop at the membrane surface. This is a more realistic assumption for practical RO systems. It differed from the situation in the unstirred batch cell in that the shear from the cross flow allows a steady-state concentration profile to develop. This nominally does not change after it is established. In the model by Gill et al., the membrane rejection was assumed to be perfect ($R = 1$). Again, the entrance velocity profile was assumed to be fully developed with a small transverse component [Berman]. The analysis utilized a perturbation series expansion based on an assumed series expansion form of the concentration, which is found in the governing convection-diffusion equation (equation 2.3). The permeate flux was also related to the concentration and osmotic pressures by equation 2.4.

$$C(x, y) = \sum_{k=0}^{\infty} C_k(x, y) \left(\frac{\pi_b}{\Delta P} \right)^k \quad (2.28)$$

$$v_w(x) = A \left(\Delta P - \pi_b \frac{C_w(x)}{C_b} \right) \quad (2.29)$$

This flux profile demonstrates the assumed linear relation between concentration and osmotic pressure. The calculations by Gill et al. showed that the previous models assuming constant wall velocity tended to overestimate the local concentration polarization at downstream locations. This is particularly the case when the assumed constant transverse velocity over the channel length is that at the inlet. In real systems, the transverse velocity decreases with axial position due to permeate fluid loss through the membrane. Gill et al. used a series perturbation method to numerically calculate the membrane wall concentration values, and found the relation for the inlet region to match reasonably well with the results presented by Dresner [1964].

Brian [1965] started with the fully developed velocity profiles of Berman [1953], as in all of the other previously described works, also allowing for variable transverse wall velocity as a function of axial position. The shape of the axial velocity is parabolic, as in simple Poiseuille flow, but it was modified at different axial positions according to a factor accounting for water withdrawal through the membrane as it flowed through the channel. Constant volumetric flux at the inlet was assumed. The membrane rejection was also assumed to be imperfect with variable R_{true} . The permeation flux rate is known through the relation between driving pressure and the osmotic pressure at the membrane surface (equation 2.4), which is linearly related to the calculated concentration. The pertinent differential equations were then solved using a finite difference method on a computer. In the case of an assumed constant permeate flux, the finite difference results showed excellent agreement with previous infinite series solutions [Sherwood 1965], lending confidence to the method. Qualitatively, the calculated results showed the salt

concentration increasing rapidly at the beginning of the channel due high permeate flux, but leveling off further downstream as the flux declines due to increasing concentration. A comparison was made between the variable flux model and that using a constant flux. The assumed constant flux was the average of the variable flux rate profile. Although the local concentration polarization differed between the two cases, the average concentration over the whole membrane length was similar. This showed that the simpler methods employed previously have utility in preliminary system design.

Srinivasan et al. [1967] developed a model similar to that of Brian [1965] for flow between two semi-permeable flat plates in which the velocity and concentration profiles were simultaneously solved. See Figure 2.3. As opposed to the previously described studies, Srinivasan assumed a uniform (flat) axial velocity and concentration profile at the entrance to the flow channel. Thus, consideration was given to the entrance region over which the momentum as well as concentration boundary layers developed. Perfect salt rejection by the membrane was assumed. One key assumption was that the concentration profile in the transverse direction takes a quadratic form at all given axial positions. In Figure 2.3, it is shown that the momentum boundary layer is much thicker than the concentration boundary layer. This is because the Schmidt number (ratio of kinematic viscosity to mass diffusivity of the salt) is large. In this work, Srinivasan developed two differential equations for the form of the momentum boundary layer and the concentration boundary layer, which must be simultaneously solved, given the appropriate boundary conditions. Equation 2.30 is the differential equation to solve for the momentum boundary layer and equation 2.31 is the differential equation to solve for the concentration boundary layer. Initial solutions can be found at small x , which then serve as a starting point for numerical calculation of the solution at larger x . This is necessary because calculations at $x = 0$ are indeterminate. The solutions are then found until the momentum boundary layer is fully developed, i.e. $\Delta = h$. This means that the two momentum boundary layers from the top and bottom membranes meet at the center of the channel. At this point, because $\partial \Delta / \partial y = 0$, some modification to the numerical scheme is required. This modified calculation

then continues until $\delta = h$, meaning the concentration polarization boundary layer has fully developed.

Equation 2.32 applies for this region.

For the region where the momentum boundary layer is developing:

$$\frac{\partial \Delta'}{\partial x} = \frac{\frac{2}{\Delta'} + v_w' \left(\frac{9}{5} \frac{\Delta'}{3 - \Delta'} - 1 \right)}{\left(\frac{1 - \int_0^{x'} v_w' dx'}{3 - \Delta'} \right) \left(\frac{2}{5} + \frac{9}{5} \frac{\Delta'}{3 - \Delta'} \right)} \quad (2.30)$$

$$\frac{\partial \delta'}{\partial x'} = \frac{\left[\frac{12(1-a_1)}{Sc} \frac{\Delta'^2}{\delta'} - 6v_w' \Delta'^2 (1-a_1) + \delta'^2 \bar{U}' (1-a_1) \frac{\partial \Delta'}{\partial x'} - (1-a_1) \delta'^2 \Delta' \frac{\partial \bar{U}'}{\partial x'} \right]}{\bar{U}' \delta' \Delta' [2(1-a_1) - \delta' \phi(\delta')]} \quad (2.31)$$

For the region after the momentum layer has fully developed:

$$\frac{\partial \delta'}{\partial x'} = \frac{\left[\frac{12(1-a_1)}{(Sc)(\delta')} + \frac{B_1}{Sc} (1-B_2 a_1) (1-a_1) \left(\frac{3}{2} \delta'^2 - 6 \right) \right]}{\bar{U}' \delta' [2(1-a_1) - \delta' \phi(\delta')]} \quad (2.32)$$

Here, Δ' is the non-dimensional thickness of the momentum boundary layer, v_w' is the non-dimensional permeate flux rate at the membrane surface, x' is the non-dimensional axial position, Sc is the Schmidt number of the dissolved salt in water, a_1 is a coefficient in the assumed parabolic form of the transverse concentration profile, δ' is the non-dimensional thickness of the concentration polarization boundary layer, $B_1 = A(\Delta P)h/D_s$, $B_2 = \pi_b/(\Delta P)$, $\bar{U}'$ is the non-dimensionalized core axial velocity, and $\phi(\delta')$ is a function of δ' , which is solved according to equation 26 in [Srinivasan 1967].

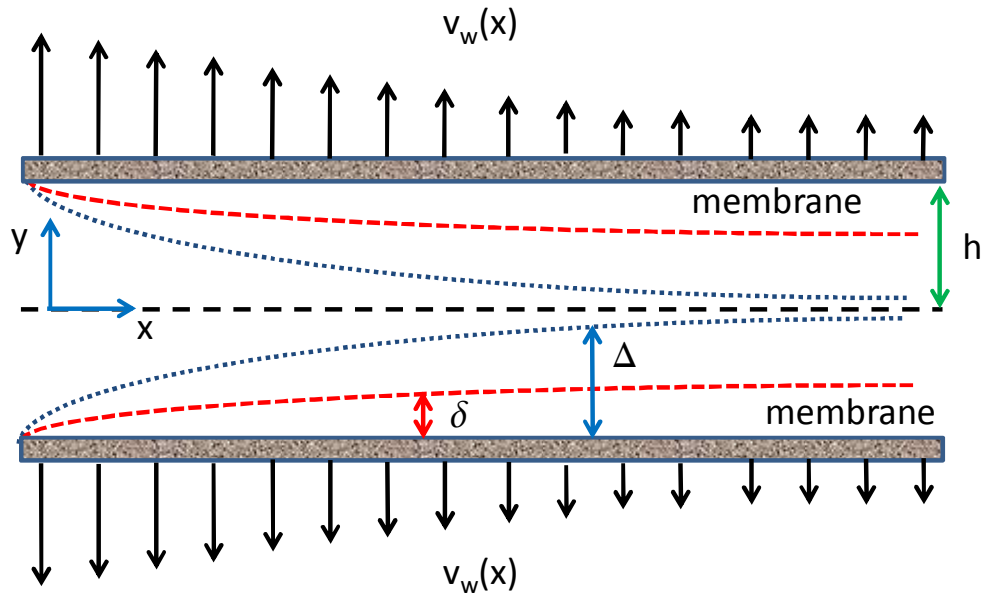


Figure 2.3: Geometry of flat sheet module and variable permeation velocities/concentration profiles analyzed by Srinivasan et al. [1967]. δ (dashed lines) represents the thickness of the concentration polarization boundary layer, and Δ (dotted lines) represents the thickness of the velocity momentum boundary layer.

Several papers have been written that address the microscopic phenomena occurring in mass transport through the membrane, and how this manifests itself in the form of concentration polarization. One of the key issues in such an analysis is that the value of the rejection is no longer considered a constant, but rather depends on the local conditions. The magnitude of the rejection then in turn influences the local conditions. Therefore, ion and solvent transport through the membrane and the development of concentration polarization in the feed stream are coupled phenomena. Bhattacharjee et al. [2001] presented such a coupled model in order to determine the concentration profile during cross-flow nanofiltration of a ternary ionic feed solution. Figure 2.4 demonstrates the basic concept of the CP/pore-transport interdependence.

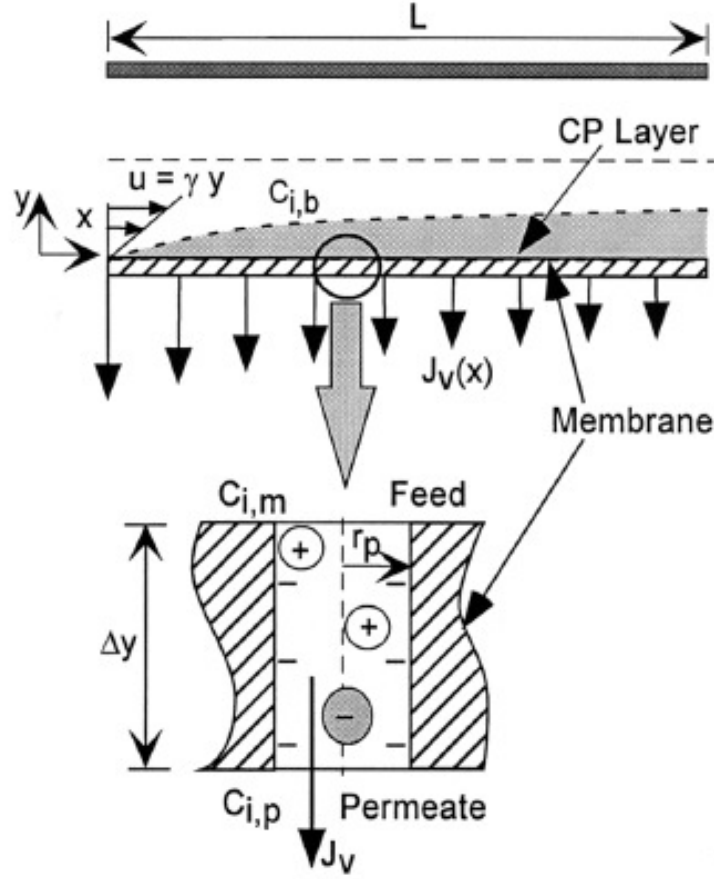


Figure 2.4: Schematic demonstrating interdependence of coupled concentration polarization and pore transport models for cross flow filtration. The top section of the figure represents concentration polarization as a function of axial position in the flow channel. The bottom section of the figure depicts ion transport through the pores [Bhattacharjee 2001].

Computational simulations were performed to calculate the rejection of an aqueous solution containing NaCl and Na₂SO₄ salts, which yields three types of solute ions: Na⁺, Cl⁻, SO₄²⁻. It was assumed that the solution is dilute and that the ions are non-interacting. Thus, the following equations can be used to set boundary conditions:

$$R_i v_w C_{i,w} = -D_{s,i} \frac{\partial C_i}{\partial y} \text{ at } y = 0 \quad (2.33)$$

$$\sum_i z_i C_i = 0 \quad (2.34)$$

$$v_w = L_p (\Delta P - \sigma_0 \Delta \pi_w) \quad (2.35)$$

Equation 2.33 represents the mass balance of each solute component, i , at the membrane surface, with the left-hand side representing convective transport and the right-hand side representing back-diffusion to the bulk solution. Equation 2.34 enforces electroneutrality of all ions in the solution, where z_i is the valence of ion i . Equation 2.35 is the standard equation for the permeate flux through the membrane as a function driving pressure and membrane surface osmotic pressure. The term σ_0 is an osmotic reflection parameter, accounting for non-idealities in the rejection. L_p is the pure water permeability of the membrane (similar to the membrane constant A in equation 2.4). These equations deal with the concentration and flow profile in the feed stream. They are then coupled to the intrinsic rejection by the membrane pores, for each given ion in the solution, by means of the extended Nernst-Planck Theory. This theory accounts for transport and resistance mechanisms for flow through nanoscale pores, which are modeled as small tubes with diameters on the order of a few nanometers. The physical process is modeled as a 1D transport problem accounting for convective, steric, and electric effects on the transport of the ions through the membrane. The fundamental equation used by Bhattacharjee for calculating intrinsic rejection is the following:

$$j_i = -D_{s_hindered,i} \frac{\partial c_i}{\partial y_{pore}} + K_{hindered,i} c_i v_w - \frac{z_i c_i D_{s_hindered,i} F}{RT} \frac{\partial \psi_m}{\partial y_{pore}} \quad (2.36)$$

Where j_i is the flux of ion i through the pore, c_i is the ionic concentration within the pore as a function of position, y_{pore} is the position coordinate within the pore, $D_{s_hindered,i}$ is a hindered diffusion coefficient for ion i within the constrained volume of the pore, $K_{hindered,i}$ is a convective hindrance factor, F is the Faraday constant, R is the ideal gas constant, T is the temperature, and $\partial \psi / \partial y_{pore}$ is the electrical potential gradient within the pore. This equation is used to calculate local rejection, which is then coupled to equation 2.33. The solution to the problem involves matching boundary conditions at the membrane-surface/pore inlet,

and simultaneously solving the convection-diffusion and Nernst-Planck equations, yielding a local 1D mass transport profile. Solutions along the axial direction are then iterated using continuity and conservation of solute between neighboring locations. The simulation solution matched well with previously reported experimental data in the literature.

Similar analyses based on microscopic transport mechanisms have been performed to analyze the form of concentration polarization. These are based on varying assumptions concerning module geometry, cross flow conditions, and mass transport kinetics, and typically use computational schemes developed in-house to generate solutions. See [Déon 2007, de Pinho 2002, Geraldès 2007]. Work has more recently been conducted using commercial computational fluid dynamics (CFD) packages, including *FLUENT* [Ahmad 2005] and *Ansys CFX* [Lyster 2009].

2.2.4. Turbulent Cross Flow

Sherwood et al. [1965] presented a theoretical treatment of the concentration polarization boundary layer when the cross flow is turbulent. This is based on the Nernst film theory model, which serves as a first and most simple description of the mass transport phenomena near the membrane surface. This method, in fact, yields a simpler analysis than that of a fully developing boundary layer found under laminar flow. In the Nernst film theory model, it is assumed that a very thin film of laminar flow is found at the surface of the membrane, caused by the no-slip boundary condition. At transverse locations above this film, the cross flow is turbulent and the concentration is assumed to be constant due to mixing. All resistance to solvent transfer to the membrane thus takes place across the thin laminar film. Figure 2.5 shows this concept schematically.

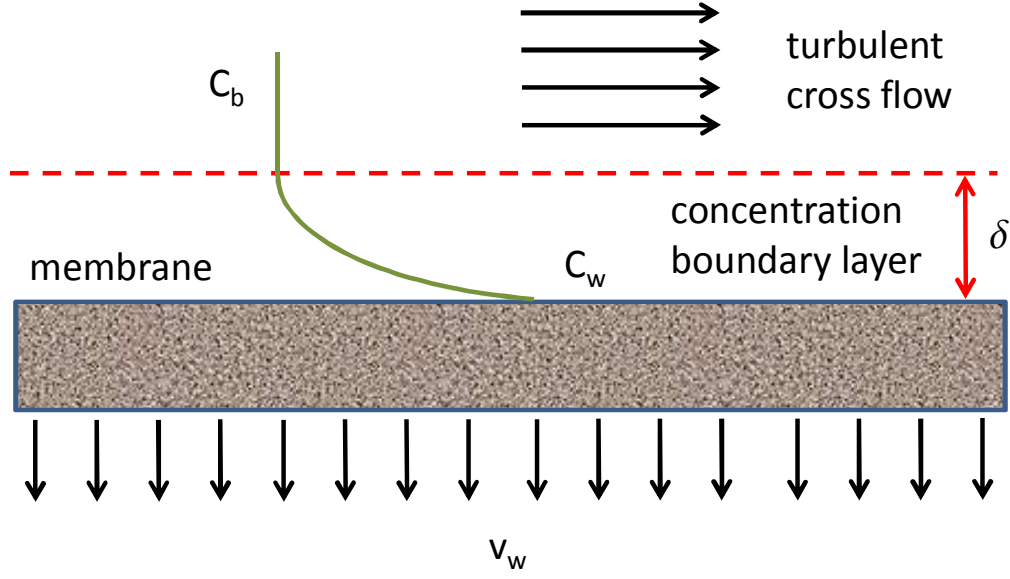


Figure 2.5: Schematic of flow and concentration profile for turbulent flow near the membrane surface in modeling using Nernst thin film theory.

In this model, mass transport is considered one-dimensional (transverse to the membrane), and occurs by convection and diffusion. No turbulence is present within the concentration boundary layer, $y < \delta$. Because the film is considered to be very thin compared to macroscopic membrane geometry, it can be applied to membranes which may not be in a flat-sheet configuration, such as spiral-wound and hollow-fiber. Simple local planar geometry can be assumed for the CP analysis.

The solution of the governing 1D convection-diffusion equation for the thin-film model is given as:

$$\frac{C_w}{C_b} = \exp\left(\frac{v_w \delta}{D_s}\right) = \exp\left(\frac{v_w}{k}\right) \quad (2.37)$$

With:

$$k = \frac{D_s}{\delta} \quad (2.38)$$

Since the boundary layer thickness, δ , cannot typically be measured directly, the experimentally determined mass transfer coefficient, k , is used. Common relations for mass transfer coefficients can be found in [Perry 1950, Sherwood 1952, Bird 1960].

Matthiasson and Sivik [1980] present an equation modifying this simplified concentration relationship in the case of imperfect membrane rejection. The passage of salt through the membrane is accounted for in the mass-balance boundary condition at the membrane surface, and yields the following result:

$$\frac{C_w}{C_b} = \frac{\exp\left(\frac{v_w \delta}{D_s}\right)}{R_{true} + (1 - R_{true}) \exp\left(\frac{v_w \delta}{D_s}\right)} \quad (2.39)$$

The simple Nernst thin film model neglects that eddy diffusion actually does occur within the boundary layer. Gill et al. [1971] took this into account and generated the following formulation for the concentration profile (equation 2.40). The relation used to describe the eddy diffusivity is found in [Gill 1961].

$$\frac{C_w}{C_b} = \frac{\exp\left(\frac{\pi v_w Sc^{3/4}}{2n_1 f^{1/2} U_b}\right)}{R_{true} + (1 - R_{true}) \exp\left(\frac{\pi v_w Sc^{3/4}}{2n_1 f^{1/2} U_b}\right)} \quad (2.40)$$

Here Sc is the Schmidt number, n_1 is a constant used in the formulation, f is the Fanning friction factor found for the flow in the laminar layer (from the Blasius relation to the Reynolds number), and U_b is the bulk cross flow velocity. Further works involving theoretical models of turbulent concentration polarization can be found in the review by Matthiasson and Sivik [1980].

2.3. Modeling of Fouling

2.3.1. Fundamentals of Fouling

In the previous section we discussed various theoretical descriptions of the forms concentration polarization may take under different operating conditions and module geometries. In many of these cases, general descriptions can apply to different types of filtration processes, such as ultra- and microfiltration of particulates and colloids, or reverse osmosis and nanofiltration of dissolved inorganic salts. In most cases, the descriptions of the concentration profiles apply to solutions that are relatively dilute. Over the course of the filtration process, however, material will deposit on the membrane surface and block pores. This may be due to gradual pore blockage by adsorption, or may occur when the solute exceeds a certain concentration limit. The result is the formation of a fouling layer, and developing means to prevent or control fouling pose one of the greatest challenges in industrial filtration processes. In this section we discuss some of the typical forms of fouling that occur, and mathematical methods of predicting fouling development and the effect on permeate flux. The theories underlying the formation and growth of these different types of layers vary, but the end effect is that all reduce permeate flux and process efficiency. The concept of ‘resistance in series’ is important in the analysis of the effect of fouling on permeate flux behavior. Different forms of fouling will cause different behaviors, and the goal is determining an expression to describe the resistance, for each mechanism. The following equation demonstrates this concept [Carrère 2000].

$$J = \frac{\Delta P}{\mu(R_m + R_a + R_c + R_{cp})} \quad (2.41)$$

Where J is the permeate flux, ΔP is the trans-membrane pressure, μ is the fluid viscosity, R_m is the pure-water membrane resistance, R_a is the resistance of adsorbed species on the membrane, R_c is cake layer resistance, and R_{cp} is resistance due to concentration polarization. R_{cp} can also be replaced by subtracting

osmotic pressure due to concentration polarization from the driving pressure in the numerator. The following sections discuss some of these fouling mechanisms and how they have been analyzed.

2.3.2. Micro- and Ultrafiltration

Micro- and ultrafiltration utilize appropriately sized pores in the membrane to form a sieve for removing large molecules and particulates. Microfiltration (MF) membranes typically contain pores ranging from 0.1 μm to 10 μm , and operate at relatively low pressures. Ultrafiltration works in the same way, but typically has smaller pores (1 nm to 100 nm) for separating smaller particles and macromolecules [Osada 1992].

A few significant methods have been developed to model fouling during ultrafiltration and microfiltration, yielding phenomenological relations involving constants that must be determined from empirical data. These data depend of the material properties of the membrane, the solvent, and the foulant, as well as operating conditions. Many of these analyses are reduced to determining the permeate flow by Darcy's Law, which in its fundamental form is the following [Bolton 2006]:

$$Q = \frac{PA}{\mu R} \quad (2.42)$$

Where Q is the volumetric flow rate, P is the trans-membrane pressure, R is the resistance to flow, A is the area through which permeation occurs, and μ is the solution viscosity. The key to this problem is then to determine the form the resistance takes and whether constant pressure or constant flow rate boundary conditions are present.

2.3.2.1. Standard Blocking Model

In the standard blocking model, it is assumed that the pores through the membrane are cylindrical and straight, and that solid matter accumulates on the pore walls over the course of a filtration. This

constriction reduces the diameter of the pores, thus increasing the resistance to flow. Grace [1956] was one of the first to explore this model and later significant work utilizing this model was presented by Hermia [1982]. These studies assumed that the amount of deposition on the inner walls of the cylindrical pores was a function of the volume of fluid processed; thus, the membrane resistance could be calculated as a function of time:

$$R = R_0 \left(1 + \frac{K_s J_0 t}{2} \right)^2 \quad (2.43)$$

Here, R_0 is the initial resistance to filtration at time 0, J_0 is the initial permeate flux, K_s is an empirical standard blocking coefficient, and t is time.

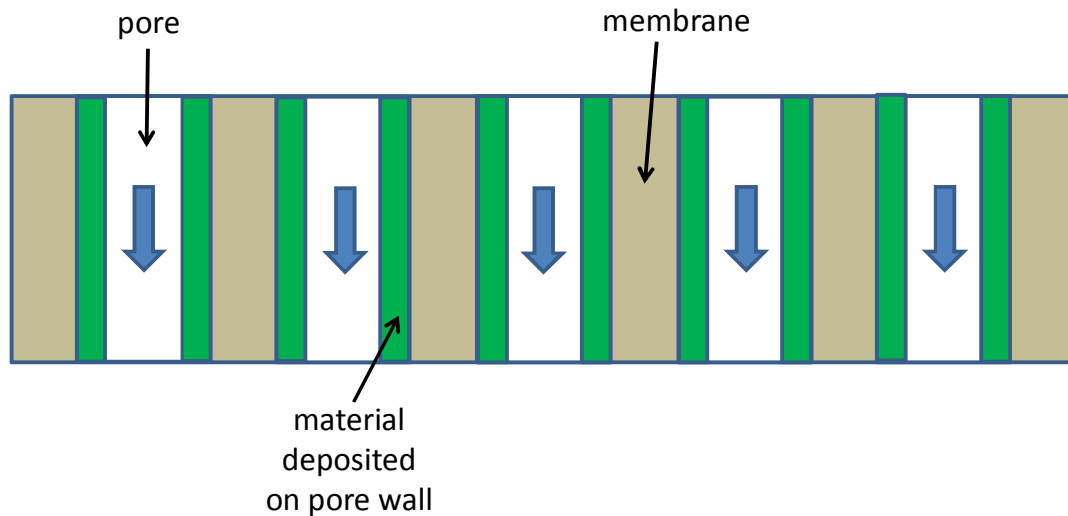


Figure 2.6: Schematic of standard blocking model for membrane fouling during ultra- and microfiltration.

2.3.2.2. Intermediate and Complete Blocking Models

Hermia [1982] also considered intermediate and complete blocking mechanisms as means to describe fouling in micro- and ultrafiltration. These mechanisms assume that as more feed solution is processed, increasing areas of the membrane become completely impermeable due to pore blockage.

Equations 2.43 and 2.44 relate permeable area reduction versus processed fluid volume for these two mechanisms. Both terms represent the same physical mechanism, area blockage, but are represented by different mathematical forms (linear and exponential). Equation 2.44 is the complete blocking model, and Equation 2.45 is the intermediate blocking model, both for constant pressure operation. These fouling mechanisms can also be referred to as the surface blockage model.

$$\frac{A}{A_0} = 1 - \frac{K_b}{J_0} V \quad (2.44)$$

$$\frac{A}{A_0} = \exp(-K_i V) \quad (2.45)$$

Where A is the available membrane area, A_0 is the initial total membrane area, K_b is a complete blocking constant, J_0 is the initial flux, V is the volume of processed fluid, and K_i is an intermediate blocking constant. These equations can then be inserted into Darcy's Law (equation 2.42) and integrated to yield the filtered volumes as a function of time for complete and intermediate blocking, respectively:

$$V = \frac{J_0}{K_b} [1 - \exp(-K_b t)] \quad (2.46)$$

$$V = \frac{1}{K_i} \ln(1 + K_i J_0 t) \quad (2.47)$$

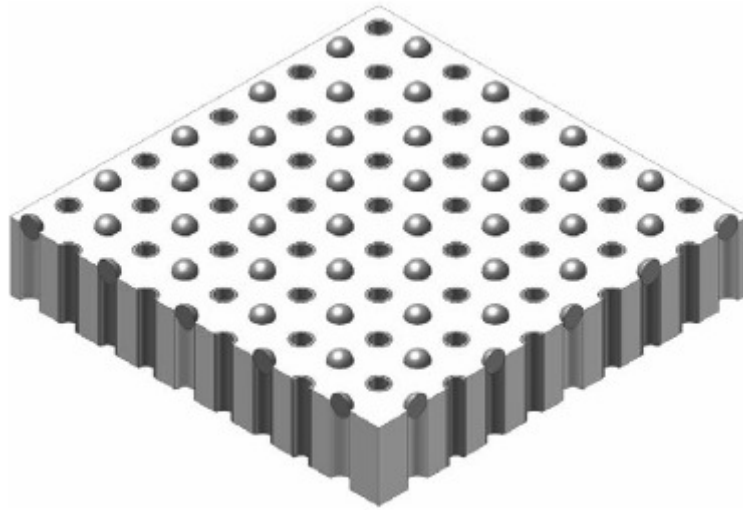


Figure 2.7: Schematic of complete/intermediate blocking model [Bolton 2006].

2.3.2.3. Cake Filtration Model

The cake filtration model is one of the many means of describing membrane fouling for micro-/ultrafiltration as well as reverse osmosis/nanofiltration. According to the cake filtration model, the rejected species accumulates on the surface of the membrane, forming a porous ‘cake’ layer which resists the flow of permeating fluid. The fluid, as well as suspended particles, must now flow not only through the membrane itself, but also through this dense layer of deposited particles. Bolton et al. give a mathematical representation of the cake layer resistance [Bolton 2006]:

$$\frac{R}{R_0} = \sqrt{1 + 2K_c J_0^2 t} \quad (2.48)$$

Here R is the current resistance to flow, R_0 is the initial resistance, K_c is an empirical cake filtration constant, J_0 is the initial permeate flux, and t is time. This representation thus relates the resistance due to the development of a cake layer as an empirical function of flow rate and volume of fluid processed.

Ho and Zydney [2002] presented the following power-law relation for the form of cake layer resistance in the filtration of compressible biological components, such as bovine serum albumin.

$$R' = k_p \left(\frac{\Delta P}{1 \text{ Pa}} \right)^S \quad (2.49)$$

Where R' is the specific cake layer resistance, k_p is an empirical resistance proportionality constant, ΔP is the trans-membrane pressure (the term in parentheses is non-dimensionalized by normalizing to a pressure of 1 Pascal) and S is a cake layer compressibility factor. $S = 0$ corresponds to an incompressible cake, and $S = 1$ corresponds to a highly compressible cake.

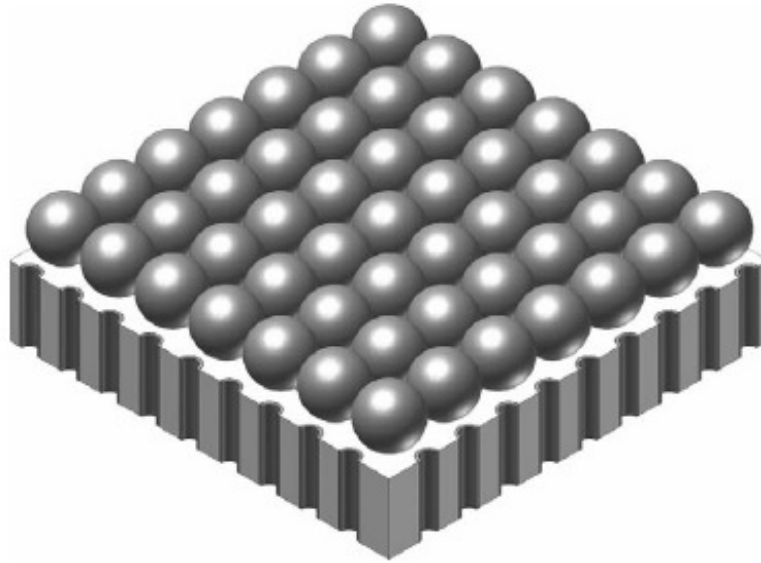


Figure 2.8: Schematic of cake filtration model [Bolton 2006].

2.3.2.4. Gel Polarization Model

During ultrafiltration of macromolecular solutions, it is often assumed that a gel layer forms at the membrane surface [Osada 1992, Matthiasson 1980]. Certain macromolecular solutes may have highly concentration-dependent viscosities, low diffusivities and low osmotic pressure due to large molecular

weight. At high concentrations, the degrees of freedom of molecular movement may become limited, resulting in a gel-like film.

This theory was first introduced and analyzed by Michaels [1968], who solved the convection-diffusion equation, assuming constant solvent and solute properties. Under certain conditions with certain solutions, this method was found to reasonably match experimental data for design purposes. The key downside was that this method was limited to only certain applications.

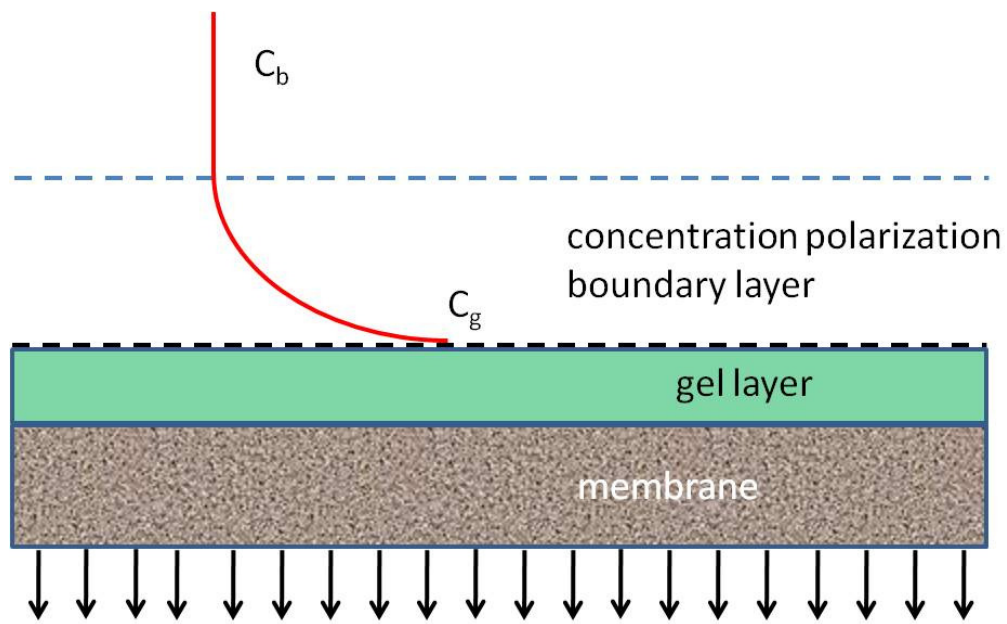


Figure 2.9: Schematic of gel layer model. Following [Matthiasson 1980].

A simple description of permeate flux is given by the film-transport model. This is similar to the film transport CP relation (equations 2.7 and 2.37), except that the concentration at the membrane surface, C_w , is replaced with the constant gelation concentration at the top of the gel layer, C_g [Matthiasson 1980].

$$J_v = K \ln \left(\frac{C_g}{C_b} \right) \quad (2.50)$$

Here K is the mass transfer coefficient, C_g is the limiting gel concentration, and C_b is the bulk solute concentration. It is assumed that the gel layer exists at steady state due to a balance of solute back-diffusion into the bulk solution and convection of solute to the gel layer. In a cross-flow configuration, the Leveque solution can be used to determine the mass-transfer coefficient for laminar cross flow [Matthiasson 1980]:

$$Sh = \frac{KD_h}{D_s} = 1.62 \left(Re \cdot Sc \frac{D_h}{L} \right)^{1/3} \quad (2.51)$$

Where Sh is the Sherwood number, D_h is the hydraulic diameter of the flow channel, D_s is the diffusivity of the solute, Re is the Reynolds number, Sc is the Schmidt number and L is the axial position in the flow channel.

Experimentally, the permeate flux is linearly related to applied pressure only up to a certain limiting pressure. This can be explained by the gel layer model. Above the limiting pressure, the macromolecular solution may reach a gelation concentration near the membrane, and a gel layer will form. The resistance to the flow is then limited by the resistance of the gel layer [Shen 1977].

The method developed by Shen and Probstein [1977] was essentially the same as that developed by Michaels [1968], except that a numerical solution was calculated accounting for variation in the diffusivity of the solute as a function of concentration, including diffusivity at the gelation concentration. Shen and Probstein presented the following semi-empirical relationship for the limiting permeate flux under cross-flow filtration. The solution is not rigorous, but can be used for design purposes:

$$v_{w,\lim} = n \left(\frac{D_g}{D_b} \right)^{2/3} \left(\frac{uD_b^2}{hL} \right)^{1/3} \ln \left(\frac{C_g}{C_b} \right) \quad (2.52)$$

Here $v_{w,lim}$ is the gel-limited permeate flux rate, n is an empirical fitting parameter, u is the laminar cross flow velocity, h is the height of the flow channel, L is the axial position in the flow channel, D_g is the diffusion of the solute at the gelation concentration, and C_g is the gelation concentration. Shen and Probstein also accounted for variable viscosity as a function of concentration, which can occur as the concentration approaches the gelation concentration. This consideration, in effect, couples the mass transport and momentum transport near the membrane surface. It was found that exact numerical solution matched the simple semi-empirical solution well, demonstrating the utility of the rough model for design.

Trettin and Doshi [1980] performed a similar analysis to Shen and Probstein [1977], but solved the convection-diffusion equation using a direct integral method. This yielded the following non-dimensional equation:

$$v_w = \frac{F_g - 1}{F_g} \left(\frac{2n^2 F_g}{(n+1)(n+2)} \right)^{1/2} \bar{D}_g^{2/3} \quad (2.53)$$

Where:

$$v_w = J_v \left(\frac{D_b a}{3x} \right)^{-1/3} \quad (2.54)$$

$$F_g = \frac{C_g}{C_b} \quad (2.55)$$

$$\bar{D}_g = \frac{D_g}{D_b} \quad (2.56)$$

$$a = \frac{3U_b}{h} \quad (2.57)$$

$$n = f(F_g) \quad (2.58)$$

This model accounts variation in the diffusivity as a function of concentration. Agreement between the exact numerical solution and the analytical solution were found to be within 1%, and results matched those reported in [Shen 1977].

2.3.2.5. Combined Models

Due to the fact that fouling in real systems is actually due to multiple mechanisms, several papers have been reported providing analyses of combined fouling models. Ho and Zydney [2002] presented such a model incorporating combined pore blocking and cake filtration mechanisms for the microfiltration of proteins in a constant-flux (as opposed to constant-pressure) mode. It was assumed that initially, areas of the membrane would become blocked, and that a cake layer of protein aggregates would form a compressible cake layer on top of the membrane. The model thus incorporates internal as well as external fouling modes. It was also assumed that a small flow is able to pass through the blocked pores. The model demonstrated that microfiltration systems operate most efficiently for low permeate flux rate with larger membrane surface area.

Bolton et al. [2006] presented a paper analyzing additional combined mechanisms including 1) cake-filtration / complete-blocking, 2) cake-filtration / intermediate-blocking, 3) complete-blocking / standard-blocking, 4) intermediate-blocking / standard-blocking, and 5) cake-filtration / standard-blocking. These model solutions were then fitted to separate experimental ultrafiltrations involving solutions of bovine serum albumin and human plasma IgG. The numerical scheme for determining fitting parameters was somewhat less complex than that presented by Ho and Zydney [2002], but still demonstrated practical utility. The experimental results showed the combined cake-filtration/complete-blocking model to be the most accurate in describing the fouling mechanisms for these systems. This represented a good phenomenological fit for the majority of data sets.

2.3.3. Inorganic Scaling

Reverse osmosis and nanofiltration are the most commonly employed methods for membrane-based filtration of inorganic salts which are dissolved in solution. Since these salts consist of dissociated ions in the solution phase, the growth mechanisms of inorganic scaling layers are significantly different than those involved in the formation of colloidal or biological fouling layers. As with other types of fouling, the concentration of the rejected species is greater at the membrane surface than in the bulk due to concentration polarization. In the separation of inorganic salts, however, a clear saturation concentration can be defined. When the concentration exceeds this value near the membrane surface, the salt will begin to precipitate from solution. Fouling modes can then include surface crystallization at nucleation sites on the membrane and bulk precipitation on crystal or particulate nuclei in the feed. Calcium sulfate is the model scalant used in the experiments discussed in this thesis. There is a large literature on crystal growth kinetics of calcium sulfate. Some significant references include Cowan [1976], Schierholtz [1958], Liu [1970 b], Liu [1971], Smith [1971], Packter [1974], Christoffersen [1976], Alimi [2003], and Wang [2010]. The growth kinetics can be dependent of flow rates, pressure, temperature and solution composition. Despite the significant differences in fouling layer formation between reverse osmosis and ultra-/microfiltration, some similar modeling methods can be used to predict flux rates.

One of the key challenges in reverse osmosis desalination is the formation of scaling layers on the membrane due to precipitation of sparingly soluble salts. These salts, such as calcite, calcium sulfate, barite, silica and calcium carbonate [Lyster 2009, Okazaki 1984] precipitate at much lower concentrations than sodium chloride, which is the major dissolved component found in seawater. It is therefore of great interest to understand the mass transport and crystal growth behavior of sparingly soluble salts. Many studies have therefore been performed using calcium sulfate as a model inorganic scalant in order to better understand and predict these properties for use in the design of more efficient filtration systems.

Okazaki and Kimura [1984] used a resistance-in-series cake filtration model to explain flux decline in a batch-type RO filtration module:

$$J_v = \frac{P - \Delta\pi}{\mu \left(R_m + R_f \frac{m}{A_0} \right)} \quad (2.59)$$

$$R_m = \frac{1}{\mu L_p} \quad (2.59)$$

Where J_v is the permeate flux, P is the applied pressure, $\Delta\pi$ is the osmotic pressure, R_m is the membrane resistance, μ is the solution viscosity, R_f is the specific hydraulic resistance of the cake layer, m is the deposited mass, A_0 is the full area of the membrane, and L_p is the pure-water permeability of the membrane.

Okazaki and Kimura performed RO filtration experiments using a saturated calcium sulfate feed solution. Excess calcium sulfate crystals (40 to 120 μm needles) were suspended in the solution to serve as nucleation seeds. Thus, the feed took the form of a calcium sulfate slurry, which deposited as a crystalline cake layer on the membrane surface, and continued to grow via crystallization from the saturated solution. The aim of this study was to investigate the effect of a bulk precipitated crystalline cake on flux rates.

Gilron and Hasson [1987] argued that the simple cake filtration model of Okazaki and Kimura was, by itself, not the best explanation for flux decline in realistic cross-flow RO filtration systems. Gilron's explanation was that flux decline occurs more by the nucleation and lateral growth of crystals on the membrane surface. The areas that become covered are thus rendered impermeable to solvent flow, and describe a surface blocking model. The following relations express this mechanism:

$$FD = \frac{Q_0 - Q}{Q_0} \quad (2.60)$$

$$\frac{FD}{1 - FD} = \mu R_f L_p \frac{m}{A_0} \quad (2.61)$$

Here FD is the percentage flux decline, Q is the current volumetric flux rate, Q_0 is the initial volumetric flux rate, m is the mass of deposited scalant, and A_0 is the initial membrane area. Gilron and Hasson claimed that the data presented by Okazaki and Kimura demonstrated a flux decline of 65% with a very small mass deposit, $m/A_0 = 0.7 \text{ mg/cm}^2$. This corresponds to a crystalline cake with a thickness of only 5 μm . Application of the Kozeny-Carmen equation for determining flow resistance through porous media shows that the sheet would have to be almost solid crystal. This did not match with the observed fouling, demonstrating the need for an alternate explanation. Gilron and Hasson used the lateral surface blockage model described above. Figure 2.10 demonstrates the difference between the two forms of fouling. The surface blockage model yields the following equation for permeate flux decline.

$$FD = 1 - \frac{Q}{Q_0} = \frac{A_{crystal}}{A_0} = N\pi r^2 = \frac{m/A_0}{\rho_{crystal} h} \quad (2.62)$$

Where $A_{crystal}$ is the total membrane area covered by scalant crystals, N is the number of nucleation sites (assumed to be uniformly distributed), r is the current radius of each crystal rosette cluster, $\rho_{crystal}$ is the crystal density and h is the crystal height. Recorded flux values, along with post-mortem analysis of the scaling pattern for flat-sheet filtrations demonstrated that this model matched well with recorded permeate flux rates and made a good approximation of the observed growth pattern (Figure 2.11). Calcium sulfate crystals grow as small platelets in rosette clusters, with an approximate limiting growth height. Mass deposition occurs primarily in the radial directions, close to the membrane surface where concentration is greatest.

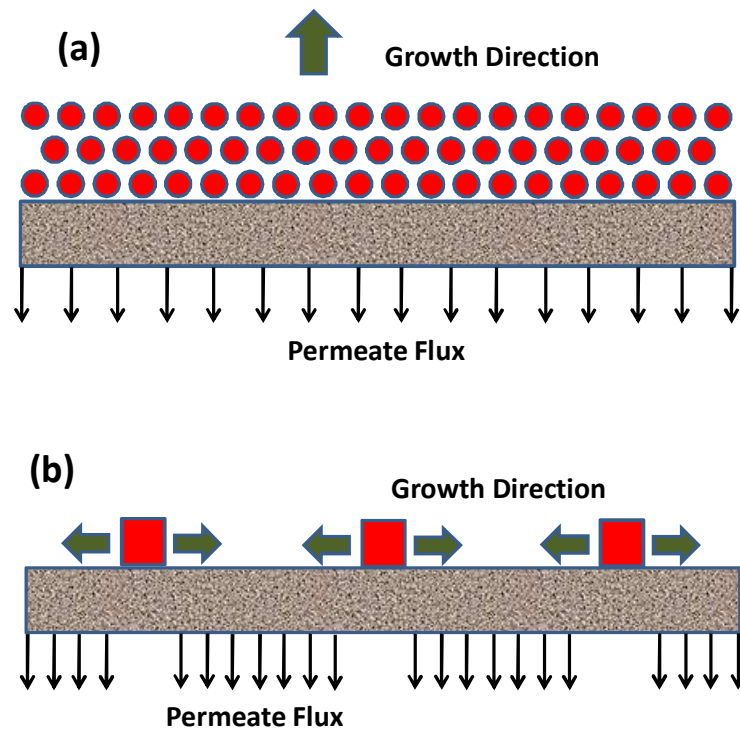


Figure 2.10: (a) cake filtration model which assumes vertical growth of a cake layer with constant porosity. (b) surface blockage assumes crystals of a given height expanding laterally and completely blocking the surface to permeation where covered. Following [Gilron 1987].

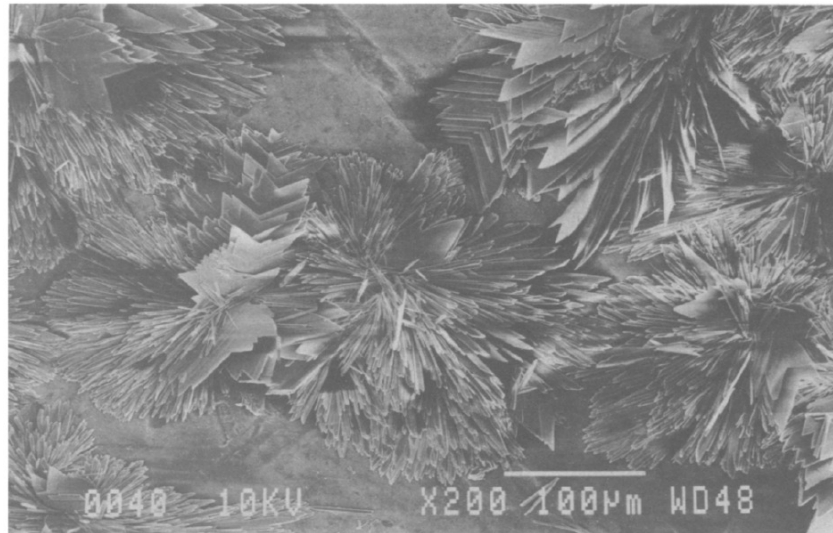


Figure 2.11: SEM image of calcium sulfate rosette growth pattern demonstrates a good approximation for Gilron and Hasson's surface blocking flux decline model [Gilron 1987].

In a related publication, Gilron and Hasson [1986] also presented a detailed mathematical model focusing on the interaction between scaling layer deposition and concentration polarization during laminar cross flow reverse osmosis. This paper considered relaxation of the concentration polarization at the membrane surface as mass is deposited on the membrane. The mass deposition rate is expressed by the following widely adopted relation for crystal growth:

$$\dot{m}_d = k_r (C_w - C_s)^n \quad (2.63)$$

Where $\dot{m}_d$ is the mass deposition rate, k_r is the precipitation rate constant, C_w is the solute concentration at the membrane surface, C_s is the solute saturation concentration, and n is the crystal kinetic growth order ($n=1$ or 2). Lateral crystal growth from uniformly spaced nucleation sites was considered, such as in [Gilron 1987], but a finite resistance to flow through the scaling deposits is included here. This model described the time-domain development of membrane scaling and concentration polarization based on the interdependence between the two phenomena. The calculated results compared well with concentration polarization and flux rates predicted by the method of Sherwood et al. [1965] for a saturated CaSO_4 solution immediately before formation of scalant. Equation 2.64 is an approximate analytical expression relating the boundary layer thickness $\bar{\Delta}$, the distance from flow channel inlet $\bar{x}$, water recovery factor S , and membrane surface concentration $\bar{C}_w$. The bars above the terms refer to the fact that the terms in the solution are non-dimensional [Gilron 1986].

$$\frac{\partial \bar{\Delta}}{\partial \bar{x}} = \frac{\bar{v}_w [\bar{\Delta}^2 (\bar{C}_w - 1) + 4(1 - \bar{C}_w \bar{m}_d)]}{(1 - S) \bar{\Delta} \left[2(\bar{C}_w - 1) + \bar{\Delta} \frac{\partial \bar{C}_w}{\partial \bar{\Delta}} \right]} \quad (2.64)$$

$$S = \int_0^{\bar{x}} \bar{v}_w d\bar{x} \quad (2.65)$$

Here the term, S , accounts for water lost due to permeation over the length of the flow channel, and is used to determine variation in local cross-flow velocity as a function of axial position. Based on the results, the total mass deposition over time was then computationally solved at each location and time using Euler's method:

$$m_d(x,t) = \int_0^t \dot{m}_d(x,t) dt \quad (2.66)$$

This relation can be also applied for a two-salt system, in which the second salt is not precipitating; a feed containing precipitating CaSO_4 and non precipitating NaCl , for example. For the non-precipitating salt, the mass deposition rate is simply set to zero.

Lee et al. [1999] performed a theoretical and experimental investigation into scaling modes of calcium sulfate in unstirred batch modules, as well as cross-flow modules operating under both turbulent (spiral-wound configuration) and laminar (flat-sheet) conditions. In this work, two possible calcium sulfate scaling mechanisms were considered. The first assumed that the calcium sulfate precipitates in the bulk phase while supersaturated in the concentration polarization boundary layer, and deposits on the membrane leaving a porous crystalline deposit. This represents a situation similar to that demonstrated by Okazaki and Kimura [1984], where the flux resistance is in the form of a porous crystalline cake layer. The second mechanism is the surface blocking model, described by Gilron and Hasson [1987], where nucleation sites are present on the membrane surface, and crystals of a given height form directly on the surface, expanding radially. The blocked areas completely prevent local permeation. Lee et al. combined the following two equations:

$$J = \frac{P - \Delta\pi}{\eta(R_m + R_c)} \quad (2.67)$$

$$J = \frac{P - \Delta\pi}{\eta R_m} \frac{A_{free}}{A_t} \quad (2.68)$$

Here equation 2.67 is the cake filtration resistance-in-series model and equation 2.68 is the independent surface blockage model. In these equations, J is the flux, η is the fluid viscosity, R_m is the membrane resistance, R_c is the cake layer resistance, A_{free} is the free unblocked membrane area, and A_t is the total membrane area. The combined equation is simply the following:

$$J = \frac{P - \Delta\pi}{\eta(R_m + R_c)} \frac{A_{free}}{A_t} \quad (2.69)$$

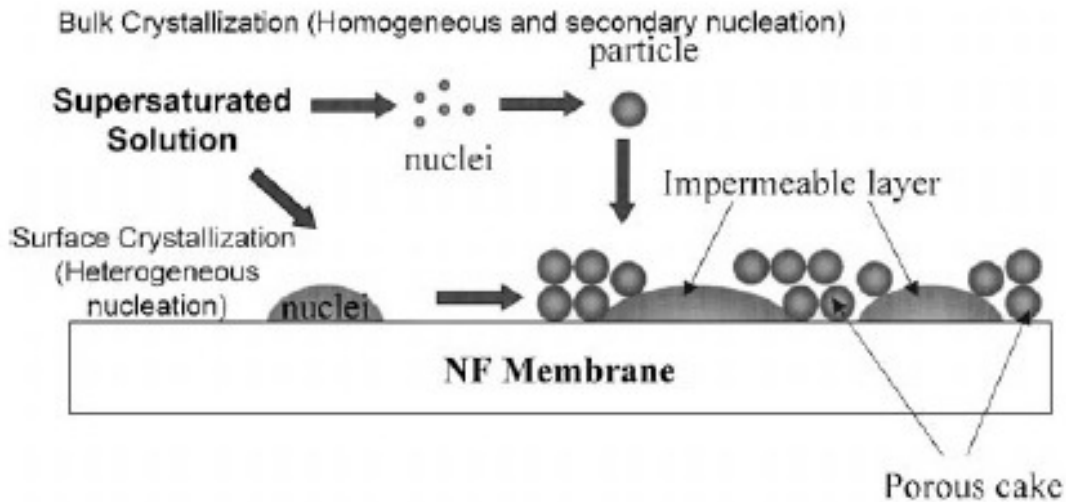


Figure 2.12: Combined cake-filtration and surface-blockage scaling model [Lee 1999].

Experiments attempted to separate the effects of bulk precipitation and surface crystallization on the overall flux. Bulk crystallization was characterized by monitoring the turbidity of the retentate solution. These results demonstrated that in batch filtration, surface crystallization was the dominant scaling mechanism due to the severe concentration polarization in the dead-end configuration. Results from cross flow filtration tests varied between differing module geometries, with spiral-wound modules

being more affected by bulk precipitation than tubular or flat-sheet systems. Correspondingly, installation of a pre-filter to remove crystals yielded the largest improvements in flux rates for the spiral-wound modules. The key contribution of this work is that it demonstrated that precipitation scaling does occur and has a significantly different effect on flux rates from surface crystallization. The relative influence of each of these mechanisms was assessed and found to vary for different module geometries and operating conditions.

Lyster et al. [2009] used a computational fluid dynamics (CFD) package (CFX, Ansys), in concert with optical images of scaling deposits from experiments on a flat-sheet membrane, to develop a coupled 3D finite-element model of the hydrodynamic flow field and mass transport in the flow channel. The analysis was based on simultaneous solution of the Navier-Stokes equation for the flow field and the convection-diffusion equation for solute mass transport. Digital optical images of the membrane surface were taken at 15 minute intervals in order to reveal scaled areas on the membrane surface. The images were digitized and the observed scaled areas were incorporated into the finite element model. The observed scaled areas were considered impermeable, following the surface-blocking model proposed in [Gilon 1987]. Thus, a 3D profile of the concentration polarization over the entire membrane surface was computed based on each of these images in order to demonstrate the interaction between concentration polarization and membrane scaling over a 24 hour filtration run. This work considered relaxation of the concentration polarization during scaling formation, with scaled areas presenting a boundary condition having a saturation ratio of 1. In the absence of scaling, concentration saturation indexes could be significantly greater (SR ~2-3) at the given locations. Figure 2.13 demonstrates this comparison.

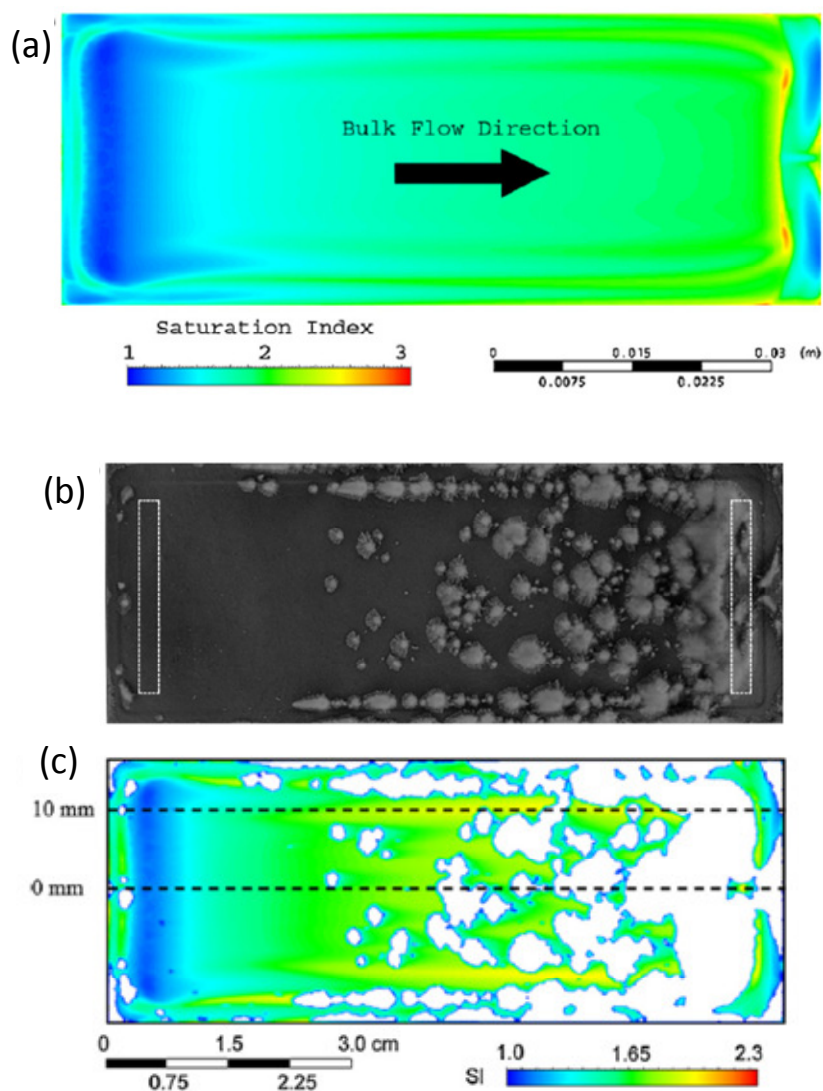


Figure 2.13: (a) Finite element model of membrane surface saturation index with no scaling present. (b) digitized image of membrane surface with scaling. (c) finite element model of membrane surface saturation index with corresponding scaling present [Lyster 2009].

This work built on a 2D finite element model developed by the same authors [Lyster 2007]. Although significantly more computationally intensive (3D model required 11 node Dell Power Edge cluster with 64 Gb memory; typical simulations required 40-60 hours of computation time), the 3D version was able to provide detailed insight into entrance and exit region hydrodynamics, and demonstrated that the lateral concentration and scaling profiles (z-direction) were not uniform. Figure 2.14 is an image of the computed hydrodynamic field at the entrance and exit regions. Uniform scaling as

a function of axial position had been a common assumption in previous approaches to modeling concentration polarization and scaling. The no-slip condition at the flow channel side walls, for example, was shown to be a cause of large saturation index, whereas adjacent areas with greater flow velocities had a much lower saturation index. The modeled predictions for permeate flux matched well with experimental values (within 2%), demonstrating the viability of this method for application to design of practical systems.

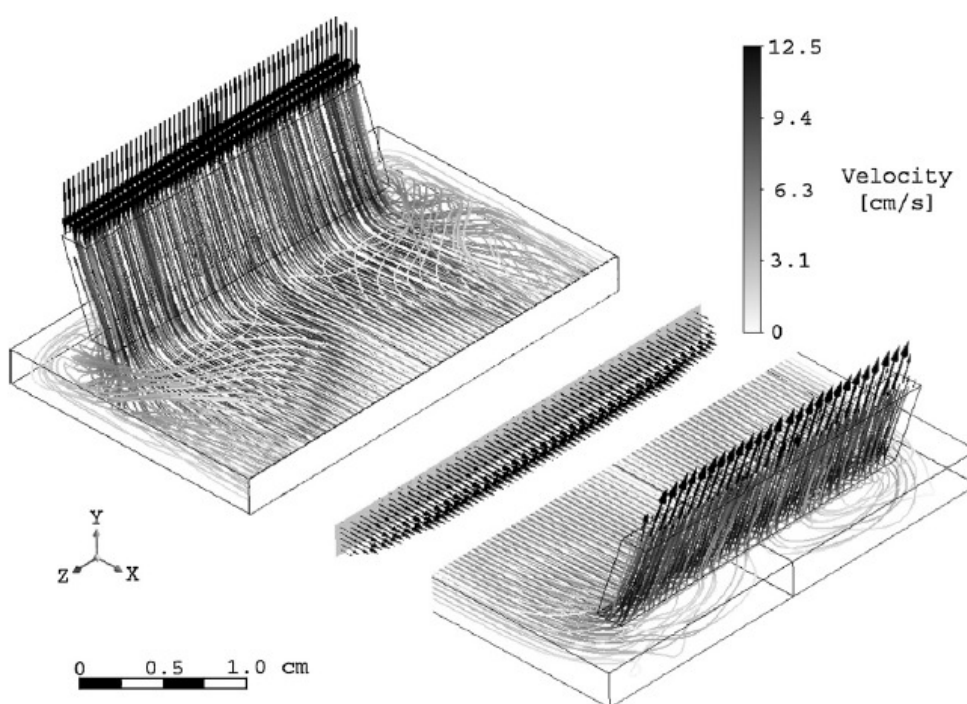


Figure 2.14: Fluid streamlines and velocity vectors in 3D membrane flow channel [Lyster 2009].

2.4. Nondestructive Monitoring of Concentration Polarization and Fouling

Several non-destructive methods have been investigated over the past several decades as means for monitoring the concentration polarization and fouling during membrane-based liquid separations. A good review is presented by Chen [2004]. These studies aimed to develop tools which can be used to investigate the fundamental behavior of concentration polarization and modes of fouling growth. Despite

the abundant theoretical and ex-situ experimental treatments of CP and fouling, there is still much that is not well understood [Kujundzic 2006]. CP and fouling phenomena are very complex, depending on the types of foulants, the feed concentration, membrane type, oxidation/reduction conditions, temperature, pH, ionic strength, and separation system hydrodynamics [Greenberg 2003]. In-situ, non-destructive sensing tools and techniques may not only help elucidate the process mechanics at play, but may also be used to improve the efficiency of industrial applications. In this section, we highlight representative studies that demonstrate key concepts in the field.

2.4.1. Optical Methods

Observation by optical means has been utilized to non-destructively monitor concentration polarization and fouling phenomena in real-time during filtration processes. In order to carry out these observations, the filtration module must be constructed of a transparent material or contain transparent windows. Information is then gathered either by direct microscopy or by analysis of light which passes through the module.

Vilker et al. [1981 a,b] presented an optical shadowgraph method for observing concentration polarization near the membrane surface in an unstirred batch cell. Ultrafiltration of bovine serum albumen (BSA) was performed and concentration gradients were directly observed. The premise behind shadowgraphic measurement is that the index of the refraction of a solution will vary depending on the concentration of the solute. Thus, when a beam of light passes through the solution near the membrane, the gradient in refractive index will cause the beam to deflect. This deflection can then be monitored on an imaging plane outside the filtration module. A schematic of the ultrafiltration cell and light path is shown in Figure 2.15. The profile of the index of refraction can then be calculated using ray tracing algorithms. In this work, a reticule mask pattern (with a size of several mm) was placed on one window on the UF batch module, and was illuminated by a collimated beam of light which passed through the cell. The light then exited through the opposite side of the cell, and was monitored on an imaging plane

using a video recorder. Due to the bending of the light through the fluid, the reticule shadow image was distorted. In separate calibration tests, the refractive index of the BSA was found to vary linearly with BSA concentration. Because the beam is bent toward the membrane, direct measured results were only available for vertical locations 200 μm above the membrane. The concentration profile had to be extrapolated for values below.

One potential source of error in this particular study was the possibility of gel layer formation. The models used to extrapolate concentration at vertical heights below 200 μm account only for the situation where there is completely free motion of the solute in the solvent. The possibility existed that the concentration very close to the surface could be high enough to form a thin gel layer, which would in turn affect the entire concentration profile.

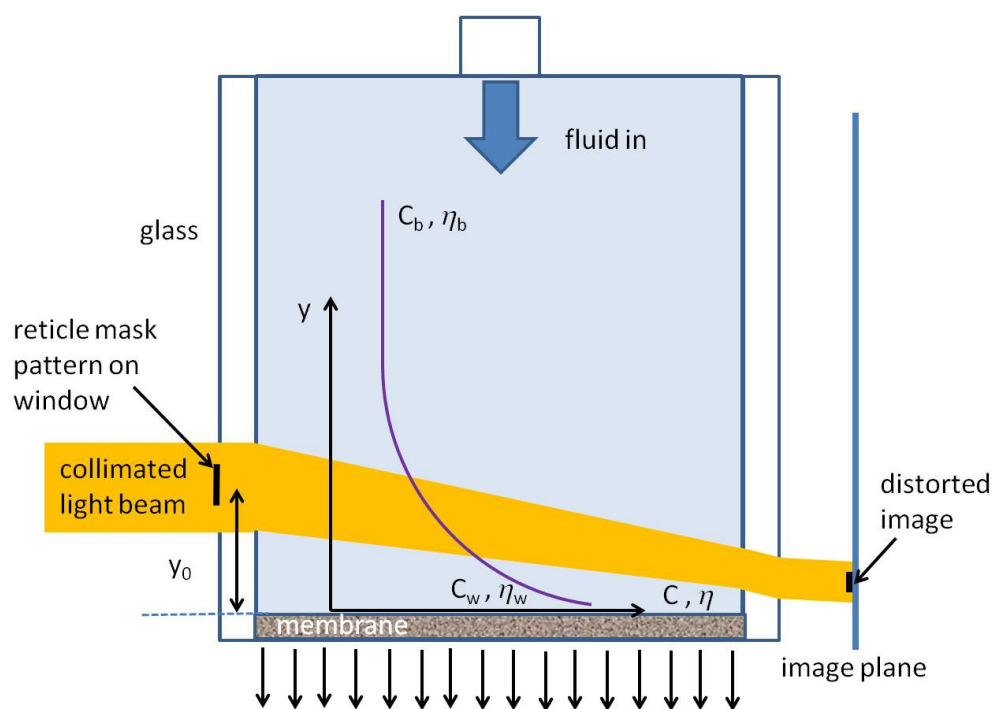


Figure 2.15: Schematic of cell used by Vilker et al. [Vilker 1981a] in shadowgraphic measurement of BSA concentration polarization.

Ethier and Lin [1992] used a refractometric method, which was very similar to that presented by Vilker et al. Instead of using a large diameter beam (several mm) to analyze the shadow from a reticule mask pattern, Ethier and Lin used a small diameter He-Ne laser beam which passed through the solution in the filtration module. The diameter of the beam in this experiment was 127 μm , and could be moved in 5 μm vertical increments. The experimental system was an unstirred batch cell for ultrafiltration of hyaluronic acid and the module was divided into two chambers by an optically transparent wall. One chamber contained a reference solution, and the second chamber contained the solution that was being filtered. The laser beam passed first through the reference chamber, through the dividing wall, and then through the filtration chamber. This configuration allowed for deflection of the beam in two directions: deflection in the y -direction (coordinates as defined on the imaging plane) was due to the difference in concentration between the two chambers, and deflection in the x -direction was due to the vertical concentration gradient in the filtration chamber. This refractometric method improved upon the shadowgraphic method in that it allowed simultaneous measurement of absolute concentration as well as concentration gradient. It also permitted a more refined measurement due to the smaller laser beam diameter. Experimental errors included optical drift over time and uncertainty in beam positioning. Like the shadowgraphic technique, this method is limited in the minimum vertical position that can be probed because of beam refraction toward the membrane. The possible formation a gel layer would have resulted in error, yielding a different concentration polarization profile than expected. This may have accounted for differences between the experimental results and the modeled index of refraction profile.

Mores and Davis [2001] directly observed deposition and cleaning of yeast on a microfiltration membrane in a laminar cross-flow system. A microscope was mounted directly above a flat-sheet cross flow module with a transparent top plate. Images of the membrane surface were recorded by a color video camera. The model foulant was *saccharomyces cerevisiae* (Fleischmann's Active Dry Yeast), dyed with Coomassie brilliant blue R-250 dye. Quantitative area coverage measurements were obtained using *Image J* software, and results were compared with continuously monitored permeate flux rates. A direct

correlation between membrane surface coverage and permeate flux rate was found, and a model for this form of microfiltration fouling and cleaning was proposed.

Uchymiak et al. [2007] also performed direct observation with a microscope mounted over a filtration module. This study, however, involved visually monitoring a flat-sheet reverse osmosis membrane used for desalination of sparingly soluble salts. The flat-sheet cross flow module was manufactured with an optical window and was designed to withstand the high pressures necessary to perform reverse osmosis (2.4 MPa). A microscope was mounted over the module window, and the membrane surface was illuminated with high-intensity LEDs. In experiments performed by other groups, such as Mores and Davis [2001], biological agents could be observed directly because they were dyed to improve visibility. In reverse osmosis of inorganic salts, the crystal structures are semi-transparent. Special lighting conditions were necessary to ensure appropriate contrast for use with image analysis software.

A feed solution consisting of dissolved CaCl_2 , MgSO_4 , Na_2SO_4 , NaCl and TDS was used to mimic brackish agricultural water from the San Joaquin Valley. Images were taken with magnifications between 10X and 30X. During all tests, permeate flux and conductivity measurements were recorded to determine solute rejection and estimate the concentration polarization according to the classical film model. Tests were conducted in which the estimated inlet saturation ratio at the membrane surface was ~ 2 , and induction time to crystal rosette growth was determined. Flow conditions were then adjusted to reduce the saturation ratio below 1, and crystal rosette dissolution was then observed. See Figure 2.16. This method was also applied to observation of an entire membrane for the CP/scaling model presented by Lyster et al. [2009].

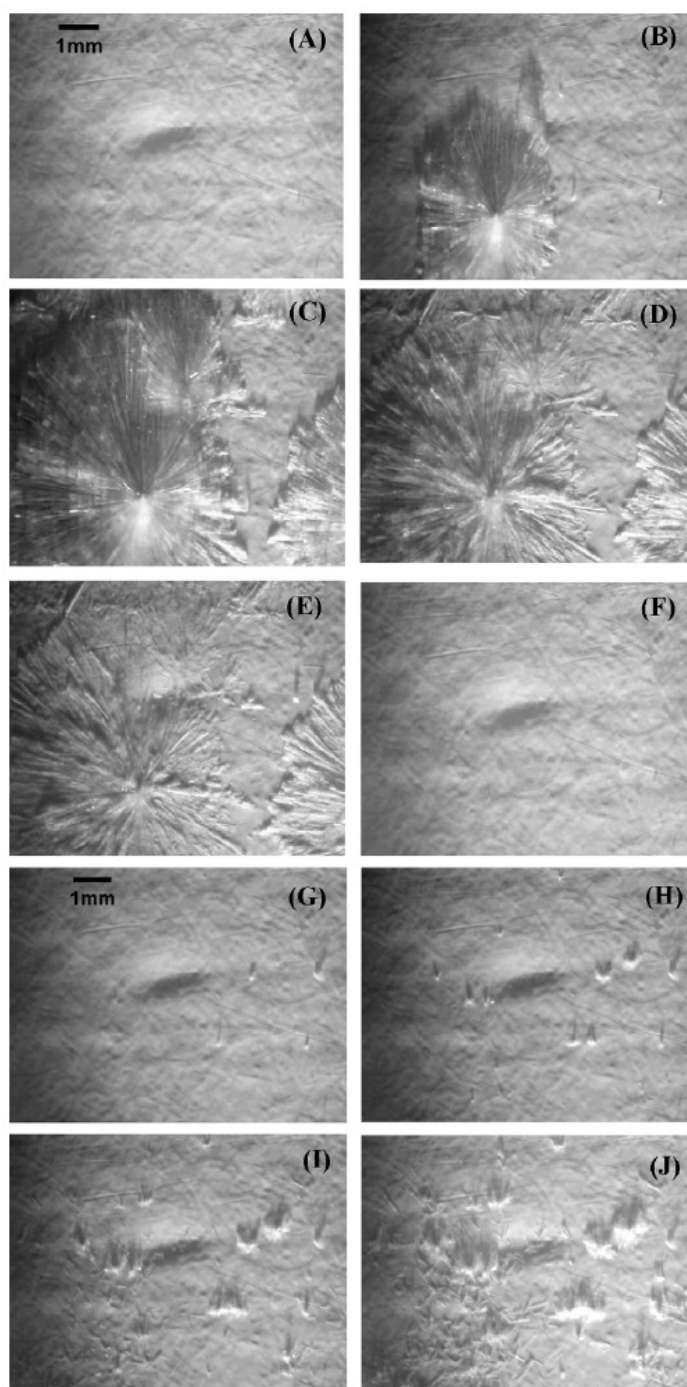


Figure 2.16: Direct visual images of calcium sulfate crystal growth (A-C), dissolution (D-F) and re-growth (G-J), [Uchymiak 2007].

2.4.2. Ultrasonic Methods

Ultrasonic time-domain reflectometry (UTDR) is another promising method that has been demonstrated for monitoring fouling growth on a membrane surface. A primary focus of the current thesis is on the use ultrasonic reflectometry in membrane monitoring, and a theoretical background is presented in Chapter 4. Ultrasonic non-destructive testing has a long history of application in a wide variety of fields. One of the first uses of UTDR for materials testing was demonstrated by Sokolov [1929], who employed a continuous ultrasonic wave in order to detect defects in solid materials. One of the first applications of ultrasonics in testing of industrial equipment was the monitoring of laminate integrity in steel boiler plates by the companies AEG and Borsig during the Second World War, in Berlin. The device used was designed by Trost and Berthold [Trost 1943].

Ultrasonics continues to be an area of ongoing research, with a large breadth of literature in a variety of areas: transducer design and construction [Bohm 1966, Hannon 1970, Crane 1978, Sleva 1990, Toda 2005, Lee 2005, Ketterling 2005, Jenkins 2005, Lu 2005], signal analysis [Kroning 2007], device miniaturization using microfabrication techniques [Sleva 1990, 1992, 1996, Fleischman 2003], materials science [Weaver 1985, Wanner 1998, Poirier 2004, Carreon 2009] and medical imaging [Herrick 1954, Emsminger 1988, Fleischman 2003, Gelat 2005, Lewin 2004, Shrimali 2010] provide a few examples.

In this section, our primary focus is on the reported literature specifically pertaining to ultrasonic monitoring of membranes used in liquid separations. The application of ultrasonic reflectometry to membrane processes has been described in several reviews [Emsminger 1988, Krautkrämer 1990, Greenberg 2003, Krantz 2008, Kujundzic 2008]. Since the pioneering studies of the use of UTDR for detecting inorganic scaling on RO membranes, there have been several studies of its application to inorganic scaling and biofouling on microfiltration (MF) and ultrafiltration (UF) membranes.

The first application of UTDR to membrane processes was that of Bond et al. [1995] who used it to study membrane compaction during permeation in real time. Mairal et al. [Mairal 1999, 2000] were the first investigators to apply UTDR for detecting membrane fouling. They applied UTDR to a flat-sheet RO membrane module to study calcium sulfate (CaSO_4) fouling from an aqueous solution. Multiple transducers were mounted on the top steel plate along the flow axis of the membrane module and the acoustic waveform associated with the reflections from the surfaces was recorded (Figure 2.17). Multiple permeate flux collection ports were installed along the flow axis of the module, allowing for correlation of the UTDR response with a localized permeate flux measurement. Time-domain analysis showed a shift in arrival time of the echoes, as well as changes in amplitude as the scaling layer formed. The time-domain changes in the echo waveforms corresponded well with declines in permeate flux. Decreases in flux at the downstream collection port correlated well with shifts in the ultrasonic waveform at the same location, indicating effective detection of early-stage fouling. The fact that the downstream transducers detected scaling before any measureable decrease in the overall permeation flux was shown to be a consequence of UTDR providing essentially a point measurement. Since the overall permeation flux is the volumetric permeation rate per unit area of membrane, it is far less sensitive to the onset of fouling.

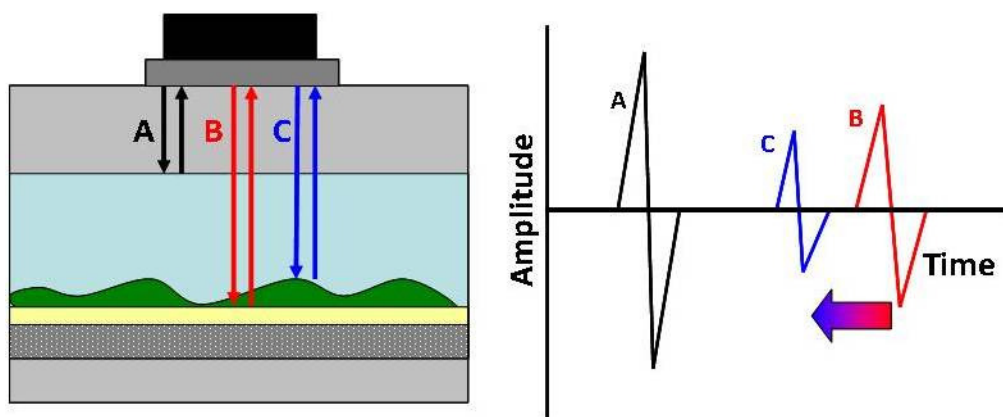


Figure 2.17: Configuration of ultrasonic transducers mounted to a flat-sheet reverse osmosis module and echo paths (left) and corresponding echo waveforms recorded on an oscilloscope (right). Following [Mairal 1999].

Sanderson et al. [2002] carried out experiments using UTDR to detect calcium carbonate scaling from a dilute aqueous solution in a flat sheet RO membrane module. The UTDR response was corroborated with concurrent measurements of the permeation flux and subsequent examination of the fouling deposits on the membrane using scanning electron microscopy.

Li et al. [2005 a] used UTDR to study calcium sulfate fouling on a flat sheet membrane for both cross-flow and dead-end flow operation. The authors corroborated their UTDR measurements with a model they developed for the fouling layer growth.

Hou et al. [2010] used UTDR to study calcium sulfate scaling in the presence of a biofilm in a flat sheet NF membrane module. The presence of a biofilm prior to the initiation of the calcium sulfate scaling resulted in a more rapid decline in the permeation flux in comparison to calcium sulfate scaling on a clean membrane surface. Here, the lower permeation flux presumably occurred in the presence of the biofilm due to enhanced CP resulting from the formation of a stagnant layer. The most interesting observation in this study was the marked difference in the morphology of the fouling layer when prior biofouling was present.

All of the aforementioned studies were performed using flat-sheet membrane modules. Large-scale water desalination uses spiral-wound membrane modules. Applying UTDR to detect scaling in a spiral-wound module is considerably more complex than for flat sheet membranes owing to multiple reflections and attenuation of the acoustic signal due to the concentric membrane, support, and spacer layers. Chai et al. [2007] used UTDR to study calcium sulfate fouling in a Koch 2521 spiral-wound membrane module. Calcium sulfate fouling and subsequent cleaning using pure water were monitored quite well using only the reflections from the outer wrapping of the module and the second and third membrane layers. The UTDR results were corroborated with permeate flux measurements and post-mortem gravimetric analysis of the fouling deposits on coupons cut from the membrane layers. Chai et al. [2003] also demonstrated that UTDR was not sensitive to concentration polarization. This is a particular

advantage of UTDR relative to permeate flux measurement, since the latter will decrease owing to concentration polarization as well as fouling; that is, UTDR is a more reliable indicator of membrane fouling.

Zhang et al. [2003, 2005] developed the concept of the acoustic signature for analyzing the complex reflection spectra associated with applying UTDR to spiral-wound membrane modules. In these studies Zhang et al. defined the acoustic signature as the root-mean-square of the displacement of successive peaks in the fouled membrane module acoustic response relative to the same peaks in the reference unfouled membrane response. The acoustic signature can be defined in terms of either the arrival time or amplitude of each peak in the acoustic response. Zhang et al. [2003, 2005] demonstrated that the acoustic signature based on either the arrival time or amplitude could track calcium sulfate fouling and subsequent cleaning in a Koch 2521 spiral-wound membrane module.

UTDR has also been used to biofouling on micro- and ultrafiltration membranes. Li et al. utilized this UTDR methodology in a flat-sheet configuration to monitor fouling during ultrafiltration (UF) of paper mill effluent [2003] as well as protein fouling on polysulfone membranes [2005 b]. The protein experiments utilized bovine serum albumen (BSA) as a model biofoulant. Ultrasonic and permeate responses were monitored versus time as a function of feed solution pH. Advanced fouling layer formation was detected by comparison of a reference echo waveform from a clean membrane to time-shifted echo waveforms from fouled membranes. Analysis of the data led to the conclusion that BSA layers grow thicker at higher pH (6.9), are more compressible at lower pH (4.9), and that permeate flux is controlled mainly by the density of the layer. Li et al. also monitored protein fouling on tubular membranes, a non-flat-sheet configuration [2006].

Recent work by Kujundzic et al. [2007] and Evans et al. [2005] has suggested that ultrasonic measurement using total reflected power (TRP) of the echo waveform is effective for monitoring the early stages of biofouling. In [Evans 2005], commercial PVDF microfiltration membranes were fouled under

laminar conditions in a flat-sheet cross flow cell. Fouling rates were quantified by recording echo waveforms while simultaneously monitoring the permeation flow rate. The reflected waves were compiled into frequency distributions by Fourier transform methods described by Ramaswamy et al. [2004, 2005]. Representative results indicated a rapid initial increase in TRP, followed by a more gradual increase. Over the same period, the permeate flow rate continuously decreased. Significant variability in TRP values were observed, which could be due to the dynamic morphology of the biofilm [Kujundzic 2008]. Biofilm morphology is dependent on microbial community structure, growth rates, age, substrate concentrations, and local hydrodynamic conditions.

2.4.3. Electrolytic Methods

Measurements of the electrical properties of the feed solution have been attempted to characterize concentration polarization of dissolved inorganic salts during desalination. Such direct measurement is a primary focus of the current thesis, and the development of theoretical background concepts is presented in Chapter 3. Here we present experimental works in the literature which attempt to utilize this method for characterizing feed concentration and concentration polarization.

Liu and Williams [Liu 1970] performed conductivity measurements in an unstirred batch cell to monitor concentration polarization of a magnesium sulfate solution during dead-end filtration. A conductivity microprobe was fabricated from platinum wire having a diameter of $\sim 72 \mu\text{m}$. The wire was inserted into a Pyrex tube which was heated and pulled to form an insulating layer over most of the wire. The protruding end of the wire was then etched to achieve a sharp tip, having a final diameter between $60 \mu\text{m}$ and $75 \mu\text{m}$. The resistance was measured between the wire probe tip and ground, with the stainless steel wall of the filtration module serving as ground. Before beginning measurements of CP, the probe was calibrated in the module with standard solutions.

In practice, the probe measured the average concentration within a sphere of several tip radii, centered at the probe tip. A circulation pump was turned on and the probe tip was placed within a few centimeters above the membrane. At the beginning of filtration tests, the circulation pump was turned off and the probe tip was lowered close to the membrane as filtration began. The operating premise of this sensor is that if a sphere is immersed in a solution of known conductivity, σ , then the total resistance measured is:

$$R_{tot} = R_{fixed} + \frac{1}{4\pi r \sigma} \quad (2.70)$$

Where R_{tot} is the total resistance measured, R_{fixed} is the fixed resistance of the wire and the steel module wall, and r is the radius of the probe tip. Since the tip was not a perfect sphere, calibration measurements were necessary.

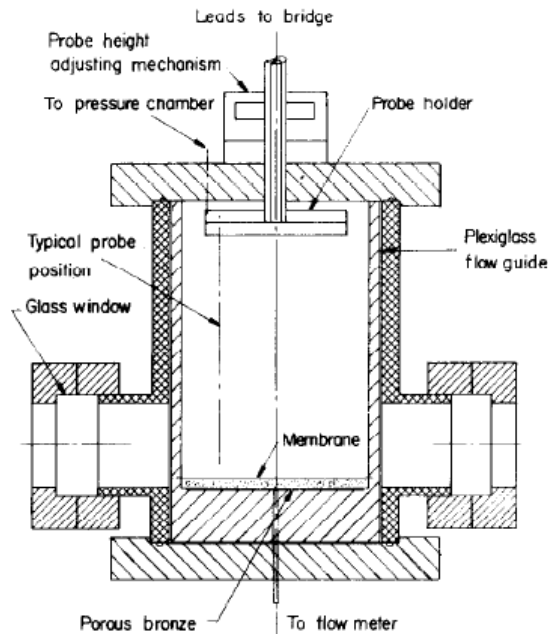


Figure 2.18: Schematic of unstirred batch cell and integrated conductivity microprobe used by Liu and Williams to measure concentration polarization in a dead-end MgSO_4 filtration [Liu 1970].

Zhang et al. [2005, 2006] developed an alternative method of monitoring the electrical properties of the electrolytic solution in the concentration polarization boundary layer. In Zhang's study, a prototype capacitive microsensor was fabricated for characterizing the vertical profile of concentration polarization boundary layers (CPBL), during flat-sheet cross flow nanofiltration of calcium sulfate (CaSO_4) solutions. The device was fabricated using MEMS (Micro-Electro-Mechanical Systems) technologies that have been developed based on integrated circuit fabrication techniques. This sensor utilized a set of interdigitated polysilicon fingers, fabricated on a silicon chip by the MUMPs Process (Multi-User MEMS Process) [MEMSCAP 2008], which is an industry standard foundry process for manufacturing MEMS structures. A 2 mm x 2 mm x 0.5 mm silicon chip served as a substrate for these devices. A thin insulating silicon nitride layer was grown on the substrate. A polysilicon layer was then grown patterned to form two of interdigitated electrodes. The thin silicon nitride layer served to electrically isolate the conductive capacitor fingers from the conductive silicon substrate (Figure 2.19).

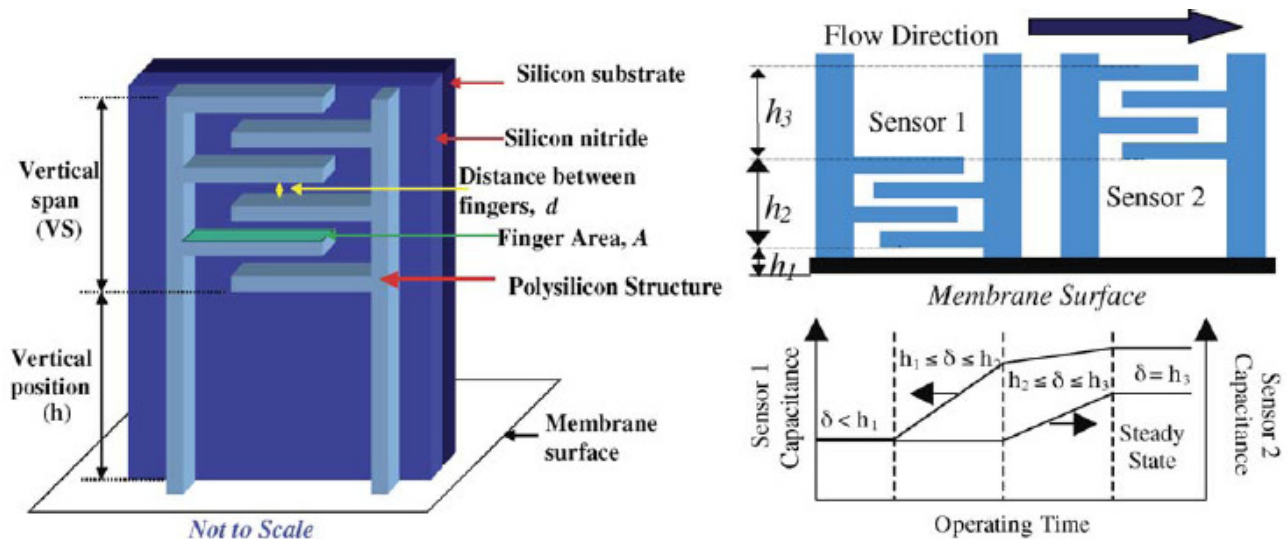


Figure 2.19: Schematic of microcapacitor used for monitoring CaSO_4 concentration polarization in cross flow reverse osmosis [Zhang 2006]. The expected capacitive response is shown in the bottom right-hand side of the figure.

The chip was mounted vertically in the module flow channel, and the profile of the cross-flow CPBL was characterized by placing capacitors on different sensors at different heights above the membrane surface. As the salt concentration varies, so does the capacitance between the fingers. Following calibration in standard calcium sulfate solutions, the individual sensors were effectively used to monitor the formation and development of concentration polarization in a flat-sheet configuration.

Two pairs of sensors were mounted on a membrane at two locations along the flow channel: mid- and downstream. One sensor in each pair had a capacitor close to the membrane surface (~ 0 mm) and the other had a capacitor 1.6 mm above the surface. The chips were then connected to copper traces on a metalized Kapton strip using conductive epoxy. Contact between the copper traces and external electronic equipment was made via feed-through pogo pins. Figure 2.20 shows representative measured concentration from each of these capacitors ($h = 0$ mm and $h = 1.6$ mm) at the two locations as a function of filtration run time. The plots of capacitance versus time follow the expected behavior of the CPBL in a flat-sheet, laminar cross flow configuration. After switching from deionized water to a calcium sulfate feed, the concentration at $h = 0$ mm clearly increased before that at $h = 1.6$ mm. This occurred at both locations (mid- and downstream). The concentration increase appeared first at the downstream location. A more gradual increase was seen at $h = 1.6$ mm. A slight decline in concentration was seen in the sensors at $h = 0$ mm as the concentration passed ~ 2.0 g/L, which is the solubility limit of calcium sulfate at 20°C [Lide 2009]. This drop was likely due to local relaxation in the supersaturated salt concentration as it precipitated out of solution.

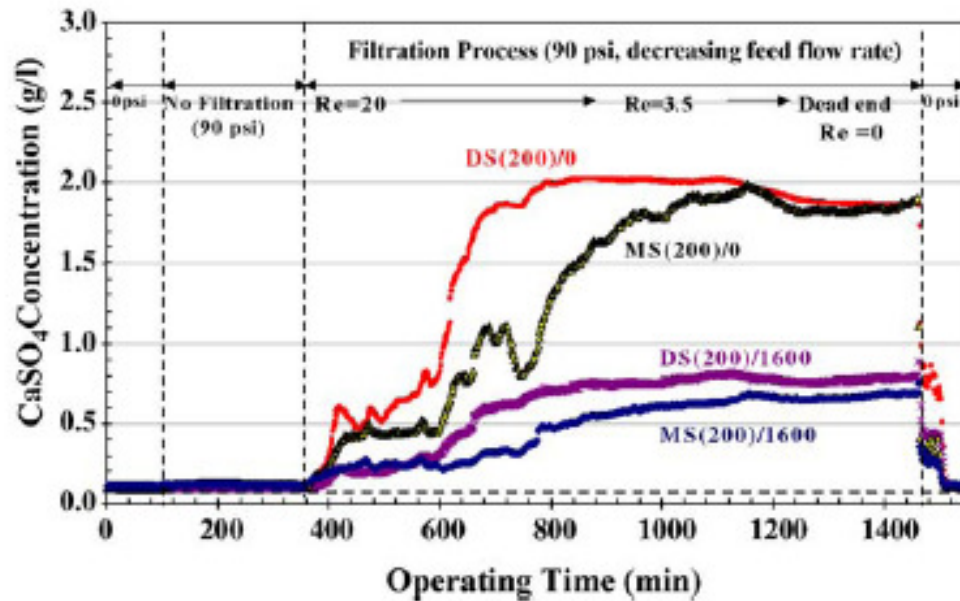


Figure 2.20: Representative capacitive response data from [Zhang 2006]. *DS* refers to downstream sensors, *MS* refers to midstream sensors, *0* refers to sensors at membrane level, and *1600* refers to sensors 1.6 mm above the membrane level.

2.5. Critique of the Literature

The aim of this thesis is to explore non-destructive methods for providing real time monitoring of the performance of membrane-based filtration systems. Most current methods of monitoring filtration system performance are based on ex-situ measurements, such as permeate flow rate, conductivity and turbidity. Such methods do not clearly show early-stage indications of the onset of fouling. Rather, a layer must be well established on the membrane surface before its presence is indicated. Remediation measures can then be costly, often requiring expensive chemical cleaning agents, system downtime, and membrane replacement. The use of in-situ sensors for providing real-time data could greatly improve membrane lifetime and overall system efficiency. They may also shed additional light on many of the fundamental phenomena at play. These are the primary motivations behind the development of such in-situ sensor systems.

The development of integrated sensor systems, however, presents a multi-disciplinary problem. It is necessary to understand the expected behavior of the membrane systems themselves in order to design appropriate sensors. A thorough review on concepts related to concentration polarization and fouling has been presented in this chapter. It is important to note that concentration polarization and fouling represent a continuum in filtration processes. They are interrelated, which was the motivation behind providing a thorough discussion of both in this chapter. The properties of the concentration polarization boundary layer (CPBL) influence the rate and density of fouling that will occur, and conversely, the properties of existing fouling layers influence the local CPBL [Gilron 1987, Lyster 2009]; fouling blocks local permeation, reducing CP. The fouling itself may be complete (standard blocking model) or just produce additional resistance to permeate flow (cake/gel layer model). Therefore, it is important to consider them to be coupled phenomena, and keep that in mind when developing sensor systems.

Although the details may vary between reverse osmosis, nano-, ultra- and microfiltration separations, concentration polarization can be described by many of the same fundamental concepts. These include the continuity equation, the Navier-Stokes equation, and the convection-diffusion equation. The simplest configuration considered is an unstirred dead-end batch cell where the CP presents a 1D mass transport problem. Even this problem is not trivial, because it requires the simultaneous solution of three differential equations with both a time and space variable. Among the first to address this problem for the unstirred batch cell, as well as for laminar cross flow, was Dresner [1964]. The introduction of cross-flow adds a tangential velocity component, which increases the complexity of the mathematical solution. Dresner assumed constant flux and perfect rejection, which is clearly unrealistic in many modern filtration processes. The work was very important, however, because it provided a foundation for more sophisticated solution approaches which came later. This included the addition of non-ideal rejection in an unstirred batch cell [Raridon 1966], and the effect of osmotic pressure [Liu 1970].

Most modern filtration systems operate in a cross-flow mode because the convective shear flow reduces the concentration polarization, thereby reducing osmotic resistance and allowing greater permeation. This can form a steady-state condition prior to the occurrence of fouling, which can be mathematically described. The cases reviewed here concern flat-sheet rectangular channels. The fluid velocity profile used by most authors for this configuration (two semi-permeable plates) was developed by Berman [1953]. Since the fluid flux rate through the membranes is typically very small compared to the cross flow rate, the approximation for simple Poiseuille flow can also be utilized. Dresner [1964] and Sherwood [1965] were among the first to fully treat this problem mathematically, assuming a membrane with perfect rejection and constant permeate flux along the length of the flow channel. Despite the fact that perfect rejections and constant permeate flux are clearly not realistic, the mathematical methodologies provided the basis for later, more refined approaches. Gill [1965] made a large step forward by performing a calculation of the concentration polarization profile where the permeate flux varied as a function of flow channel position. Each approach to modeling of concentration polarization and fouling had its own advantages and drawbacks, specifically concerning accuracy over certain periods of time or accuracy within certain regions in the flow channel.

The fundamental question posed in the fouling models is how to mathematically represent the resistance to permeate flow. The details vary between filtration type, but the general mechanisms are presented as partial pore blockage, complete pore blockage, cake layer or various combinations of these mechanisms. It should be noted that formulating detailed representations of fouling layers can be very difficult. Biofilms, for example, exhibit dynamic morphology, which is dependent on microbial community structure, growth rates, age, substrate concentrations, and local hydrodynamic conditions. Modeling by means of averaged methods, however, can be applied with certain practical utility. There is currently a focus on developing finite-element methods to explain CP and fouling in membrane modules of many different configurations [Ahmad 2005, Lyster 2009].

While there is extensive literature available on theoretical treatments of CP and fouling, there is much less work available to confirm the mechanisms assumed in these predictions with in-situ, real-time data. Most of the modeling methods have been verified by monitoring of permeate flux. Optical methods of monitoring fouling are one obvious approach, although there are many shortcomings. The use of an optical microscope was demonstrated by Mores et al. [2001] to observe fouling by stained yeast cells, and by Uchymiak et al. [2007] and Lyster et al. [2009] to observe inorganic scaling during reverse osmosis. This methodology can certainly be put to good use for system design in flat-sheet systems. This utility was clearly shown by Lyster et al. [2009], where images were coupled with a finite element analysis which explained how scaling growth can vary in the horizontal direction, as well as in the axial direction with cross flow. None of the other modeling studies take this point into account. Unfortunately, direct observation by optical microscopy is not likely to be scaled up for large volume industrial processes, particularly for desalination. It would not be especially useful in non-flat-sheet geometries, such as spiral-wound, which is the industry standard.

Ultrasonic time-domain reflectometry (UTDR) has shown promise in application to non-flat-sheet geometries. The studies employing UTDR presented in this review required no optical window or invasive integration scheme. Indeed, initial work has shown some efficacy of the method with spiral-wound modules, where the multiple windings result in more complicated analysis of the echo signal [Zhang 2003, 2005, Chai 2007]. A greater number of studies have been performed using flat sheet configurations, and have effectively demonstrated that analysis of the echo waveforms reflected from the membrane surface can indicate a change from a clean state to a fouled state. The ultrasonic transducers can be mounted externally to the module housing and replaced as desired. This consideration potentially allows for very simple installation with industrial-scale systems, which is the direction of current and future work involving UTDR monitoring. Concerns do exist, however, about response sensitivity, particularly in detection of early-stage scaling. Acoustic energy losses occur due to reflections from

interfaces, scattering and beam spread. Because of these factors, the earliest stages of scaling are often not detectable, particularly in the inner windings of a spiral-wound membrane.

There is much less work in the literature on real-time monitoring of concentration polarization than on fouling. This task is, of course, inherently much more difficult. While UTDR has been shown to be able to detect fouling, it is not sensitive enough to detect concentration polarization [Chai 2003]. The shadowgraphic and refractometric methods presented in [Vilker 1981 a, b] and [Ethier 1992] demonstrated CP observation via gradients in boundary layer refractive index in dead-end batch modules. Concentrated protein solutions were filtered, yielding very thick concentration boundary layers. Additionally, the probing beams were very limited in resolution close to the membrane surface, and the possible presence of a gel layer at the membrane surface was not accounted for in analysis of the results. A dead-end configuration is used in certain pharmaceutical applications, but not in applications where large throughput is required. Cross-flow configurations are much more commonly found precisely because they reduce the CPBL and thus resistance to permeation due to osmotic or deposition effects.

Liu and Williams [1970] reported monitoring of CP using aqueous salt solutions by means of conductivity measurements. This method involved conductivity measurement between a needle microprobe and the stainless steel wall of a dead-end RO module. Again, the module was an unstirred batch cell and the resulting CPBL was quite thick. There was also significant uncertainty in placement of the microprobe near the surface of the membrane and the module wall. This made accurate measurements very close to the membrane surface difficult. While this method demonstrated an initial success in real-time monitoring of CP, the configuration is not appropriate for the modern large-scale processes we are interested in.

Zhang et al. [2005, 2006] demonstrated direct monitoring of the CPBL in a laminar cross-flow configuration with integrated MEMS capacitive sensors. The results qualitatively matched the expected profile of a CPBL layer, with the greatest capacitive responses downstream and close to the membrane, as

expected. This work represented a large step forward in direct monitoring of concentration polarization however the tests were carried out under somewhat unrealistic conditions. The filtration module was designed with an unusually tall flow channel, both to accommodate the vertically oriented sensors, as well as to allow for flow conditions that would generate an unusually thick CPBL.

The current thesis is intended to build upon knowledge of the interrelated concentration polarization and fouling phenomena in an effort to develop next-generation integrated sensor systems which can provide real-time in-situ information. One of the primary questions concerns the degree to which the presence of a sensor inside the flow channel influences local filtration conditions. Despite any perturbation to local filtration behavior, can the sensors still be calibrated and employed as useful tools in CP monitoring and scaling detection during nanofiltration. Do the sensors provide significant advantages in terms of sensitivity to CP and early-stage scaling due to their location within the flow channel of a desalination module? Chapter 3 introduces the use of internally integrated electrolytic sensors for monitoring the concentration of sparingly soluble salts very close to the membrane surface. Chapter 4 presents the use of ultrasonic transducers that are internally mounted into the filtration module, where the transducer is in direct contact with the back-side of the membrane. This configuration serves as an attempt to improve sensitivity to early stage scaling. In both Chapters 3 and 4 we present background theoretical information essential to understanding the functioning of the respective sensing mechanisms (electrolytic, acoustic).

Chapter 3

Integrated Electrolytic Sensors for Monitoring of Concentration Polarization

3.1. Motivation and Sensor Design Guidelines

In this chapter, the development and application of integrated sensors for real-time, in-situ monitoring of concentration polarization (CP) at the membrane surface during cross-flow desalination is described. It is of great interest to study concentration polarization experimentally, since CP is always the precursor to scaling formation. Scaling during reverse osmosis (RO) separations results from precipitation and crystal growth on nucleation sites located within the supersaturated boundary layer near the membrane surface. A thorough overview of concentration polarization concepts was presented in the literature review in Chapter 2. In this chapter concepts concerning electronic measurements for solute concentration characterization in electrolytic solutions are presented.

Several physical models have been proposed and described to mathematically explain CP phenomena in an assortment of physical configurations. These configurations include dead-end, laminar cross-flow and turbulent cross-flow filtrations, which may be performed under batch, flat-sheet, spiral-wound or hollow-fiber geometries. Many of these model predictions have been verified via permeate flux measurements. Very little work exists, however, with the purpose of directly observing the concentration polarization boundary layer (CPBL) by experimental means. Many of the experiments reported in the literature concerning direct observation of CP involve configurations that are very different from those found in industrial desalination processing. The reported examples of direct CP monitoring typically involve operating conditions under which very thick concentration boundary layers form. Often macromolecules or colloidal solutions are used.

Commercial desalination, on the other hand, is typically performed in spiral-wound modules; the feed cross-flow velocity is much greater and the CPBL is much thinner. In practice, sparingly soluble salts such as calcium sulfate, calcium carbonate and barium sulfate are particularly problematic because they precipitate at low concentrations [Lyster 2009]. The aim of the work presented in this chapter is to develop a sensor system that can function under conditions closer to those encountered in commercial desalination. The primary sensor design guidelines are as follows:

- The presence of the sensor itself must not have a significant influence on the overall operation of the filtration system, nor significantly disturb the local conditions where it is located.
- The sensor must sample the fluid properties as close to the surface of the membrane as possible. The sensing area should be immersed within the concentration polarization boundary layer (CPBL), so that the sensor is not simply the bulk feed.
- The sensor design must demonstrate feasibility for future use in a realistic large-scale commercial desalination environment. Environmental factors include module geometry, operating pressure, cross-flow rate, feed composition, solute concentration and temperature.

3.2. Fundamentals of Electrolytic Conductivity Measurements

Most common commercially available conductivity probes employ two electrodes that are immersed in the electrolytic solution under test. The electrodes are connected across an external AC voltage source, and the resulting complex impedance magnitude and phase angle are recorded. Electronic parameters such as capacitance, resistance, conductance and inductance can then be derived by the measurement device.

Commercial conductivity probes typically operate in a mode that minimizes the influence of electrode surface impedance effects including the capacitive electric double layer and complex electrochemical reactions [He 2001, 2005]. Electrochemical reactions, often referred to as Faradaic processes [Bard 2001], are minimized by using low applied voltage and selection of an inert electrode material. Platinum and palladium are common choices [Bard 200, He 2001]. The equivalent circuit most commonly used for the analysis of conductivity cells is shown in Figure 3.1. The impedance due to the

capacitive electric double layer can be controlled by choice of operating voltage and frequency. The resistance is primarily controlled by cell geometry. Equations 3.1 and 3.2 give the relations for electrical impedance of resistive and capacitive circuit elements, respectively. Considering a circuit in terms of total impedance on the complex plane can often simplify analysis.

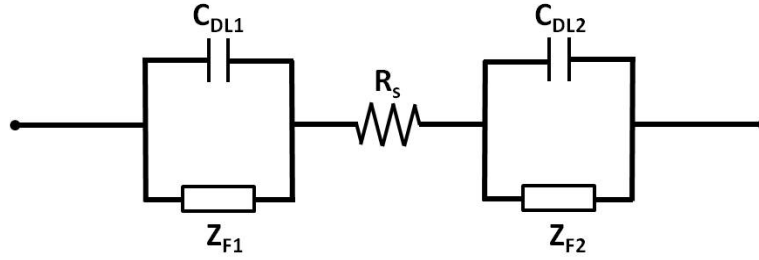


Figure 3.1: Equivalent circuit used for analysis of electrolytic conductivity cells. C_{DL} is the electrode double-layer capacitance, Z_F is the impedance due to Faradaic processes and R_s is solution resistance.

$$Z_R = R \quad (3.1)$$

$$Z_C = \frac{1}{j\omega C} \quad (3.2)$$

When an AC voltage is applied by the conductivity probe, an AC electric field develops in the region between the electrodes. Dissociated ions serve as charge carriers in the electrolytic solution, resulting in a measurable AC current. Ohm's Law can then be applied to determine the resistance, R_s , of the solution. In the current thesis, we have developed miniaturized conductivity probes for use within desalination modules. These probes are connected to an LCR meter (Agilent 4263B), which can be used to monitor multiple electronic parameters including complex impedance, phase angle, capacitance, resistance and conductance. We are interested primarily in experimental measurements and analysis of capacitance and conductance, which both vary with solute concentration. Analysis of these two parameters may provide important insights, since capacitance is largely a surface effect and conductance

is an effect of the medium between the electrodes; thus, sensor design and geometry are key factors to consider.

This raises the important concept of the cell constant for conductivity measurement. Most common commercially available conductivity probes employ a parallel plate electrode configuration (Figure 3.2). Neglecting fringing electric field effects, the parallel plate configuration can be analyzed in a very simple way. The fluid between the electrodes is a conductor with a given resistivity, ρ , which depends on the concentration of dissolved ions. The resistance can then be calculated based on the overlapping area between the electrodes and the distance between them. The relation between the measured resistance (an intrinsic property) and the fluid resistivity (an extrinsic property) is given in equation 3.3.

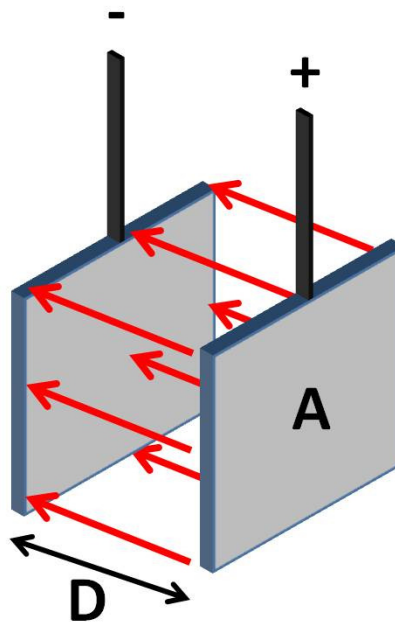


Figure 3.2: Schematic of parallel plate conductivity probe. The arrows are electric field lines between the electrodes. The fluid between the electrodes has conductivity, ρ .

$$R = \frac{\rho d}{A} = \kappa \rho \quad (3.3)$$

Here R is the resistance, d is the distance between the parallel plate electrodes and A is the overlapping area. The term κ has been introduced, and is known as the *cell constant* of the probe. Other simple electrode geometries have analytical solutions for the cell constant, while most require numerical computation.

3.3. Electrolytic Conductivity Concepts

Since this thesis is in part concerned with making direct measurements of feed solution conductivity in the near vicinity of the membrane during reverse osmosis desalination, it is worth considering fundamental mechanisms underlying the phenomenon. The molar conductivity is a property describing the efficiency of dissolved salts as electric conductors, and is given by the conductivity [S/m] divided by molar concentration [mol/m³]. Thus, the molar conductivity has the units [S·m²/mol]. It can be experimentally calculated for aqueous salt solutions, and has been shown to have a square-root dependency on concentration, as discovered by Kohlrausch [Kohlrausch 1900, Rieger 1994]:

$$\Lambda = \Lambda^0 - s\sqrt{C} \quad (3.4)$$

Where Λ is the molar conductivity, Λ^0 is the molar conductivity extrapolated to infinite dilution, C is the molar concentration of the solute, and s is a fitting parameter depending on the particular solute/solvent system. A first-order estimate of conductivity assumes the salt to be completely ionized and dilute, meaning that there are no interionic interactions. The total molar conductivity is then the sum of the molar conductivities of the individual ions:

$$\Lambda^0 = \nu_+ \Lambda_+^0 + \nu_- \Lambda_-^0 \quad (3.5)$$

The ‘+’ refers to the cations, the ‘-’ refers to the anions and ν is the number of moles of the ion for each mole of salt. This term will differ for non-symmetric salts. Another useful term is the transference number, which relates the conductivity of the individual ion species to the total conductivity of the solution, Λ . The transference numbers of the cations and anions must sum to 1.

$$t_{\pm} = \frac{\nu_{\pm} \Lambda_{\pm}}{\Lambda} \quad (3.6)$$

A relation for molar conductivity was developed by Onsager, which takes into account the effect of the ionic atmosphere surrounding each ion when an electric field is applied [Onsager 1932, Rieger 1994]. This expression has been shown to be quite useful in predicting the conductivities of aqueous electrolytes, particularly at low concentration. Ions of one charge in the electrolyte will tend to attract ions of the opposite charge, resulting in the formation of an ionic atmosphere. Onsager’s expression for molar conductivity is given in equation 3.7.

$$\Lambda = \Lambda^0 - \frac{|z_+ z_-| F^2 \Lambda^0}{12 \pi \epsilon \epsilon_0 x_A R T N_A} \frac{q}{1 + \sqrt{q}} - \frac{(|z_+| + |z_-|) F^2}{6 \pi \eta N_A x_A} \quad (3.7)$$

Where x_A is the ion atmosphere thickness, following the Debye-Hückel formulation [Rieger 1994], η is the solvent viscosity, ϵ is the dielectric constant of the solvent, ϵ_0 is the permittivity of free space, R is the ideal gas constant, T is temperature, and N_A is Avogadro’s Number. The term q is expressed as follows:

$$q = \frac{z_+ z_-}{(z_+ - z_-)(z_- t_+ - z_+ t_-)} \quad (3.8)$$

Here t is the transference number of the given ion, defined in equation 3.6. $q = 1/2$ for symmetric electrolytes. This relation is primarily valid at low concentrations, which is appropriate for the work presented in this thesis. The ionic atmosphere thickness can be solved from the following expression:

$$x_A = \sqrt{\frac{\epsilon\epsilon_0 RT}{F^2 I}} \quad (3.9)$$

Where F is Faraday's constant and I is the ionic strength:

$$I = \frac{1}{2} \sum_i z_i^2 C_i \quad (3.10)$$

The first term in the Onsager conductivity relation (equation 3.7) is the so-called ion atmosphere relaxation effect. When an ion is attracted by an electric field, it is subject to an opposing force exerted by its ion atmosphere, thus lowering its contribution to the conductance. The second term is the electrophoretic effect. When the ion moves through the fluid, it tends to pull its ionic atmosphere with it. This results in an increased viscous drag effect opposing the motion.

3.4. Double-Layer Concepts in Electrolytic Solutions

In an electrolytic solution, the dissolved salts yield charged ions that have freedom of movement within the solution, and thus serve as mobile charge carriers. When a potential difference is applied across the opposing electrodes, the electrode surface becomes charged due to either an excess or deficiency of electrons. The resulting electric field causes ions of the opposite sign to migrate toward the electrode; cations collect at the negatively charged cathode and anions collect at the positively charged anode. This accumulation of excess ions is called the double layer. The double layer can have a thickness from a few Ångstroms (high concentration, high applied voltage) to several nanometers (low concentration, low applied voltage) in aqueous solutions [Conway 1999].

A potential drop occurs across the double layers at each electrode as well as across the resistive solution between the electrodes (Figure 3.3). It is assumed that no Faradaic processes occur, meaning the electrode is considered to be *ideally polarized*. This type of capacitive/resistive device is often called an

electrochemical supercapacitor [Conway 1999] because the potential drop occurs over such a thin layer (nanometers) can provide large energy storage capacity. See [Conway 1999] for discussion of these types of devices for energy storage.

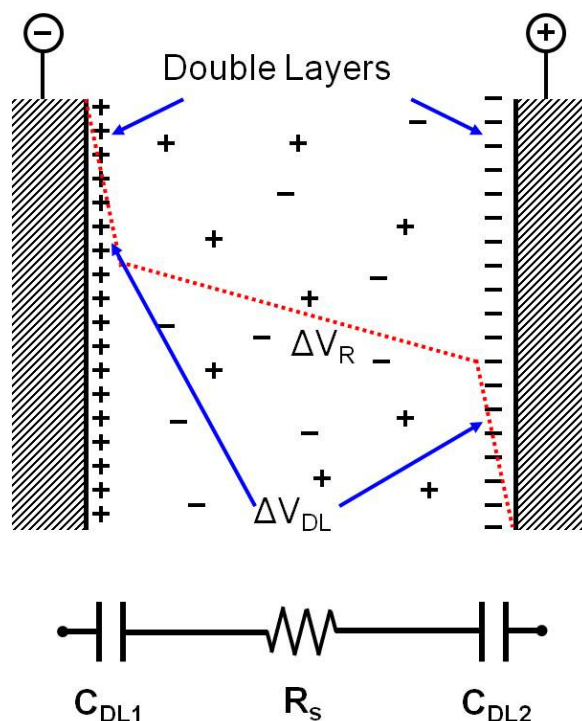


Figure 3.3: Schematic of electrolytic capacitor and corresponding voltage drops between the electrodes. ‘+’ symbols are cations, ‘-’ symbols are anions, and the dashed line represents the electric potential drop across the double-layers and electrolytic solution. Following [Conway 1999].

The first description of the ionic double layer effect was provided by Helmholtz [Helmholtz 1853, Bard 2001], who postulated that a single layer of ions adsorbed to the surface of each electrode with a thickness of a few Ångströms. The potential was assumed to drop linearly across this thin layer, fundamentally describing a parallel plate capacitor. The model was simple to explain, but did not correlate well with the results of many experiments. In particular, this formulation assumes that the capacitance is constant with concentration and applied voltage, which is not correct.

The Helmholtz model was modified by Gouy and Chapman [Gouy 1910, Chapman 1913, Bard 2001] to account for statistical thermodynamic phenomena. They explained that the ions do not form a simple monolithic layer on the electrode surface. Rather, the ions are constantly in thermal motion. An energetic balance must be expressed between the electrostatic attraction of the ions to the electrode and thermal motion. The result is a gradient in ionic concentration, which decreases with distance from the electrode. Far from the electrode, the concentration is that of the bulk.

The Gouy-Chapman model assumes that the main parameters (charge, solute concentration, electric field, electric potential) vary only with distance from the electrode, x . The ions are also assumed to be point charges with magnitude $\pm z$. The solution is divided into laminae of thickness dx , and the electric potential in these laminae varies because of masking by ions in the layers closer to the electrode. Thus, the energy levels of the ions also vary, which can be described by the Boltzmann distribution [Bard 2001]:

$$n_i = n_i^0 \exp\left(\frac{-z_i e \phi}{kT}\right) \quad (3.11)$$

Where ϕ is the local electric potential, i refers to the specific ion under consideration, n_i is the local number concentration of the ions, n_i^0 is the bulk concentration of the ions in the region far from the electrode where $\phi = 0$, z_i is the charge of ion i , e is the fundamental electric charge, k is Boltzmann's constant and T is the temperature. From this expression, we can convert ionic number density to charge density per unit volume, using the following relation:

$$\rho(x) = n_i z_i e \quad (3.12)$$

Poisson's equation is then applied. This governs the distribution of charge in a varying potential field, $\phi(x)$. The potential decreases from the surface of the electrode to zero at $x = \infty$.

$$\rho(x) = -\epsilon\epsilon_0 \frac{d^2\phi}{dx^2} \quad (3.13)$$

Combining equations 3.11 and 3.13 yields the Poisson-Boltzmann equation:

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\epsilon\epsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \phi}{kT}\right) \quad (3.14)$$

We use the following identity to recast this equation into a form which can be more easily manipulated:

$$\frac{d^2\phi}{dx^2} = \frac{1}{2} \frac{d}{d\phi} \left(\frac{d\phi}{dx} \right)^2 \quad (3.15)$$

Which yields the following form of the Poisson-Boltzmann Equation:

$$d\left(\frac{d\phi}{dx}\right)^2 = -\frac{2e}{\epsilon\epsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \phi}{kT}\right) d\phi \quad (3.16)$$

Integration gives:

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\epsilon\epsilon_0} \sum_i n_i^0 \exp\left(\frac{-z_i e \phi}{kT}\right) + const. \quad (3.17)$$

We then apply the following boundary conditions: $\phi(\infty) = 0$ and $d\phi(\infty)/dx = 0$ and obtain:

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\epsilon\epsilon_0} \sum_i n_i^0 \left[\exp\left(\frac{-z_i e \phi}{kT}\right) - 1 \right] \quad (3.18)$$

If the electrolyte is symmetric, meaning the charge of the cations and anions are the same, $z_{cation} = z_{anion}$, this equation can be solved analytically. Applying this assumption yields a first-order differential equation as follows:

$$\frac{d\phi}{dx} = -\left(\frac{8kTn^0}{\epsilon\epsilon_0}\right)^{1/2} \sinh\left(\frac{ze\phi}{2kT}\right) \quad (3.19)$$

Equation 3.19 can then be separated and integrated to yield the potential profile in the diffuse layer. The left hand side is integrated from ϕ_0 at the electrode surface to $\phi(x)$, and the right hand side is integrated from 0 to x , giving:

$$\frac{\tanh(ze\phi/4kT)}{\tanh(ze\phi_0/4kT)} = \exp(-\kappa x) \quad (3.20)$$

Where the term κ is:

$$\kappa = \left(\frac{2n^0 z^2 e^2}{\epsilon\epsilon_0 kT}\right)^{1/2} \quad (3.21)$$

The generalized relation for differential capacitance is:

$$C = \frac{d\sigma}{d\phi_0} \quad (3.22)$$

Where σ is the conductivity. In order to solve for the capacitance of the double layer, we first apply Gauss's Law with a Gaussian box enclosing the charge distribution near the electrode surface (Figure 3.4). Analysis of the electrostatic field by Gauss's Law involves the use of imaginary volumes containing the charge distribution under consideration. The classic distributions, for example, involve using a Gaussian pillbox to solve the electric field generated by a plane of charge or a Gaussian cylinder to solve

for the field generated by a charged wire (linear charge). Gauss's Law reflects the relationship between the charges contained within the imaginary Gaussian volume and the electric field flux through the surfaces of the volume. It is given in the general integral form according to equation 3.23:

$$q = \epsilon\epsilon_0 \oint_{\text{surface}} \vec{E} \cdot d\vec{S} \quad (3.23)$$

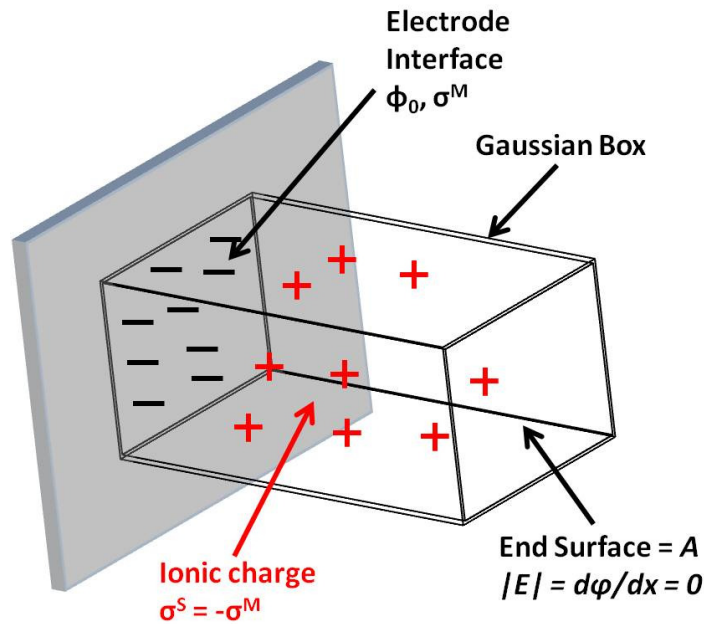


Figure 3.4: Gaussian box for relating the charge to electric field. Following [Bard 2001].

The end surface of the box is far enough away from the electrode that no electric field is assumed to pass through it ($E = d\phi/dx = 0$). The ions contained in the box therefore must balance the charge on the electrode surface. It is also assumed that the field lines are perpendicular to the electrode surface, so no electric flux passes through the side walls of the box. Therefore, the only electric flux that passes through a surface of the Gaussian box is on the electrode surface. An expression for the spatial rate of change of electric potential, $d\phi/dx$ (equation 3.19) has already been developed, and the value at $x = 0$, $(d\phi/dx)_{x=0}$, is now of interest. The expression for Gauss's Law in this configuration can be written as follows:

$$q = \epsilon \epsilon_0 \left(\frac{d\phi}{dx} \right)_{x=0} \int_{\text{surface}}^{end} dS = \epsilon \epsilon_0 A \left(\frac{d\phi}{dx} \right)_{x=0} \quad (3.24)$$

The solute charge density, σ^S , must balance the electron charge density on the metal electrode, σ^M .

$$\sigma^M = -\sigma^S = \left(8kT \epsilon \epsilon_0 n^0 \right)^{1/2} \sinh \left(\frac{ze\phi_0}{2kT} \right) \quad (3.25)$$

Applying this expression to equation 3.22 for the differential capacitance gives the following:

$$C = \frac{d\sigma^M}{d\phi_0} = \left(\frac{2z^2 e^2 \epsilon \epsilon_0 n^0}{kT} \right)^{1/2} \cosh \left(\frac{ze\phi_0}{2kT} \right) \quad (3.26)$$

The Gouy-Chapman model, however, assumes that the charges are point charges, which is not true. In response to this concern, Stern [Stern 1924] introduced the concept of a finite distance of closest approach for ions at the electrode surface, which took the form of a compact, Helmholtz-type layer (Figure 3.5). In Stern's modification to the double layer model, the compact layer at the electrode surface behaves like a parallel plate capacitor, with a thickness on the order of the ionic hydration radius. The dielectric constant of the compact layer is typically assumed to be significantly lower than that of the bulk solution ($\epsilon_{\text{water}} \sim 80$). A very strong electric field occurs within the compact Helmholtz layer because the potential drop occurs over such a short distance. Dielectric saturation is believed to occur within the compact layer (adsorbed solvent and hydrated ions) at such high field strengths [Conway 1951]. The Stern-Gouy-Chapman model takes the double layer to behave as two capacitors in series (Figure 3.5, equation 3.27).

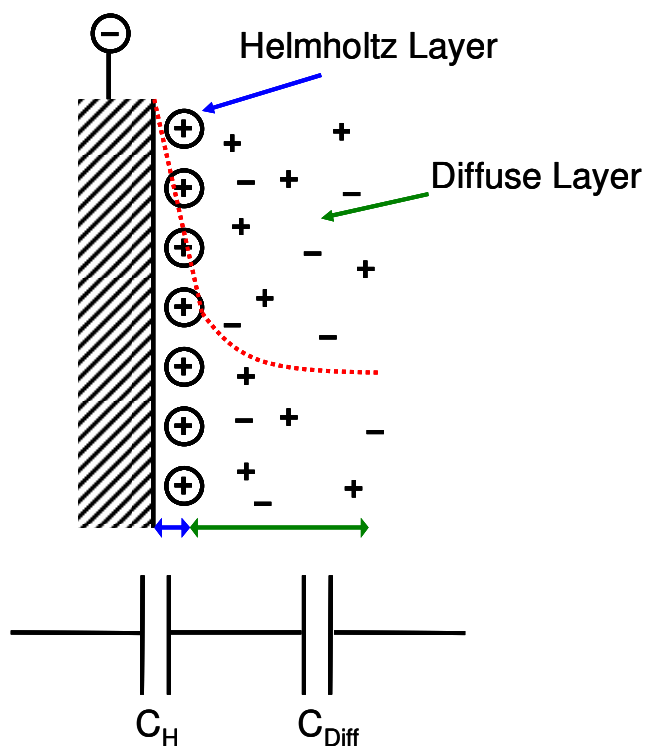


Figure 3.5: The Stern-Gouy-Chapman model of the double layer at the electrode interface. Following [Conway 1999].

$$\frac{1}{C_{DL}} = \frac{1}{C_H} + \frac{1}{C_{Diff}} \quad (3.27)$$

Additional improvements to the double-layer model have been added since the formulation of the Stern-Gouy-Chapman model. A review of electric double-layer research is given by Parsons [Parsons 1990]. One of the most important breakthroughs in double-layer modeling was presented by Grahame [Grahame 1947, Bard 2001], who defined and carefully described inner and outer Helmholtz planes (IHP and OHP). Specifically adsorbed ions on the electrode surface form the IHP, while hydrated ions are located further from the electrode, and form the OHP (Figure 3.6). In addition, solvent or other neutral molecules may become adsorbed to the electrode surface and can play a role in the overall electrical properties of the interface. Specific features of the ions and the solvent molecules themselves are accounted for in the Grahame model, including size, polarizability, and electron donor/receiver properties.

Anions, for example, receive an extra electron and are generally assumed to be larger than typical cations, which give up an electron. It is important, of course, to reference a table of ionic radii when considering specific salt systems. Cations tend to hydrate more strongly than anions [Conway 1999], meaning that the anion distance of closest approach to a positively charged electrode is often smaller than the hydrated cation distance of closest approach to a negatively charged electrode. The result is that the Helmholtz capacitance at a positively charged surface is often larger than the Helmholtz capacitance at a negatively charged surface [Conway 1999].

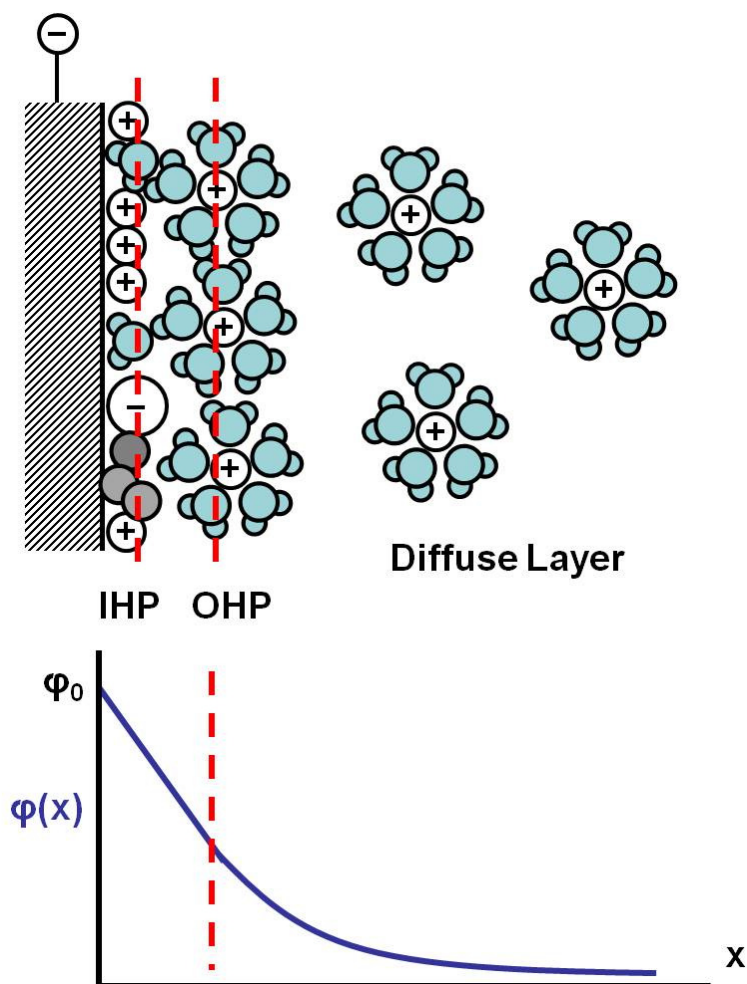


Figure 3.6: Grahame model of the double layer at the electrode surface. IHP is the inner Helmholtz plane (specifically adsorbed species), OHP is the outer Helmholtz plane (hydrated ions). Below is a plot of the electric potential, which drops to 0 far from the electrode.

3.5. Design and Fabrication of Integrated Electrolytic Sensors

3.5.1. Design Concepts

The goal of the work in this thesis is to develop an integrated sensor system that can be used to monitor the concentration of dissolved solute in a flat-sheet cross flow filtration module. It is of particular interest to be able to monitor the concentration within the concentration polarization boundary layer (CPBL) near the membrane surface. Hence, the sensor design should follow the guidelines outlined in Section 3.1.

Initial work focused a design concept similar to that reported by Zhang [Zhang 2005, 2006], incorporating interdigitated electrodes in contact with the electrolyte for capacitive measurement readings. These readings can then be calibrated to give concentration values. The sensors employed by Zhang were fabricated by the Multi-User-MEMS-Process (MUMPS). The chip (2 mm x 2 mm x 0.5 mm) consisted of a silicon substrate (500 μm) coated with a thin insulating silicon nitride layer and a conducting polysilicon layer that was micromachined to form two interdigitated electrodes. An external test system could then be connected to the electrodes via a physical electronic feed-through scheme that passed through the top wall of a flat-sheet filtration module.

These sensor chips were mounted vertically (2 mm tall) in order to monitor salt concentration at select vertical locations above the membrane surface. The sensors were able to show differences in concentration with varying axial position and height above the membrane, and the results were qualitatively consistent with expected behavior. Higher concentration was found downstream and closer to the membrane surface. The specific experimental system, however, was not representative of practical desalination units. The module was built with an unrealistically tall flow channel, and tests were conducted under conditions such that a very thick CPBL would form (several mm). One significant aspect of the current thesis is to improve upon this scheme for application under more realistic and challenging conditions.

Prototype experiments were performed first in a flat sheet module similar to that used by Zhang. Further experiments were then performed in a flat-sheet cross flow module where the estimated CPBL thickness was calculated to be on the order of 100 to 200 μm thick, with cross-flow velocities up to 8 cm/s ($\text{Re} = 188$). Silicon is one of the most common substrates used in MEMS (Micro-Electro-Mechanical Systems) fabrication. It is easily machined, has good electronic properties and is inexpensive. Silicon is also a brittle material, such that if it were thin enough to be completely immersed in the boundary layers predicted for the current work, it would certainly break. Flexing of the membrane and module housing is expected under typical operating pressures. The brittleness of silicon also makes it a poor substrate choice for future use within spiral-wound or hollow-fiber modules, since it cannot bend to conform to the curved membrane geometry.

A wide variety of flexible circuits has been manufactured for many years, and thus could serve as a basis for our sensor fabrication design. Most flexible circuits commercially produced today consist of patterned copper films on the flexible substrate, and are intended for use in telecommunications, automotive and aerospace applications, just to list a few [Gilleo 1992]. Copper, however, would be a poor electrode choice for long-term immersion in saline solutions because of corrosion [Schweitzer 2007]. We desire to manufacture very thin flexible devices, so that they would be completely immersed in the CPBL. We custom fabricated the sensors reported in this thesis at available facilities on the University of Colorado campus (University of Colorado MEMS Lab, Colorado Nanofabrication Laboratory, Nanomaterials Characterization Facility). Kapton polyimide sheets provided by Dupont were used as the flexible substrate (25 μm thick, Type 100 FPC, Dupont). Kapton makes a good substrate because it withstands most chemical and temperature conditions encountered in MEMS processing [Gilleo 1992, Dupont 2010]. Low-stress nickel electrodes were electroplated on the Kapton (Nickel Sulfamate RTU, Technic Inc.). Although not as good as platinum or palladium, nickel was chosen because it demonstrates acceptably high corrosion resistance for proof-of-concept experimentation [Schweizer 2007]. Nickel seed layers are easy to thermally evaporate on the substrate and several ready-to-use electroplating solutions

are available (Technic Inc.). Nickel plating solutions are affordable in comparison to platinum or palladium.

3.5.2. Fabrication Process

The process used to fabricate the custom flexible integrated concentration sensors is presented below. A schematic flow diagram is provided in Appendix A.

1. Place WaferGrip adhesive (Dynatex) on a 2.5 cm × 2.5 cm microscope slide, then set the slide on a hot plate (110° C). When the WaferGrip melts, place a square of Kapton sheet (25 µm thick, Type 100 FPC, Dupont) on the slide, being careful to avoid forming large bubbles under the Kapton. Remove chip from the hotplate and allow it to cool.
2. Thermally evaporate a 5 nm titanium adhesion layer followed by a 20 nm seed layer of nickel on the Kapton.
3. Deposit ~10 µm photoresist (AZ P4620, Clariant) on the chip. Lithographically pattern the resist (UV exposure, development) to form a mould for electroplating.
4. Electroplate nickel (Nickel Sulfmate RTU, Technic Inc.) with the plating solution at 45° C and stirred at 250 rpm to form the electrode structures. Plating current is determined by the area to be plated. Before plating, quickly dip the chip in nickel etchant (1-2 seconds) and rinse in deionized water to remove oxides from the seed layer surface. Plated thickness is between 4 µm and 8 µm.
5. Remove the photoresist in acetone. Rinse in isopropanol. Dry.
6. Etch the titanium/nickel seed layer that is still exposed. Etch nickel at room temperature for 25 seconds (Nickel Etchant TFB, Transene), and etch titanium at 45° C until seed layer is removed, typically 1.5 - 2 minutes (Titanium Etchant TFTN, Transene). Rinse the chip in deionized water and blow dry with nitrogen between etch steps.
7. Remove the Kapton sheet with the nickel structures from the glass slide by placing chip on hotplate to melt the WaferGrip adhesive (110° C). When melted, carefully pull the sheet off the slide.
8. Clean WaferGrip residue from the Kapton by immersing in amyl acetate at 65° C, then rinsing in acetone and isopropanol.
9. Place Kapton on thin double-sided transfer tape (Adhesive Transfer Tape 9482PC, 3M). The tape is 50 µm thick (0.002") and is on a backing. This forms a Kapton 'sticker'.
10. Cut the large Kapton 'sticker' square (2.5 cm × 2.5 cm) to form a smaller 'sticker' with the nickel electrode structures.
11. Peel Kapton/nickel electrode off the tape backing and apply to the filtration membrane.

3.5.3. Electrode Design

The following initial hypotheses were formulated to guide the geometry considerations of the sensor electrodes:

- Interdigitated electrodes should provide a large surface area exposed to the solution with a small footprint. This should yield more sensitive capacitance readings.
- Small finger and gap widths for interdigitated electrodes will reduce the vertical height above the membrane surface to which electric field lines extend. [Gevorgian 1996, Igreja 2004]. This consideration should result in readings with better resolution of conditions very close to the membrane surface, particularly for conductance measurements.
- The sensor substrate locally blocks permeation of water through the membrane resulting in perturbation of the CPBL. Convective cross-flow transport, however, should make the CPBL clearly detectable with acceptable sensitivity.

Over the course of this work, two different nickel electrode designs were tested in desalination experiments. The first was an interdigitated design, similar to that used by Zhang [Zhang 2005, 2006]. Two variants on this design were tested: one with finger and gap widths of $30\text{ }\mu\text{m}$, and one with finger and gap widths of $100\text{ }\mu\text{m}$. Figure 3.7 shows the layout design of the $100\text{ }\mu\text{m}$ finger/gap structure.

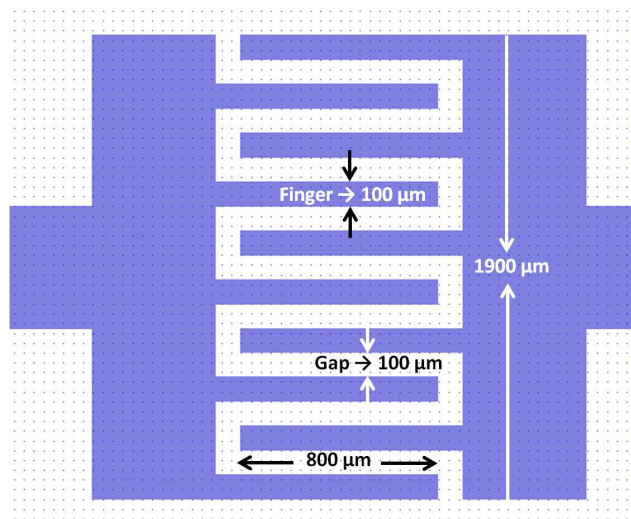


Figure 3.7: Interdigitated sensor design with finger and gap widths of $100\text{ }\mu\text{m}$.

The second design incorporated monolithic electrodes that were mounted individually to the membrane. They were placed so that a 0.5 – 1.5 mm gap of exposed membrane was present between the electrodes, forming a permeation channel. This electrode design was intended to test whether this permeate flow channel locally increased the CP index in the region between the two electrodes, reducing the effect of blockage and boundary layer perturbation. Figure 3.8 is a layout schematic of the full electrode structure, including contact pads for wiring to the external measurement equipment.

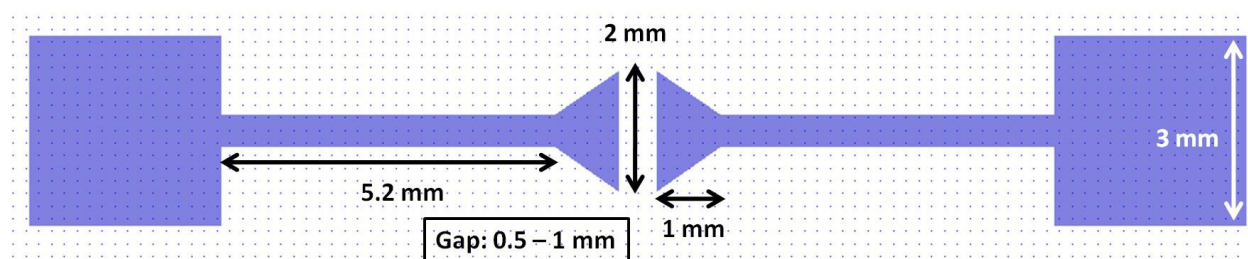


Figure 3.8: Layout schematic of full monolithic electrode structure.

3.6. Systems Integration

3.6.1. Filtration System

A stainless steel flat-sheet cross-flow cell was used in all experiments. The cell consisted of a top plate with a recessed cross-flow channel and a bottom plate with a recessed permeate-collection well. The recessed flow channel featured tapered entrance and exit regions to ensure laminar cross-flow [Mairal 1999, 2000]. The permeate channel contained many small posts, on top of which a porous steel plate was placed. The membrane was then placed on top of the porous steel support plate. The posts in the permeate channel enabled water to pass through the membrane and porous plate, and exit through the permeate collection ports with adequate clearance to insure a negligible pressure drop on the permeate side.

The top plate of the cell was placed on the bottom plate, leaving an enclosed flow channel over the membrane (7.5 cm wide by 55 cm long by 2 mm high), with 4-cm long tapered regions at the two

ends to minimize hydrodynamic entrance and exit effects. The cell had an inner o-ring to seal the flow channel and an outer o-ring for secondary sealing. The module was secured for high pressure operation with 24 evenly spaced bolts. Engineering drawings of the module plates are given in Appendix B.

A Fluid-O-Tech TMFR SS051 rotary vane pump was used in all experiments and a back-pressure regulator (Tescom) was placed on the retentate line to maintain constant pressure in the module. The retentate and permeate streams were recycled into the feed tank. The system also contained a bank of activated carbon pre-filters for removing particulates from the feed stream (CB1, OmniFilter, 0.5 μm ; PL-U.1X10UL, Serfilco, 0.1 μm). The feed stream passed through a heat exchanger to maintain a constant temperature ($\pm \sim 0.3^\circ \text{C}$) immediately before entering the flow module. The heat exchanger consisted of a 10 meter coil of stainless steel tubing, which passed through a water bath of controlled temperature. The temperature in the bath was maintained by a recirculating chiller (RTE-110, Neslab). A schematic of the fully integrated hydraulic and electronic system is presented in Appendix C.

3.6.2. Electronic Control and Data Acquisition

A custom LabView program was written to remotely carry out all electronic control and data acquisition functions required for the filtration experiments. The program incorporated LabView drivers (National Instruments) to control and acquire data from an Agilent 4263B LCR meter. The LCR meter was used to measure complex impedance, phase angle, resistance, conductance and capacitance from the integrated concentration sensors. It operated with a 10 kHz/50 mV (rms) test signal and was connected to the electrodes of each sensor via a multiplexing relay switch (ER-16, National Instruments). The LabView routine controlled multiplexer switching via a PCI-6503 digital I/O card (National Instruments) installed in the desktop computer. Data from the LCR meter was transmitted to the computer via a GPIB cable and GPIB card (National Instruments).

The following system operating parameters were also recorded: permeate flow rate (Flo-Sensor 101, MacMillan), permeate and feed conductivity (CDCN-91 Dual-Channel Conductivity Controller, Omega), pressure (PX603 Pressure Transducer, Omega) and feed temperature (J-Type Thermocouple, Omega). All of these devices generate differential voltage outputs which were calibrated to the physical parameters of interest. The device output lines were connected to a National Instruments USB-6008 Data Acquisition (DAQ) Module, which transmitted the data to the computer via a USB cable (Appendix C). The LabView control and data acquisition algorithm is outlined below. A graphical flow chart of the LabView algorithm is also shown in Figure 3.9. Parameter values from the integrated concentration sensors and all other corollary devices were recorded every 3 minutes and appended to the appropriate spreadsheet files on the desktop computer. LabView code is given in Appendix D and Matlab code for plotting the data is given in Appendix E.

1. Actuate multiplexer relay switches to close the circuit for the desired sensor.
2. Set the LCR meter function to the desired measurement parameter pair (i.e. Z, θ).
3. Record parameter values from LCR meter via GPIB and write to a spreadsheet.
4. Switch the LCR meter to next parameter pair (i.e. C, R). Record values and write to spreadsheet. Repeat steps 2 and 3 for all desired parameter pairs.
5. Switch multiplexer relay to next sensor circuit. Repeat steps 2, 3 and 4.
6. After all sensors have been sampled, set multiplexer relay switch so all circuits are open. This reduces energy use and mechanical wear of the switches.
7. Record feed pressure from the electronic pressure gauge via NI USB-6008 DAQ module.
8. Record feed conductivity from the commercial probe installed in stirred fed tank via NI USB-6008 DAQ module.
9. Record permeate conductivity from the commercial probe installed on the permeate line via NI USB-6008 DAQ module.
10. Record permeate flow rate from the electronic flow meter installed on the permeate line via NI USB-6008 DAQ module.

11. Record feed temperature from the thermocouple installed in heat-exchanger bath via NI USB – TC01 thermocouple DAQ module.
12. Wait until the pre-set measurement interval time, then repeat steps 1 through 11.
13. Terminate LabView script when filtration experiment is completed.

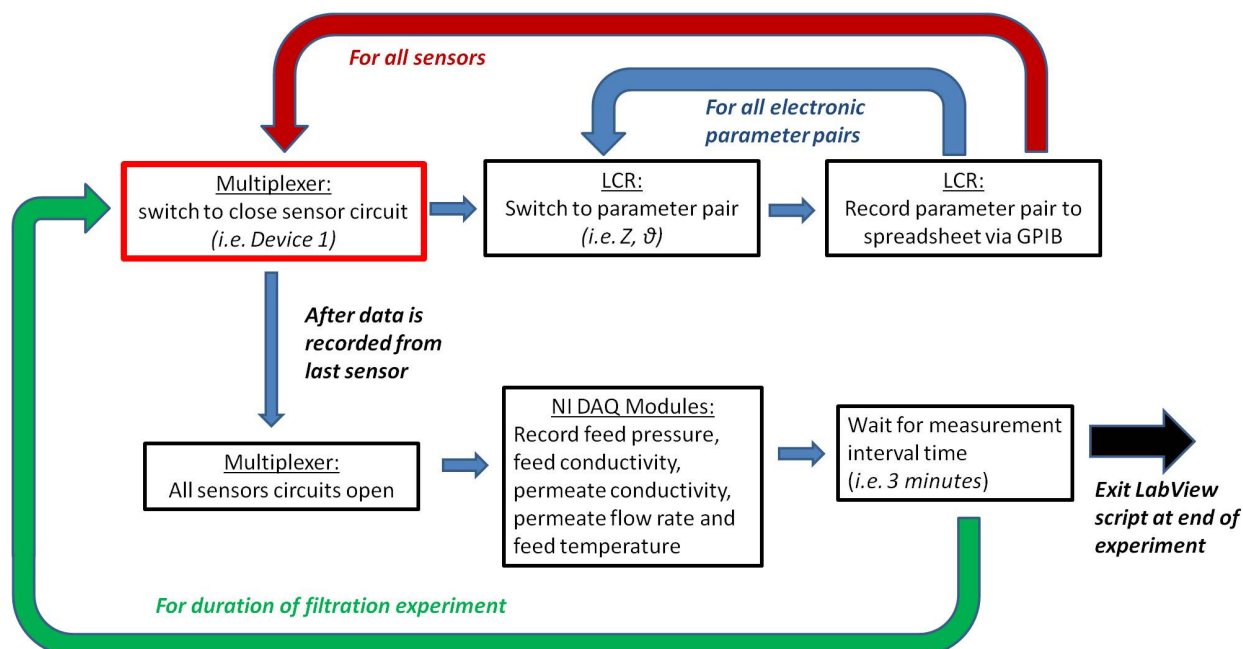


Figure 3.9: Flow chart of LabView algorithm for electronic control and data acquisition during filtration experiments.

The following LCR meter control variables were used for the experiments presented in this thesis:

- Voltage level: 50 mV (rms)
- Test signal frequency: 10 kHz
- Cable length correction: 0 m
- Measurement functions: C, R, G, Z, and θ .

3.6.3. Sensor Integration

The sensor integration scheme incorporating electronic feed-through between the flow channel and external equipment underwent several iterations over the course of this work. In this section two feed-through schemes are presented that were tested in the module with the integrated sensors. The experiments conducted in this section of the thesis included two in the short prototype module mentioned in Section 3.5.1 (one membrane, one top of flow channel) and six in the long module (three membrane, three top of flow channel). In the experiments conducted in the long filtration module, sensors were installed at up-, mid- and downstream locations. A sensor has two electrodes, so two electronic feed-through ports were required for each. The ports were drilled into the top and bottom plates of the module to allow for installation of electronic feed-through blocks. The feed-through ports were machined on the edges of the flow channel in order to minimize the impact of the feed-through assembly on the cross-flow hydrodynamics at the center of the cell, where the sensors were located.

The feed-through blocks on the bottom plate incorporated an electrically conducting component to puncture the membrane, in order to gain access to membrane sensors. Figure 3.10 shows plan view schematics of the sensors mounted on the membrane and the top wall of the flow channel. The sensors are located 14, 28 and 42 cm from the entrance of the flow channel. Figure 3.11 is a cross-sectional schematic showing the integrated sensors and cross-flow feed stream. The sensors on the membrane are immersed in the concentration polarization boundary layer and the sensors on the top wall of the flow channel are immersed in the bulk feed stream. The channel is 7.5 cm wide by 55 cm long by 2 mm high, with 4 cm tapered regions at the two ends.

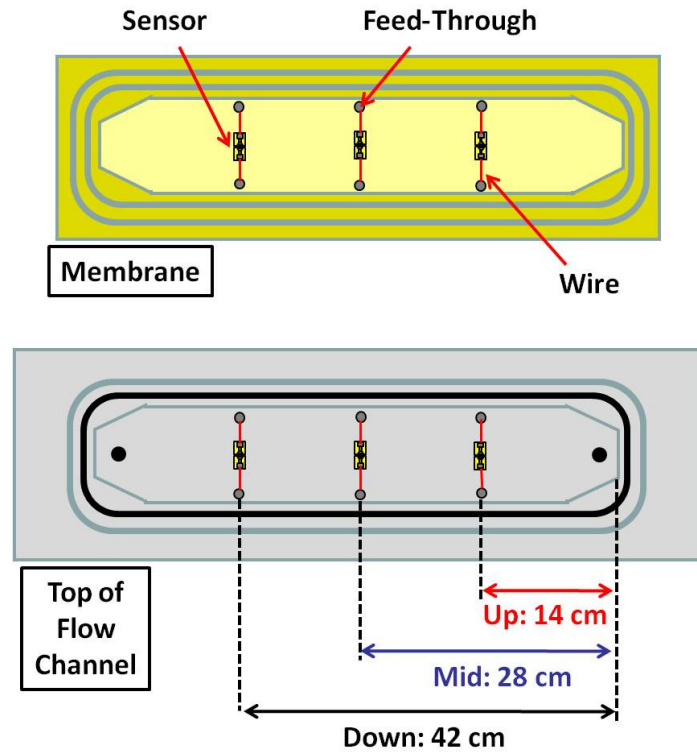


Figure 3.10: Plan view sensors mounted on the membrane (top) and the top wall of the flow channel (bottom). Not drawn to scale.

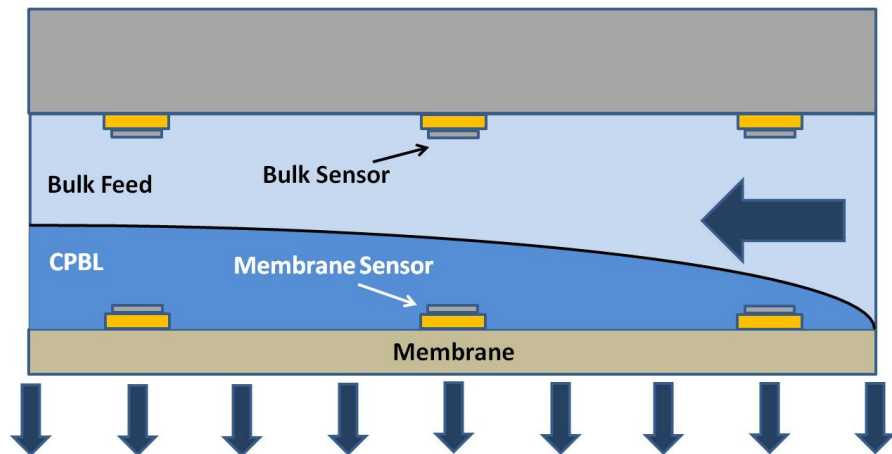


Figure 3.11: Schematic of bulk and membrane sensors. Sensors are mounted on the top wall of the flow channel to monitor the bulk feed concentration and sensors are mounted on the membrane monitor concentration within the CPBL. Not drawn to scale.

A schematic of the electronic feed-through block assembly used in initial testing (configuration 1) is shown in Figure 3.12. The feed-through blocks consisted of Teflon cylinders (7 mm diameter) with a groove in the center for placement of an O-ring. When installed into the feed-through ports in the filtration module, the O-rings prevent leaking. A hole was drilled through the center of the Teflon blocks, and pogo-pin receptacles (SPR-25W-2L, Everett Charles Technologies) were press-fit. 24-gauge solid core wire was cut so that the end was sharp in order to puncture the membrane and gain access to the integrated sensors. This wire was then soldered into the pogo-pin receptacle. Wire wrap (30-gauge) was stripped at the end and wrapped around the 24 gauge solid core wire. The other end of the wire was then secured to the nickel contact pads on the flexible sensor electrodes with conductive epoxy. The 24-gauge wire was folded over and secured to a Kapton base with conductive epoxy. The feed-through assembly and the contact pads of the sensors were then coated with silicone sealant (734 Flowable Sealant, Dow Corning) so that only the desired nickel sensing area was exposed to the solution. On the external side of the filtration module plate, wires were soldered to the receptacle pins to provide contact to the LCR meter (Agilent) via the multiplexer (National Instruments). The pins were insulated with heat shrink tubing to prevent accidental contact to the metallic housing.

A second feed-through configuration was also tested (configuration 2) in an attempt to improve simplicity and reliability (Figure 3.13). Most components are the same as in configuration 1, except that instead of using a sharp wire to puncture the membrane, a sharpened screw was used. The inside of the open end of the pogo-pin receptacle was tapped so that a small screw (0-80 type, 0.05"/~1.5 mm diameter) could be installed. Wire wrap (30 gauge) was then stripped at the end, wrapped around the screw and secured with a nut. The other end of the wire was then secured to the nickel contact pads on the sensor electrodes with conductive epoxy, as in configuration 1. All exposed metal areas, except the sensing electrodes, were coated with silicone sealant.

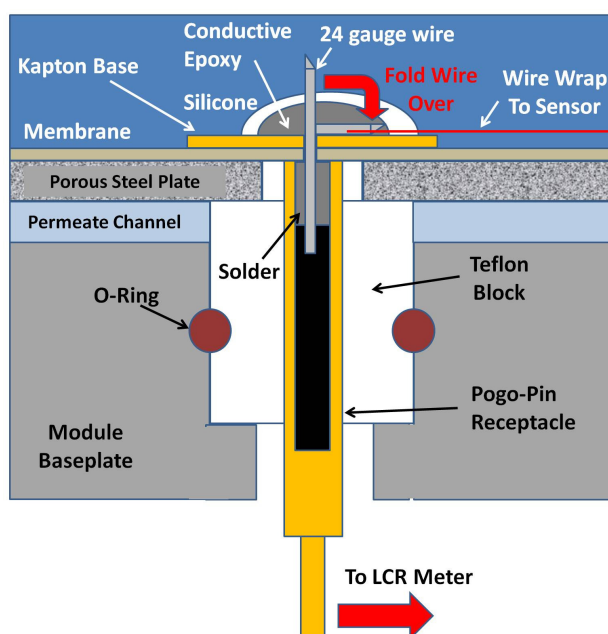


Figure 3.12: Electronic feed-through integration scheme used in initial testing of integrated concentration sensors. Configuration 1.

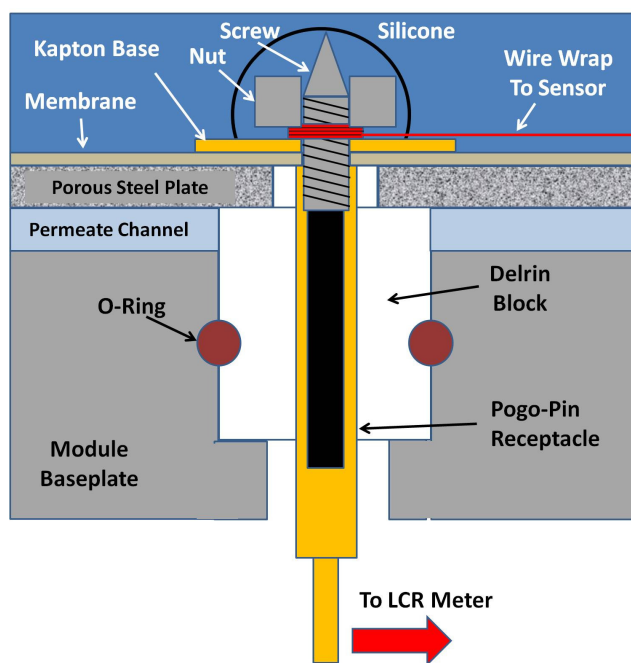


Figure 3.13: Schematic of screw-terminal type feed-through block assembly. Configuration 2.

3.7. Multiple Integrated Sensors: Experimental Design

3.7.1. Concentration Polarization Model

The primary operating parameters controlled in a filtration experiment are solute concentration, pressure and cross-flow velocity which influence permeate flux rate, CPBL thickness and CP strength at the membrane surface. A mathematical model was utilized to select the appropriate operating conditions for effective experimental design. It is important to show that sensors installed on the membrane can sense the position dependence of concentration polarization, as well as scaling and cleaning. A numerical model of the concentration profile at the membrane surface was used to predict the solute mass-transport and scaling patterns on a membrane in the flat-sheet module. The predicted concentration profile is based on the classical one-dimensional film theory mass-transport model given by equation 3.28 [Osada 1992]:

$$CP = \frac{\Delta\pi_m}{\Delta\pi_b} = (1 - R) + R \cdot \exp\left(\frac{J_v}{k_d}\right) \quad (3.28)$$

Where CP is the concentration polarization index, $\Delta\pi_m$ and $\Delta\pi_b$ are the osmotic pressures at the feed side of the membrane surface and in the bulk solution, respectively, R is the solute rejection coefficient of the membrane, J_v is permeate flux, and k_d is the local mass-transfer coefficient.

The permeate flux rate, J_v , is determined from:

$$J_v = L_p (P - \Delta\pi_m) \quad (3.29)$$

Where L_p is the pure water permeability of the membrane and P is the applied trans-membrane pressure. The influence of cross-flow on mass transport is expressed through the mass-transfer coefficient, k_d , which is described by the Graetz solution for flow in a thin rectangular channel [Osada 1992].

$$Sh = 1.85 \left(Re \cdot Sc \frac{h}{x} \right)^{1/3} \quad (3.30)$$

$$k_d = \frac{2Sh \cdot D_s}{3h} \quad (3.31)$$

Where Sh is the Sherwood number, Re is the cross-flow Reynolds number, Sc is the Schmidt number, h is the height of the flow channel, x is the axial position, and D_s is the solute diffusion coefficient. Equations 3.28 and 3.29 can be solved simultaneously using equations 3.30 and 3.31 to determine the local mass-transfer coefficient in order to predict the concentration profile. The definition of CPBL thickness is based on the local mass transfer coefficient and the solute diffusivity:

$$\Delta = \frac{D_s}{k_d} \quad (3.32)$$

The concentration polarization profile is calculated as a function of axial position. Mass-transport properties are numerically calculated at discrete points along the length of the flow channel axis. Initial conditions at the channel entrance assume no CP, i.e., the concentration at the membrane surface equals that of the bulk feed. The cross-flow velocity, and hence the Reynolds number, are then appropriately adjusted over the axial length of the flow channel by subtracting the flux removed by permeation at the previous axial location.

This model was verified by comparison of the predicted permeate flux rate, averaged over the entire permeable area, with measured flux rates under known operating conditions (pressure, cross-flow velocity, feed concentration). The results showed that the measured and predicted permeate flux rates matched within 10% indicating that this model is a viable tool for experimental design.

Tests were conducted with a cross-flow velocity of 8.2 cm/s ($Re = 188$), at a variety of concentrations ranging between 0.02 and 0.7 g/L $CaSO_4$. All tests were performed at 551 kPa (80 psi). The key mass transport parameters include permeate flux, saturation ratio at the membrane surface ($SR = C_{memb}/C_{sat}$) and thickness of the CPBL. These mass transport parameters are shown in Figure 3.14, and assume a rejection coefficient of $R = 1$. The cross-flow velocity is constant at 8.2 cm/s ($Re = 188$), and the pressure is constant at 551 kPa (80 psi). Calcium sulfate concentration is variable.

Additional tests involved scaling and cleaning of the membrane. Modeling plots for a feed concentration of 0.7 g/L calcium sulfate at variable cross-flow velocities are included. These cross-flow velocities are lower than that used in the concentration monitoring tests (Figure 3.14). See Figure 3.15. The high concentration and low cross-flow rates significantly increases the supersaturation, thereby inducing more rapid scaling. Tests should be conducted indicating whether the integrated sensors can provide a scaling induction time that qualitatively matches the expected behavior. It is interesting to note that the CPBL thickness is strongly dependent on cross-flow velocity but not on concentration.

3.7.2. Experimental Protocol

In this section, the experimental protocol is described for testing of multiple integrated concentration sensors in the long flow module. The major goals of this work include the following:

- Test the response of the sensors to salt solutions of variable concentration.
- Verify that the membrane-mounted sensors do respond to concentration polarization, and demonstrate the axial dependence of CP.
- Assess the ability of the sensors to detect scale formation and cleaning.

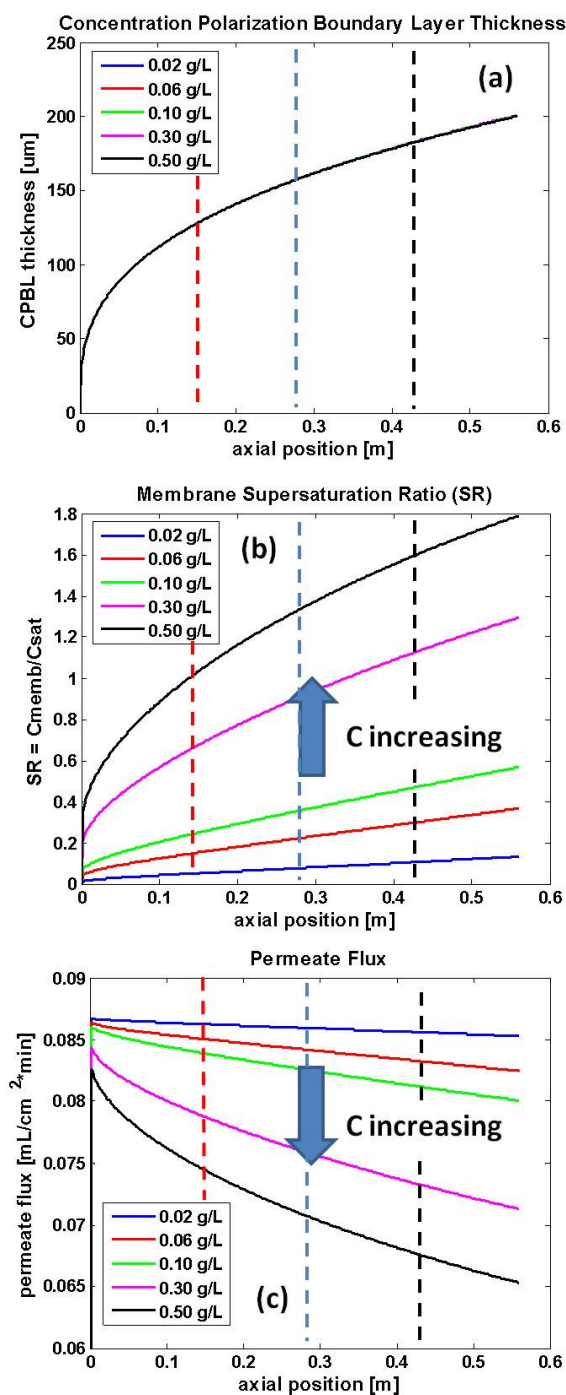


Figure 3.14: Mass-transfer modeling predictions as a function of axial position for concentration monitoring tests performed in flat-sheet cross flow module; variable feed concentration, constant pressure (551 kPa = 80 psi), constant cross-flow velocity (8.2 cm/s, $\text{Re} = 188$). The dashed lines correspond to the integrated sensor locations. (a) CPBL thickness. (b) Membrane supersaturation ratio. (c) Permeate flux.

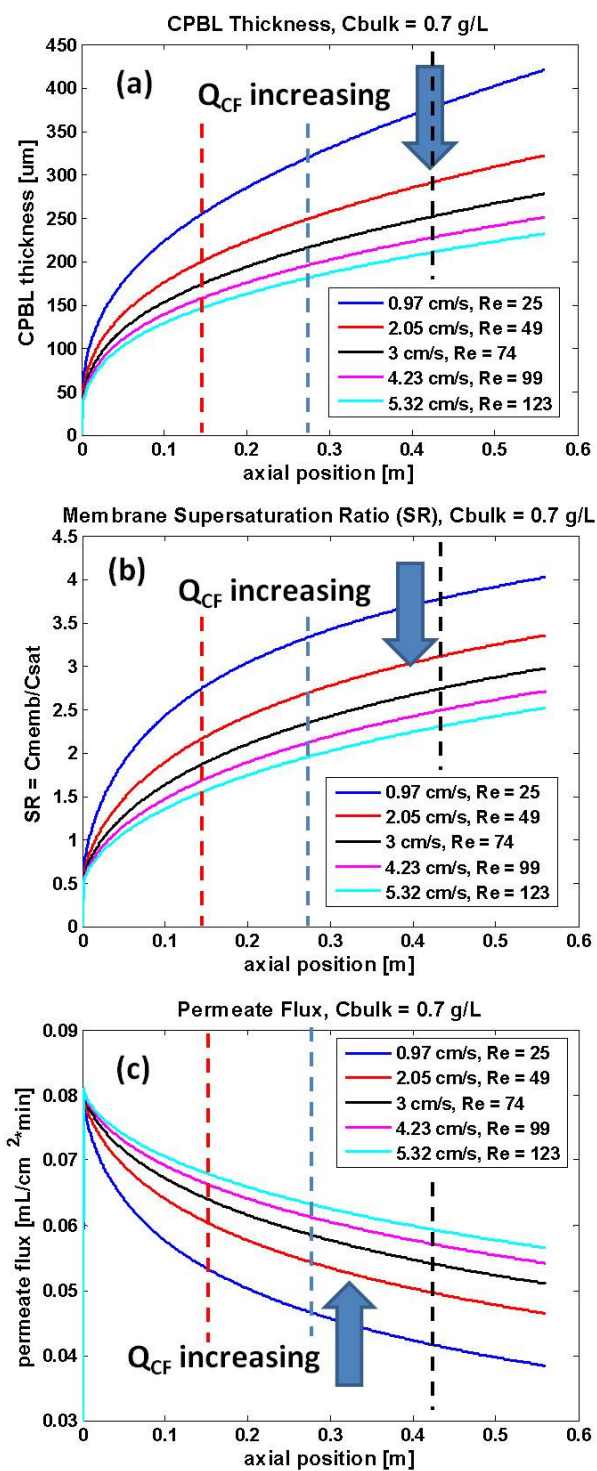


Figure 3.15: Mass transfer modeling for scaling tests performed in flat-sheet cross flow module, as a function of axial position. Variable cross-flow rate, constant pressure (551 kPa = 80 psi), constant concentration (0.7 g/L CaSO_4). The dashed lines correspond to integrated sensor locations. (a) CPBL thickness. (b) membrane supersaturation ratio. (c) permeate flux.

CP Experiments

All experiments described in this thesis were started by running the system with deionized (DI) water for at least 16 hours to compact the membrane. All CP experiments were performed at 551kPa (80 psi) with a cross-flow velocity of 8.2 cm/s ($Re = 188$), using a Dow FilmTec NF 90 nanofiltration membrane. Readings from all sensors were recorded with permeation (CP) and under pure cross-flow. The responses obtained under pure cross-flow are to serve as calibration points under known concentration, particularly for the membrane mounted sensors. The electronic readings from the membrane sensors should change when the permeate valve is open, because they are then sampling a solution of unknown concentration in the CPBL. The sensors mounted on the top wall of the flow channel should continue to monitor the bulk feed solution, and thus the readings should remain unchanged. When permeation is stopped, the module is operating in a pure cross-flow mode meaning that all sensors are sampling the bulk feed solution. Pure-cross flow operation was enabled simply by closing a valve on the permeate stream line. Permeation was permitted by opening the valve.

The salt concentration of the feed was increased by removing a defined volume of solution from the feed tank, and replacing it with the same volume of a 0.79 g/L CaSO_4 stock solution (equivalent to 1.0 g/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The required volume of solution to exchange was calculated based on the starting concentration, the desired concentration, and the volume of fluid in the entire system (feed tank, pre-filters, tubing, module). Conversely, if the feed solution was to be diluted, the appropriate quantity of feed to be replaced with DI water could be calculated in a similar fashion. Because there inherently is uncertainty in determining the true feed concentration using this method, the feed conductivity was monitored and fit against a linear concentration calibration. The calibration was performed with smaller quantities of solution and better concentration control.

After any change in feed concentration, the module was operated under pure cross-flow for at least an hour to allow the feed to fully mix. Solution mixing was also monitored with a commercial

conductivity probe installed in the feed tank. The permeate valve was then opened, allowing the membrane sensors to record the conditions in the presence of CP. This condition was also maintained for at least an hour. The permeate valve was then closed again to demonstrate that the membrane sensors would record the same values as previously observed under pure cross-flow at the same concentration. This procedure was repeated for all concentrations tested.

Scaling Experiment

In order to demonstrate sensor response due to scaling, an experiment was performed with a feed concentration of 0.7 g/L CaSO_4 at a reduced cross-flow velocity (2.2 cm/s, $\text{Re} = 53$). This combination of high concentration and lower cross-flow rates yields much larger supersaturation ratios at the membrane surface, resulting in reduced scaling induction times. The experiment was stopped after the electronic parameters indicated scaling, and the membrane was removed for post-mortem analysis.

3.7.3. Data Analysis Protocol

Data collected from the LCR meter (Z , θ , C , R , G) during pure cross-flow operation provided calibration points for each sensor under known solution concentrations. Calibration curves were then fitted to these points for use in determining concentration during operation where CP was present at the membrane surface. A cubic-spline interpolant fit was generated for each of the electronic parameters for each sensor using Matlab. This analysis procedure calibrates each individual sensor for a given experiment, removing the effects of uncertainties such as gap spacing between electrodes (monolithic electrodes) and exposed electrode area. The electrodes were placed manually (membrane and top wall of flow channel), resulting in uncertainty in the gap. The silicone covering the nickel electrode arm between the contact pad and the sensing area was also applied manually, resulting in uncertainty in the electrode area exposed to the solution.

It is of interest in this work to analyze a variety of different electronic parameters, because of the complex physical system actually sampled by the sensors. The equivalent circuit and physical sensor configuration (monolithic electrodes, Figure 3.8) is shown in Figure 3.16.

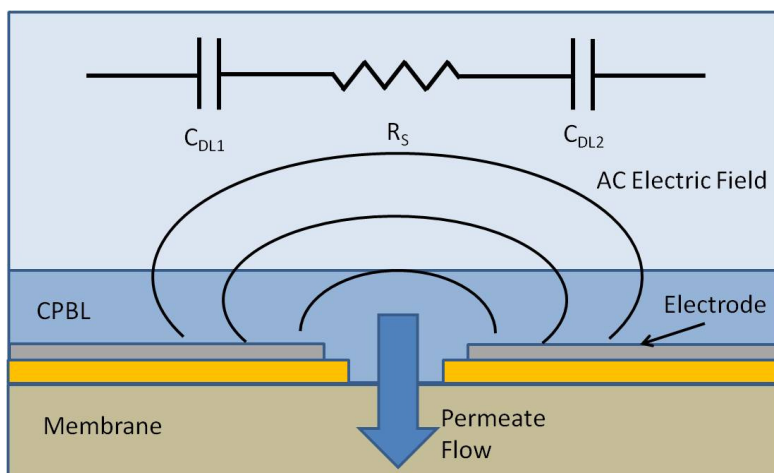


Figure 3.16: Equivalent circuit and physical configuration with monolithic electrodes.

The primary electronic components of the equivalent circuit include the capacitive electric double layers at each electrode, as well as the AC resistance of the solution between the electrodes. The resistance depends on the cell constant of the sensor, as discussed in Section 3.2, and thus depends on the path of the electric field lines between the electrodes. These pass through both the CPBL, since the nickel electrodes are immersed in the CPBL, and the bulk feed. It should be reiterated here that the CPBL represents a continuous gradient in solute concentration between the membrane surface and the bulk solution, not a discrete step change. The definition of CPBL thickness in equation 3.32 is used by convention. It is important to understand that the electric field lines between the two electrodes pass through a space of variable solute concentration. The presence of the sensor also creates a perturbation to the CPBL, meaning it is of interest to measure multiple parameters and experimentally determine which ones demonstrate the greatest sensitivity to changes in solute concentration and the presence of scaling.

3.8. Results and Discussion

3.8.1. System Development - Prototype Module

Initial testing of the integrated electrolytic sensors was performed in a prototype Plexiglas module similar to that used by Zhang [Zhang 2005, 2006]. The module has a flow channel measuring 18.5 cm long by 10 cm wide by 0.9 cm high, and was used in the development of sensor integration and electronic feed-through schemes, incorporating one sensor on the membrane and one on the top of the flow channel.

Early Electronic Feed-through Configurations

Design and test the electronic feed-through schemes represented one of the major time and effort investments in this work. The electronic feed-through represented a major component of a complex electronic packaging problem, since measurements must be made by external devices (LCR meter), while the sensors are installed in a pressurized fluidic environment with flow. Feed-through configurations were tested within the prototype flow cell prior to those shown in Figure 3.12 and Figure 3.13, and are briefly reviewed here. Tests incorporating the latter configurations were ultimately successful in detecting the presence or lack of concentration polarization.

The first of the initial electronic feed-through schemes is shown in Figure 3.17, and incorporated two electrically insulating blocks that were fabricated from Delrin; one for the sensor installed on the membrane and one for the sensor on top of the flow channel. Each block contained two holes into which tungsten needle probes were inserted. The needles were secured into the block by potting with epoxy, which also prevented leaking. An O-ring was placed on the block, which was then pressed into a seat in the bottom (or top) plate of the module.

The bottom (membrane) feed-through assembly had two bosses on the top of the Delrin block where the needle probes were located. These bosses were inserted into holes in the porous steel support plate, helping to reduce the area of the feed-through assembly which would otherwise block permeation.

The sharp tips of these needle probes punctured the membrane as well as the nickel contact pads of the flexible capacitor devices. Before installation of the flexible sensor on the membrane, a thin, water resistant, double-sided-tape (9482PC, 2 mil thick, 3M) was adhered to the back (non-metalized) side of the Kapton. The pins were separated by 5 mm, in order to match the spacing of the sensor nickel contact pads. Conductive epoxy was used to electrically connect and mechanically secure the pins to nickel contact pads. The epoxy and remaining exposed nickel area was coated with silicone (734 Flowable Sealant, Dow Corning) so that the conducting surfaces not in the interdigitated sensing area do not contribute stray capacitance to the total reading. This approach was taken to enable better control of quantitative measurements from different sensors of the same design.

Random loss of the capacitance reading proved to be one of the major problems to be solved in developing designs for electrical feedthrough between sensors in the module and external equipment. In several tests, the capacitance readings would at times randomly drop from reasonable value (following double-layer capacitance modeling) to near zero, and then return to initial values. This was likely a symptom of poor mechanical contact between the small, sharp needle probe tips and the conductive epoxy adhering the needles to the nickel sensor contact pads. The surface area of the needle tips is very small, protruding 2 mm into the flow channel with a diameter of 0.5 mm. Post-mortem analysis showed that contact could be broken by the inevitable flexing that occurs in the module under operating conditions. Post-mortem analysis did not support the hypothesis that the reliability issue was due to corrosion, scaling or particulate deposition on the exposed interdigitated sensor area.

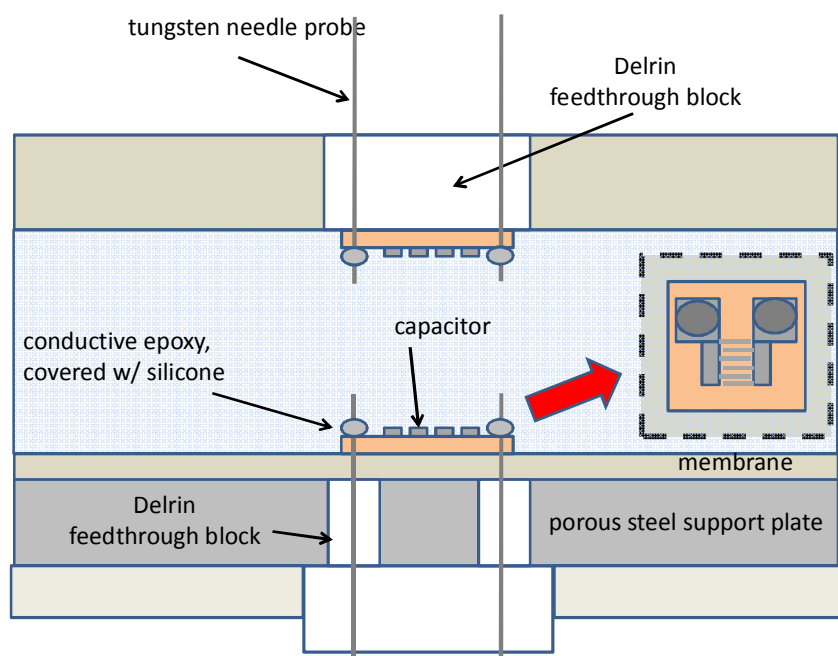


Figure 3.17: Sensor is adhered to membrane with water-resistant double-sided tape. Two tungsten needle probes are held in place in a Delrin feedthrough block and puncture the membrane and nickel contact pads on the flexible Kapton/nickel sensor.

In an attempt to improve reliability of the electrical contact between the tungsten needle probes and the epoxy joining it to the sensor, Delrin caps were manufactured to cover the pins (Figure 3.18). These caps were intended to help distribute mechanical loads on the epoxy/needle junction more effectively. The caps consisted of small cylinders, 3 mm in diameter and 3 mm tall. The needle tip was inserted into a 0.5 mm diameter hole in the center of the cap. The tip of the needle was coated with conductive epoxy so that when the cap was placed over the tip, the hole in the cap was filled. The epoxy that squeezed out on the bottom of the cap provided contact to the nickel electrode pads.

One of the primary means of testing the efficacy of the thin flexible sensors on the membrane surface was to run the system with the permeate valve open as well as closed. When the permeate valve is closed, water is unable to pass through the membrane, and the membrane sensor is assumed to be sampling the only the bulk solution - ostensibly the same as that being sampled by the sensor on the top wall of the flow channel. When the permeate valve is open, permeation is allowed to occur, and a

concentration polarization boundary layer (CPBL) exists. In this case, the sensor on the membrane should respond to the change, while the top sensor should not. During testing employing the feed-through configuration shown in Figure 3.18, the capacitance readings from the membrane sensor showed no significant changes when switching between these two operating conditions. The sensor reliably responded to changes in the bulk concentration but not to presence or lack of CP. In addition, the random loss of contact continued to be observed, demonstrating that the Delrin caps on the tungsten needle probes did not solve the reliability problem.

A lack of real concentration polarization at the interdigitated sensing area may one possible explanation for the lack of significant response from the membrane sensor when opening the permeate valve. Up to this point, it had repeatedly been shown that all sensors responded reliably to known changes in the bulk feed concentration. Since the sensor appeared to be working correctly, there may not have been any detectable local CP. The real possibility exists that the capped needle probe tips perturbed the cross flow field significantly enough that the otherwise expected CP does not develop locally at the sensing area. In this configuration, the caps were placed in close proximity to the interdigitated structure (~2-3mm) to simplify the overall integration scheme.

The feed-through configuration was then modified by separating the single central block into two separate blocks. Each was moved to the edge of the flow channel in order to reduce interference with the flow field at the sensor location in the center of the channel. See Figure 3.19. The flexible sensor itself was also modified by moving the nickel contact pads on the Kapton further outward, away from the interdigitated sensing area; this reduced the perturbation of the flow field caused by the now-smaller conductive epoxy/silicone bump on the nickel contact pad. In this new sensor layout, the nickel contact pads were separated by 16 mm. Enameled magnet wire (38 AWG) was used to connect the tungsten needle probes on the edges of the flow channel to the nickel electrode contact pads. The first tests with the separated feed-through blocks continued to use Delrin caps to secure the wires and conductive epoxy to

the needle probes. The caps and conductive epoxy were coated with silicone to isolate them from the feed solution. The magnet wires were also coated with silicone to help secure them to the membrane.

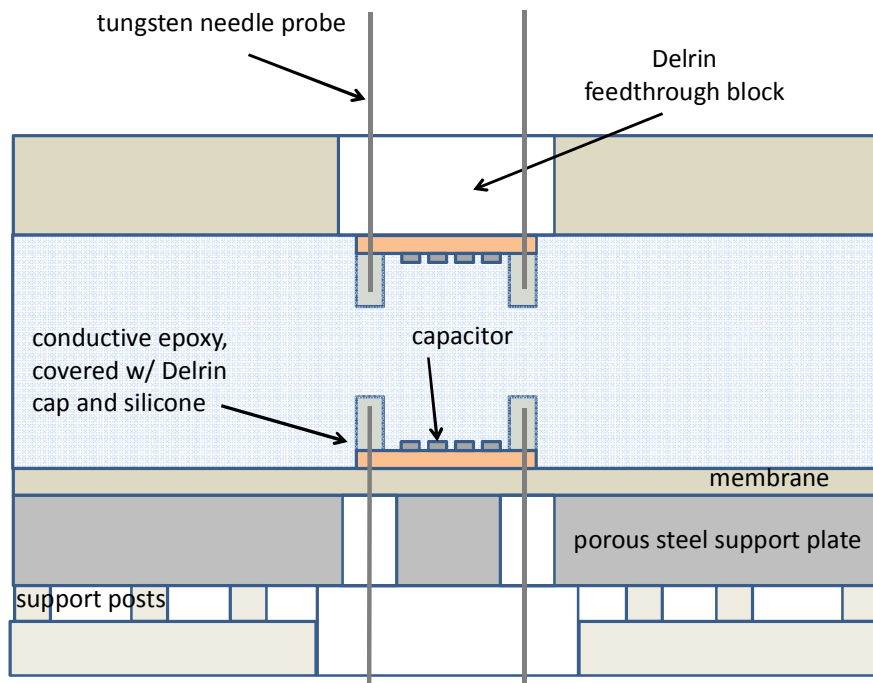


Figure 3.18: Delrin caps were added to the feed-through to help distribute mechanical loads on the needle/epoxy junction with the aim of improving mechanical reliability.

An additional significant change to the sensor integration scheme was introduced at this stage; a 1 cm x 1 cm area of the porous steel support plate was reduced by approximately $75\text{ }\mu\text{m}$ (3 mil) to form a small recess at the location where the flexible sensor would be installed. This was done so that when the module is pressurized, the membrane, as well as the flexible sensor, is pushed down into this recess, bringing the sensing area closer to the ‘zero-height’ level of the surrounding membrane surface. The concentration in the boundary layer is greatest at the surface, and thus the higher the vertical position of the sensing area within the layer, the lower the difference in concentration between the bulk and the stratum actually being monitored. In some situations the sensing area may even be located above the CPBL, i.e. in the bulk flow. Strong CP could potentially exist, and fouling could occur without the sensor

having detected any change from the initial condition. This feature was incorporated in later experiments. This electronic feed-through configuration demonstrated significant and repeatable responses to the opening and closing of the permeate valve (i.e. CP). The problem with reliability persisted, however, prompting the design modification shown in Figure 3.12.

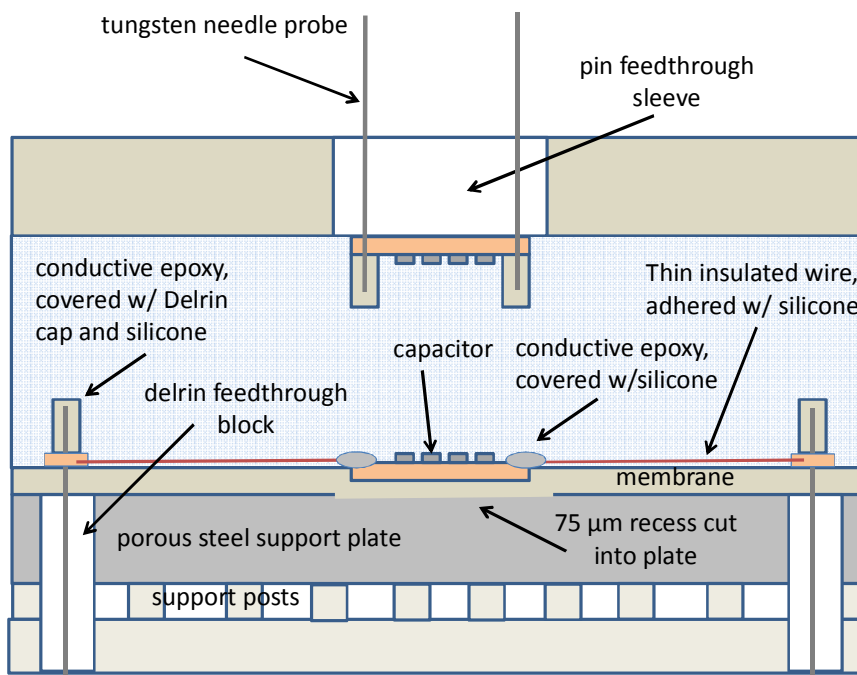


Figure 3.19: Tungsten needle probes with Delrin caps are still used, but the feedthrough blocks on the bottom have been separated and moved to the edges of the flow channel. A 75 μm recess has been cut into the porous steel support plate at the sensor location in order to place the active sensing area closer to the 'zero-height' level.

In addition to the tests described above, an important aspect of the work was to verify that the sensor responses obtained were due to changes in concentration and not other systematic factors. Thus, we performed a test in which a blank Kapton square was mounted to the membrane. The use of this 'dummy' sensor was the only difference between this test and the previous tests. All of the electrical feed-through components were still present, including the needle probes, Delrin caps, conductive epoxy, and magnet wire, with all coated in silicone. Results showed negligible responses with changing salt concentration, compared to those recorded with working sensors.

Prototype Flow Channel Design

The entrance and exit regions of the flow channel initially consisted of a single hole at either end (Figure 3.20 (a)). This configuration made characterization of the axial laminar cross flow regime difficult due to entrance and exit hydrodynamics, which were not clearly defined. The entrance and exit regions extended over a significant portion of the channel, which was verified by post-mortem observation of scaling patterns on the membrane. This uncertainty in the entrance and exit effects made use of the numerical CPBL model, described in Section 3.7.1, inappropriate for design of experiments to quantitatively measure membrane surface concentration.

An attempt was made to mitigate the entrance and exit effects by modifying the feed inlet and outlet ports. Several additional holes were added to the ports along the width of the channel, as shown in Figure 3.20 (b). Post-mortem observation of scaling patterns still demonstrated the uneven nature of the flow field. Lyster et al. [Lyster 2009] have presented a detailed finite-element model demonstrating the complex nature of the flow field in the entrance and exit regions of a channel similar to Figure 3.20 (b).

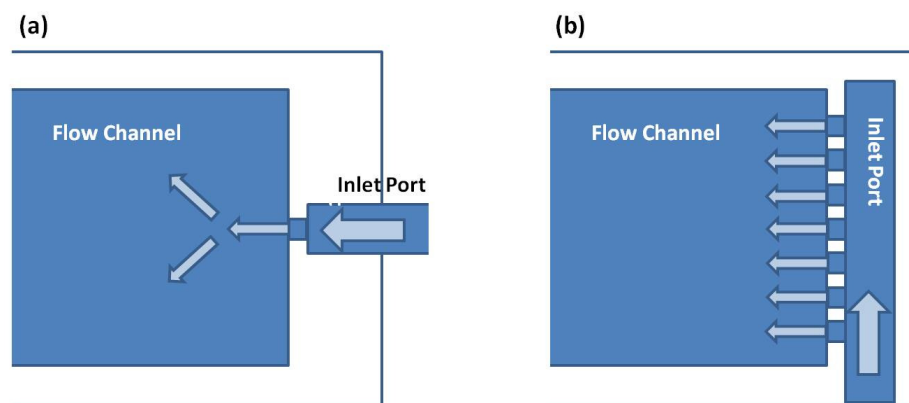


Figure 3.20: Inlet/outlet designs used in prototype flat-sheet module. (a) initial single-inlet port design. (b) modified multiple inlet port design.

Prototype Sensors and Results

Initial sensor testing employed the interdigitated electrode design with finger and gap widths of $100\text{ }\mu\text{m}$. An optical micrograph is shown in Figure 3.21. Feed-through configuration 1 was used to make electronic contact to the LCR meter. Experiments were performed with a variety of salt concentrations at a pressure of 551 kPa (80 psi) and a cross-flow velocity of $\sim 1\text{ cm/s}$ ($\text{Re} \sim 130$). The electronic system, however, proved to be somewhat unreliable. The capacitance response would be at a reasonable value for a period of time, as verified by the analysis to be given in Section 3.8.4. The capacitance would appropriately respond to changes in salt concentration, increasing with greater concentration and decreasing with reduced concentration. Occasionally, however, the response unexpectedly dropped to near-zero. The readings would then randomly fluctuate between the real value and zero. Post-mortem mechanical analysis of sensors indicated that in several instances, several nickel fingers demonstrated poor adhesion to the flexible Kapton substrate. This prompted a redesign in the electrodes, by expanding the finger and gap widths to $100\text{ }\mu\text{m}$ (Figure 3.7) with the overall footprint and exposed electrode area of the sensors remaining the same. This modification to the design significantly improved the yield of the sensor fabrication process, as well as reliability in the prototype module.

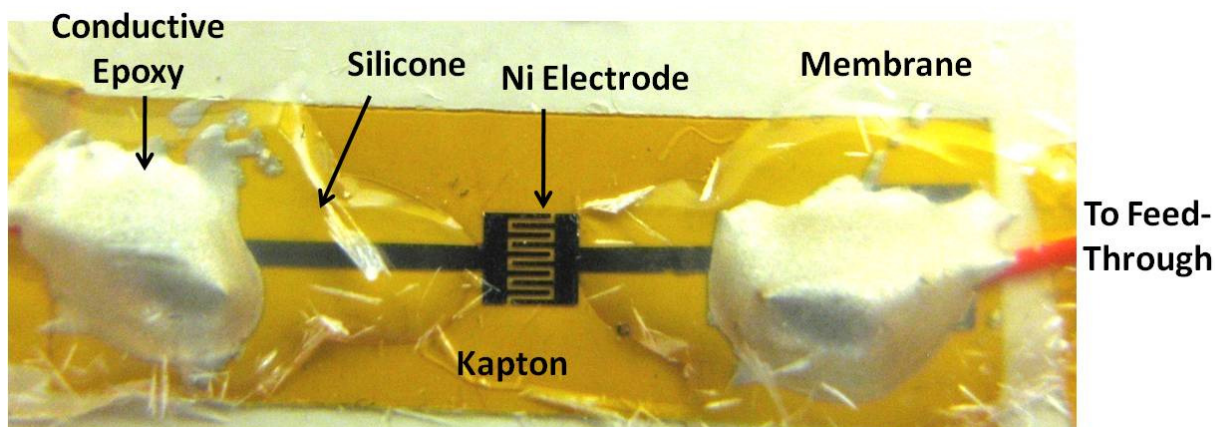


Figure 3.21: Optical micrograph of interdigitated sensors with $100\text{ }\mu\text{m}$ finger and gap widths.

Prototype testing demonstrated that a sensor mounted on the membrane surface detected concentration polarization, while a sensor mounted on the top of the flow cell did not. Figure 3.22 (a) shows the response from the membrane sensor. When the permeate valve was opened, CP developed and the capacitance increased in response to the local increase in solute concentration. No such response was observed from the sensor on the top of the flow channel (Figure 3.22 (b)). The concentration polarization boundary layer was particularly thick, estimated between $\sim 0.5 - 1.0$ mm, as it was in the work performed by Zhang [Zhang 2005, 2006]. In addition to showing electronic measurement of concentration polarization, testing in the prototype module demonstrated negligible response in the capacitance readings to changes in cross-flow velocity or pressure while under pure cross-flow conditions. This demonstrates that the primary parameter manifested in the capacitance readings is the solute concentration.

Having demonstrated these key features of the integrated sensor system, we determined that a new module with a much longer flow channel would be necessary to test sensor readings as a function of axial position (Section 3.6.1). A much thinner flow channel would provide a more realistic test of the sensor design, owing to increased cross-flow rates and thinner concentration polarization boundary layers.

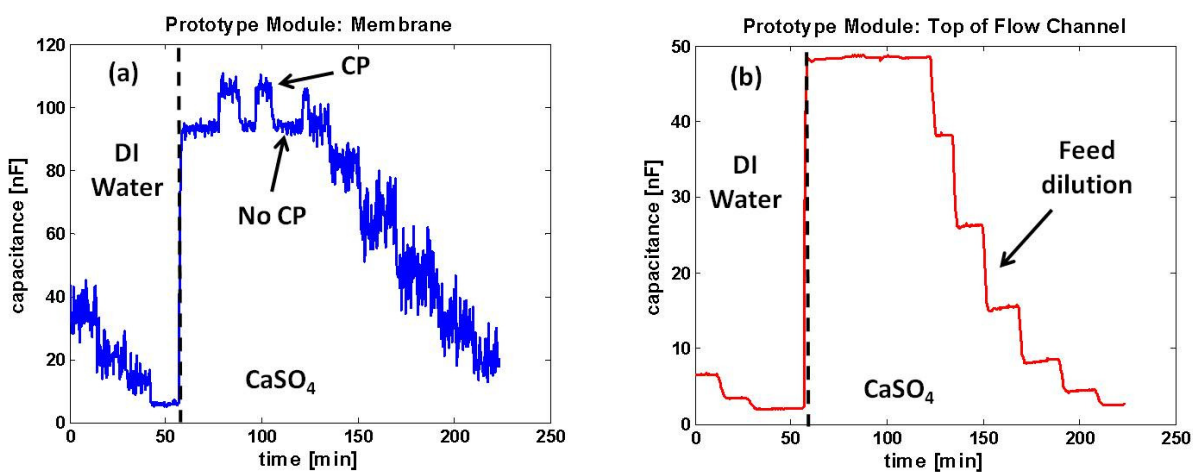


Figure 3.22: Capacitance data from sensors mounted (a) on membrane surface and (b) top of prototype flow channel, demonstrating the ability to detect CP.

3.8.2. System Performance - Multiple Integrated Sensors

The long filtration module was first tested with all sensor integration components in place, but no nickel sensing electrodes. This test was performed in order to determine the influence of the electronics connecting the sensors to the LCR meter. The following components were present: LCR cables, feed-through block and wiring to the center of the flow channel. The integration wiring (wire wrap, 30 gauge) was adhered to a blank Kapton square with conductive epoxy. This experiment was carried out in the same fashion as those with functioning sensors. Electronic feed-through configuration 1 (Figure 3.12) was used in this test.

The feed and permeate conductivities, as recorded by the commercial conductivity meters (CDCN-91, Omega) are shown in Figure 3.23. Figure 3.23 (a) is the feed conductivity and Figure 3.23 (b) is the permeate conductivity. The corresponding capacitance results from the integrated sensors are shown in Figure 3.24. The feed solution was switched from deionized water to 0.16 g/L CaSO_4 , and while the change in conductivity is clearly indicated by the commercial probes, only a very minor change in capacitance responses from the sensor data streams (a few pF) is observed. This response is negligible compared to those observed with nickel sensors present (tens of nF), indicating that changes in the signal corresponding with changes in feed concentration are due to the nickel sensing structures that are exposed to the feed solution.

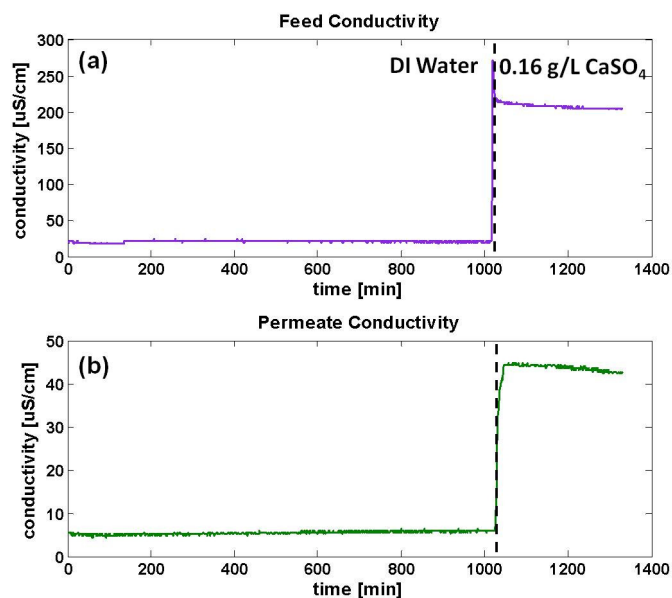


Figure 3.23: (a) Feed conductivity. (b) permeate conductivity. Both recorded by CDCN-91 conductivity meter.

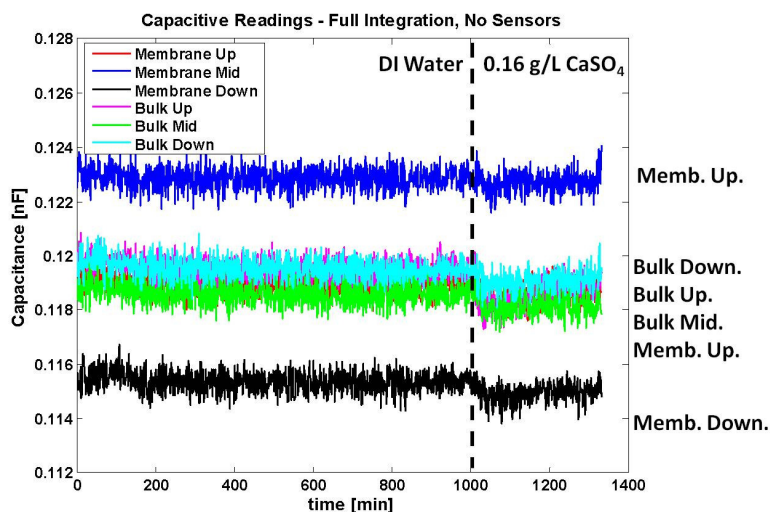


Figure 3.24: Sensor capacitance response with full integration scheme, but no nickel structures exposed to the feed solution. Each data trace is read from the different sensor locations.

Two initial tests were performed with working sensors using feed-through configuration 1 and interdigitated electrodes with 100 μm finger/gap widths. In these initial tests, we focused on capacitive readings, following the methodology of Zhang. Representative results from the membrane and bulk feed

sensors are shown in Figure 3.25. Figure 3.25 (a) shows a clear change in capacitive response from the membrane sensors when the permeate valve is opened, i.e. when CP is present. The readings from the bulk sensors, mounted on the top of the flow channel, do not show such a change, indicating that they continuously monitor the bulk feed stream (Figure 3.25 (b)).

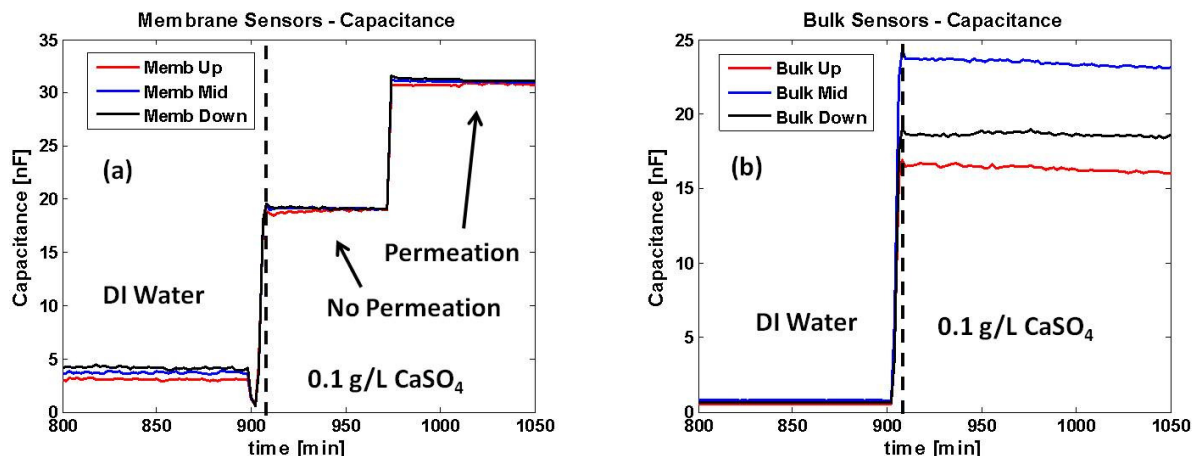


Figure 3.25: Capacitance results from representative test of integrated concentration sensors. (a) Sensors mounted on the membrane surface. Notice the response to concentration polarization. (b) Sensors mounted on the top of the flow channel. No change in readings occurs when permeate valve is opened.

All of the membrane sensors responded to the presence or lack of concentration polarization, while the sensors mounted on the top wall of the flow channel continuously sampled the bulk feed stream. During these initial two experiments, however, we continued to observe occasional spurious of the capacitance readings from of a few sensors, similar to the situation in the prototype module described in Section 3.8.1.

We pursued two different solutions to this problem. One potential cause of problem may have been fracture of the epoxy at the feed-through location where the sharp 24-gauge wire punctures the membrane. The plate in the long module may have flexed more than in the shorter prototype module. This issue was addressed by installing the screw-terminal type feed-through shown in Figure 3.13. After introduction of the screw-terminal type feedthrough, reliability significantly improved, although the

occasional drop-out of the capacitance readings from certain sensors still occurred. Subsequent mechanical post-mortem analysis of the nickel interdigitated electrode structures showed that in some instances, the adhesion of the fingers to the Kapton substrate was still poor. Immediately after concluding a test, it could be seen to the naked eye that a few fingers on a few sensors had lifted off the substrate. This may have been a result of greater cross-flow velocities in the long module. This observation prompted the fabrication of the monolithic electrode design, shown in Figure 3.8. A photograph of the fabricated sensors is shown in Figure 3.26. These sensors showed significantly greater reliability over the course of multi-day experiments.

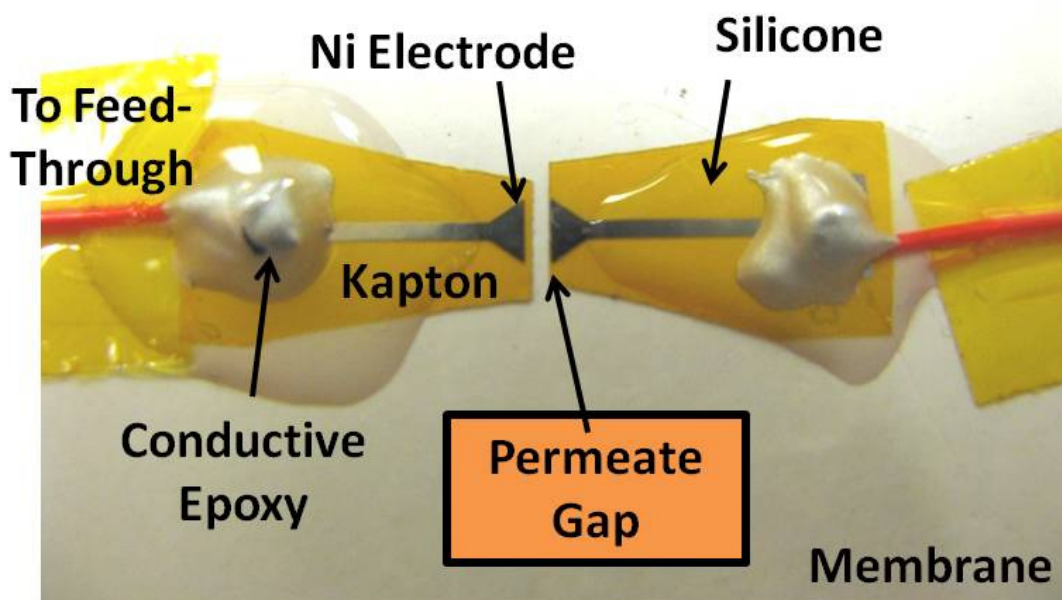


Figure 3.26: Optical micrograph of monolithic sensor with permeate gap between electrodes.

3.8.3. Axial Dependence of Concentration Polarization

The interdigitated sensors on the membrane were able to detect the presence or lack of concentration polarization, but they did not clearly indicate the dependence of CP strength on axial position within the flow channel. The reason for this may have had to do with the fact that the sensors themselves locally blocked permeation through the membrane, resulting in perturbation of the CPBL. The CPBL was still detectable due to the convective cross-flow, but it may have been perturbed to a point where the difference between CP strength at the upstream location was not distinguishable from that at the downstream location.

An experiment conducted with the monolithic electrode sensors, however, was able to experimentally demonstrate the dependence of concentration polarization strength on axial position. The numerical CP film model described in Section 3.7.1 was used to guide experimental design. A pressure of 551 kPa (80 psi) and cross-flow rate of 8.2 cm/s was used in this experiment. The following concentrations were tested: 0.02, 0.04, 0.06, 0.08 and 0.1 g/L CaSO_4 . See Figure 3.15 for the predicted concentration polarization profiles.

For this test we modified the data acquisition system to record multiple electronic parameters from the LCR meter, including capacitance, resistance, complex impedance and phase angle. This was done to allow a comparison of multiple parameters in order to ascertain whether one parameter demonstrates significantly greater sensitivity and/or reliability than another. The finite thickness of the sensor (approximately 75 μm) means it is not possible to sample the concentration of the fluid exactly at the surface of the membrane. The presence of the sensor will still result in some perturbation of local concentration polarization boundary layer, introducing a further complication. These issues were addressed by calibrating the sensors, as described in Section 3.7.3. The concentration calibration curves are shown for each sensor for capacitance, resistance, impedance and phase angle in Figure 3.27.

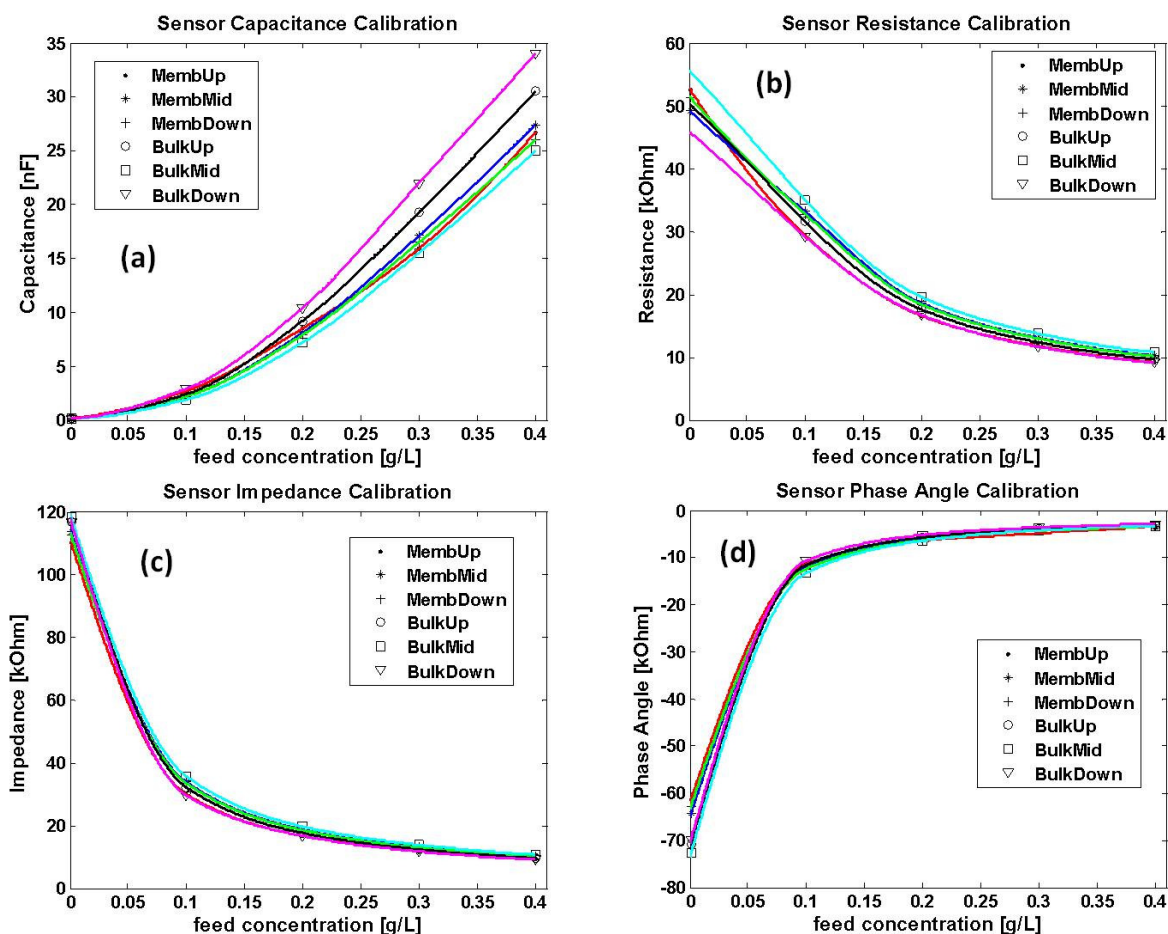


Figure 3.27: Concentration calibration curves for each of the sensors in terms of (a) capacitance, (b) resistance, (c) complex impedance, and (d) impedance phase angle.

Analysis of the responses from the sensors showed that capacitance and impedance readings demonstrated a meaningful difference between the concentration at the upstream and downstream locations that follows the expected behavior. Results are shown in Figure 3.28 and Figure 3.29. Figure 3.28 (top) shows the measured concentration, as determined by the capacitance calibration curves, respectively, and Figure 3.28 (bottom) express these results in terms of concentration polarization factor, where $CP = 1$ indicates that the sensor is measuring the bulk concentration. The form of the impedance calibrated results presented in Figure 3.29 is the same. The results show that impedance appeared to be a better metric at very low concentration (0.02 g/L), as it yielded bulk sensor CP factors of 1 and membrane sensor factors clearly above this, as expected. At this concentration there was significant error in the

capacitance reading, which gave CP values below 1 for all of the sensors. Both capacitance and impedance measurements showed the bulk sensors to read close to a CP of 1 under all tested concentrations (except capacitance, 0.02 g/L).

The most interesting item to note is that the downstream membrane sensors provided the highest CP factor at all concentrations (except for capacitance at 0.02 g/L and impedance at 0.04 g/L). Although the experimentally determined CP factor is not that which was predicted by the numerical model, the results likely indicate that we are directly observing the change in concentration, which increases from the upstream position to the downstream position.

The likely reasons for measuring a lower CP value than expected include the sensor height and perturbation of the flow field due to the presence of the sensor itself. In addition, the rejection coefficient of the membrane was below 1, which will tend to reduce the concentration at the membrane surface. Rejection was calculated using the conductivities recorded by the feed and permeate conductivity probes to be around 75%.

Effect of Variable Cross-Flow Velocity

In addition to the results discussed above, the cross-flow velocity was also varied under constant pressure to observe the sensor responses. All results for this aspect of the work were obtained under 551 kPa (80 psi) pressure and concentrations of 0, 0.02, 0.04, and 0.08 g/L. The analysis of electronic responses is the same as that described above. The values of the different electronic parameters were recorded for each sensor under each condition (combination of flow rate and concentration), and compared against the calibration curves.

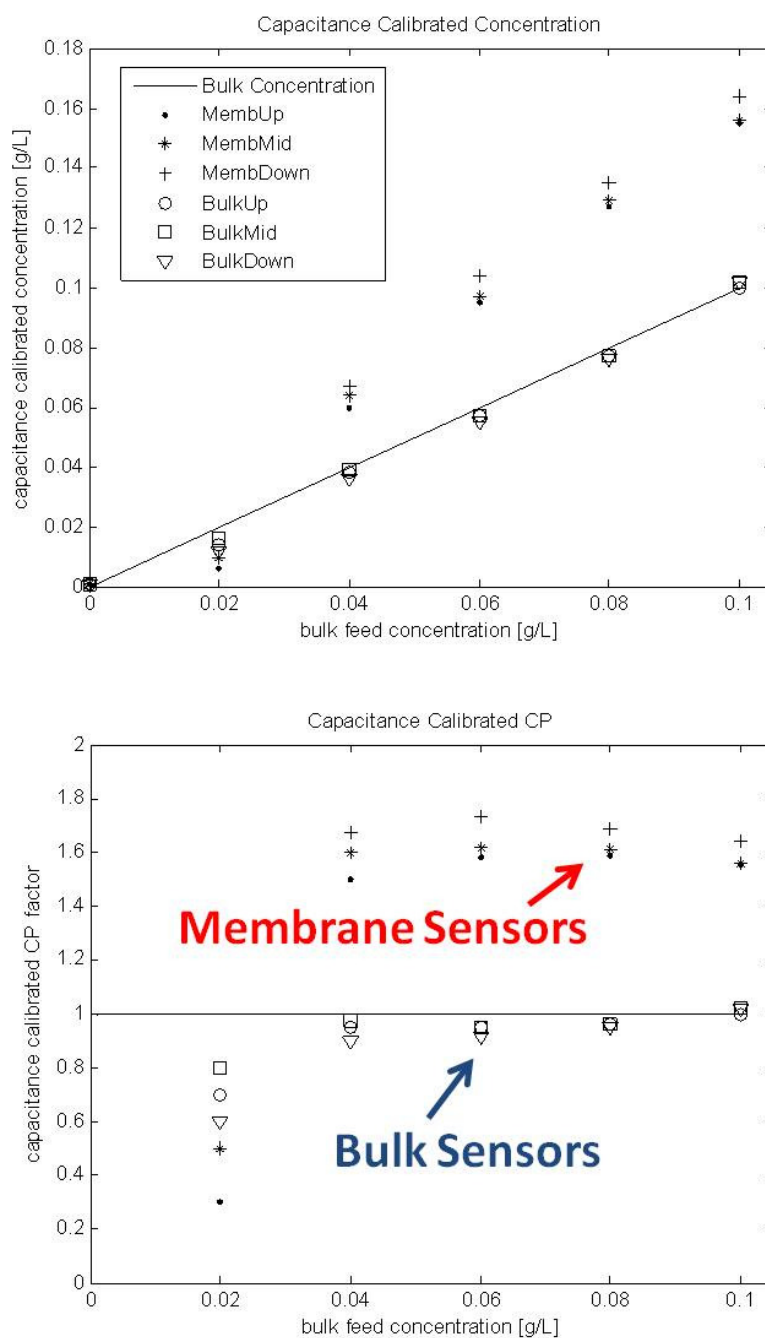


Figure 3.28: Concentration data from sensors according to calibration fitting. (Top) capacitance calibrated concentration readings. (Bottom) Corresponding calculated CP factors. Note that the calibrated bulk sensors read close to the bulk concentration, while the membrane sensors read notably higher. The downstream membrane sensor reads the highest concentration for both capacitance and impedance (+ symbol).

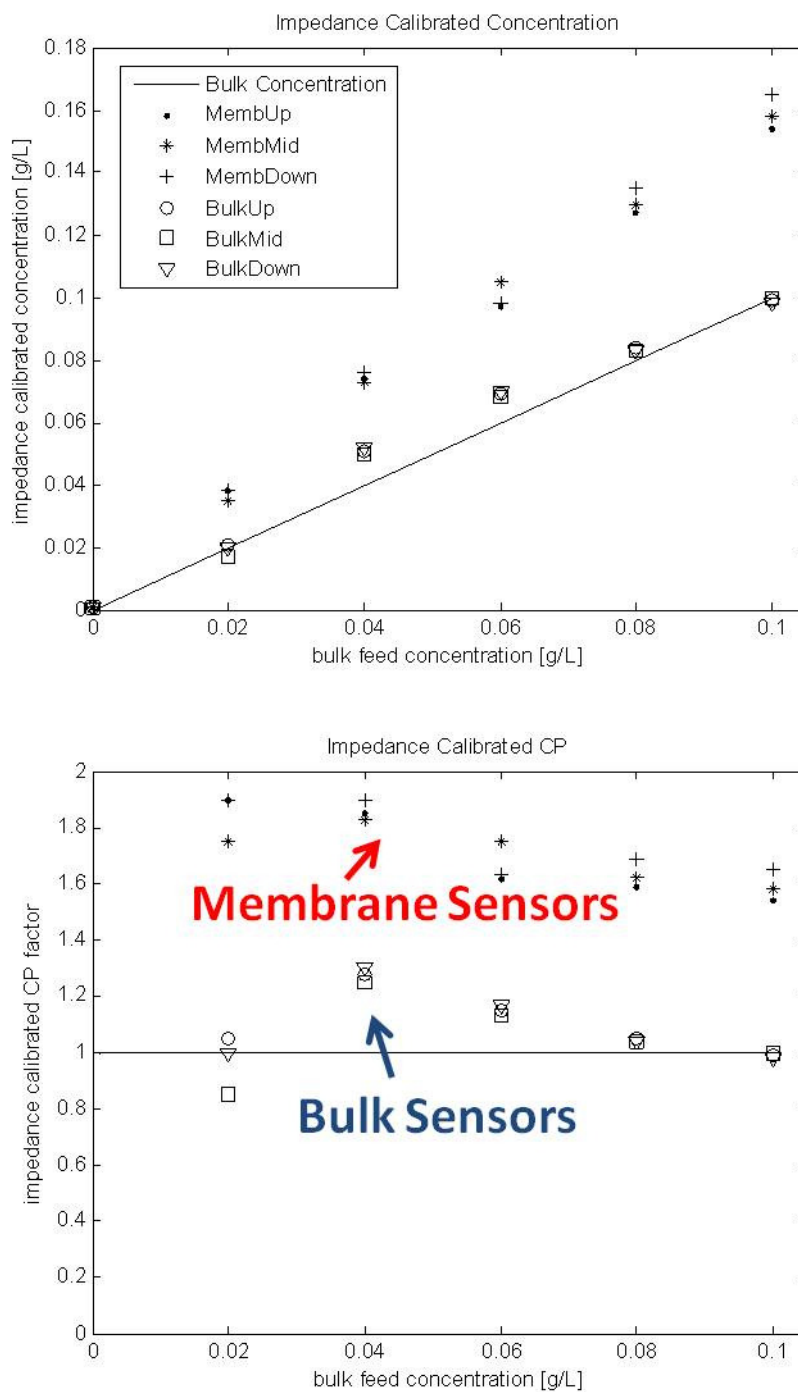


Figure 3.29: Concentration data from sensors according to calibration fitting. (Top) impedance calibrated concentration readings. (Bottom) Corresponding calculated CP factors. Note that the calibrated bulk sensors read close to the bulk concentration, while the membrane sensors read notably higher. The downstream membrane sensor reads the highest concentration for both capacitance and impedance (+ symbol).

The results show that the membrane sensors are strongly responsive to changing cross flow velocity, where the concentration decreases with increasing velocity. Both the capacitance calibrated results and the impedance calibrated results behaved in a similar fashion. Plots of the capacitance calibrated CP as a function of cross-flow velocity at 0.02, 0.04 and 0.08 g/L are shown in Figure 3.30. It is particularly interesting to note that the downstream membrane sensor always showed the greatest CP, but it was more notable at slower cross-flow velocity. The highest velocity in these plots (8.2 cm/s, $Re = 188$) was the same as that used in the calibration test described in the section above, and these results are similar to those presented in Figure 3.28.

Quantitative Analysis of CP Values

It can be seen from the plots of concentration polarization in Figure 3.28, Figure 3.29, and Figure 3.30 show that the measured CP values are significantly lower than that expected by the numerical CP model. These figures show the expected CP profile in terms of the saturation ratio at the membrane surface, but the CP factor can be easily calculated by dividing the surface concentration by the known bulk concentration. One major factor to consider is that the sensors, while thin, still have a finite thickness. The CPBL is predicted in the models to be on the order of 200 μm thick, while the sensor stack thickness (transfer tape plus Kapton substrate) is $\sim 75 \mu\text{m}$. Therefore, the nickel sensing area is elevated above the membrane surface, and will experience a lower CP level than what is actually at the membrane. Therefore, in order to provide some more insight into the actual CP readings experimentally provided by the sensors, estimates of the CP value at vertical positions above the membrane surface can be made (Figure 3.31).

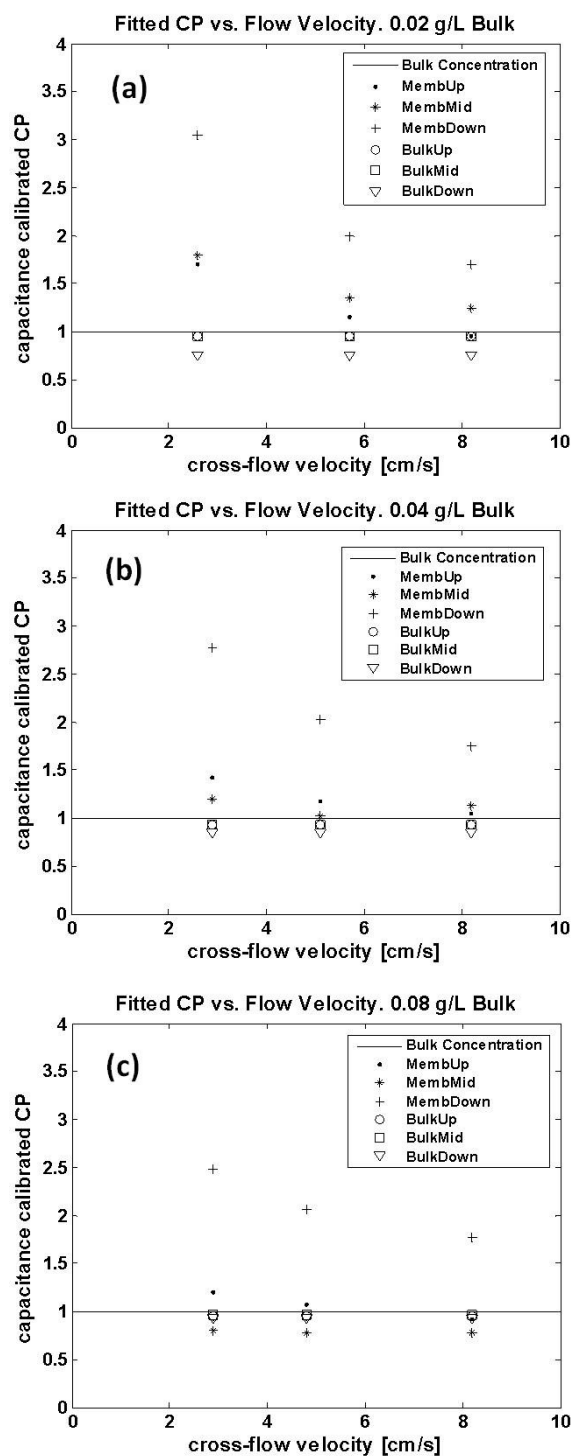


Figure 3.30: CP results based on capacitance calibration for the six sensors as a function of cross-flow velocity. (a) 0.02 g/L bulk CaSO_4 feed. (b) 0.04 g/L. (c) 0.08 g/L. Note that the downstream sensor (+ symbol) always has the greatest CP value, which decreases with increasing velocity. The bulk sensors remain close to a CP of 1 for all velocities.

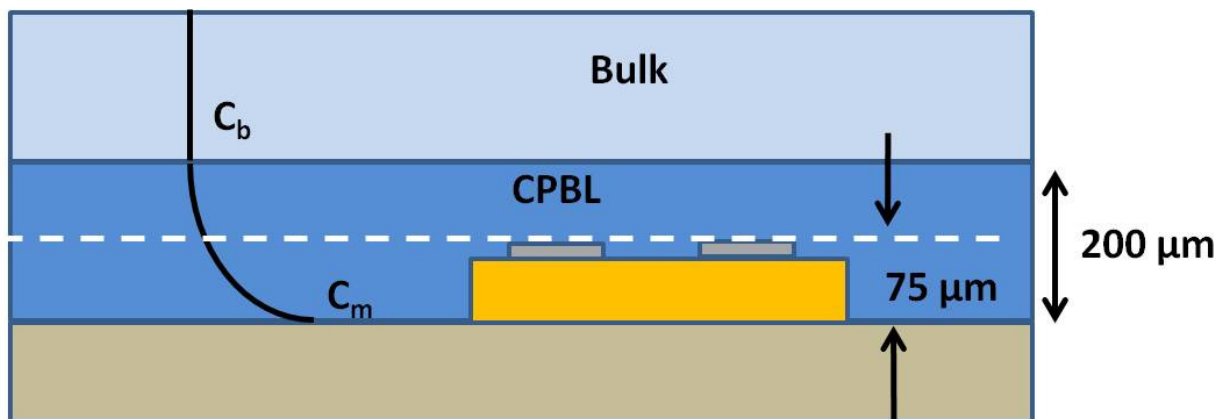


Figure 3.31: Schematic demonstrating vertical dependence of CP and location of nickel sensing structure.

These estimates were made by applying an exponential fit to the CP profile at each of the sensor locations under each of the bulk concentrations tested (8.2 cm/s cross-flow, corresponding to results shown in Figure 3.28). Each fit was calculated using the model-estimate CP value at $z = 0 \mu\text{m}$, and a CP value of 1 at the local CPBL thickness. The CP at $75 \mu\text{m}$ was then calculated based on the exponential fit. The three columns on the right of Table 3.1 show these estimated CP values at the elevated vertical location, and show them to be significantly reduced, ranging between ~ 1.9 (upstream) and ~ 2.6 (downstream). Note that the experimental CP values measured by the membrane sensors in these figures range between ~ 1.5 and ~ 1.9 , which is much closer to the estimated CP at $75 \mu\text{m}$ than at $0 \mu\text{m}$. Local perturbation of the flow field caused by the presence of the sensors likely accounts for the remaining mismatch between estimated and measured values.

In addition to this, possible uncertainty in the exact vertical height was accounted for by taking the average CP values at each location at each concentration, over the vertical range between $65 \mu\text{m}$ and $85 \mu\text{m}$ (i.e. uncertainty of $\pm 10 \mu\text{m}$). Again, this average is based on the exponential fit. The resulting CP values differed only very slightly from the value calculated exactly at $75 \mu\text{m}$, between 0.05 and 0.1. Thus, the values presented in Table 3.1 are acceptable estimates of the influence of vertical position.

Table 3.1: CP values at membrane surface and 75 μm above membrane (highlighted values). Based on numerical CP model for the experiment shown in Figure 3.28. Vertical profile based on exponential fit.

C_{bulk} [g/L]	CP ($z = 0 \mu\text{m}$)			CPBL Thickness [μm]			CP (75 μm)		
	Up	Mid	Down	Up	Mid	Down	Up	Mid	Down
0.02	5.27	8.13	11.01	125	158	182	1.94	2.32	2.62
0.04	5.21	7.95	10.65	125	158	182	1.93	2.3	2.6
0.06	5.15	7.79	10.32	125	158	182	1.93	2.27	2.54
0.08	5.1	7.63	10.02	125	158	182	1.92	2.25	2.51
0.1	5.04	7.49	9.74	125	158	182	1.91	2.24	2.49

3.8.4. Analysis of Capacitance Responses

A thorough analysis of capacitance values recorded by the interdigitated sensors was performed to verify that the values did indeed correlate well with expected values given by theory. This analysis incorporated data recorded from both 100 μm finger/gap (long module) and 30 μm finger/gap (short module) sensors, under pure cross-flow where the concentration sampled by all sensors was known. Although the two sets of sensors have differing finger and gap widths, the total electrode area exposed to the feed solution is the same. Assuming constant concentration and test signal voltage, the total double-layer capacitance varies with electrode area.

The process for changing feed concentration during the experiments, as described in Section 3.7.2, introduced uncertainty into the actual value of the concentration. Therefore, the true concentrations were determined by calibration conductivity with concentration with better controlled solution samples. Although the procedure was aimed at providing feed solution concentrations of specific values in the many tests performed (i.e. exactly 0.1, 0.2, 0.6... g/L), a data set of capacitance values corresponding to a range of concentrations was developed, with concentrations between 0 and 1.4 g/L. In order to statistically analyze the sensor responses to concentration, the data points were grouped into bins of 0.1 g/L, centered about 0, 0.1, 0.2, 0.3, ... 1.4 g/L CaSO_4 . The mean capacitance and standard deviation on the mean were calculated for all data points in each bin. These experimental values are shown in Figure

3.32. The error bars are of different size at each concentration because the number of points and standard deviation of the points in each bin varies.

A model of the total sensor capacitance was then developed following the Stern-Gouy-Chapman formulation presented in Section 3.4. Because this work was never intended as an extremely well controlled set of electrochemical experiments, the model contains several parameters with significant uncertainty. These include potential at the Outer Helmholtz Plane (OHP), thickness of Helmholtz plane, and effective dielectric constant of the Helmholtz plane. Thus, the model is plotted as a range, incorporating these uncertainties. The solid lines in Figure 3.32 show the capacitance range as a function of concentration for an Outer Helmholtz potential spanning 0 to 25 mV. The experiments were conducted with a 50 mV (rms) test signal from the LCR meter, which is the total potential difference between the two electrodes. Thus we assume that up to half of this potential drop can occur across each double layer. This assumption is clearly not quite true, because there is a potential drop across the resistive solution, but it provides an outer bound. The uncertainty in the other terms, including Helmholtz layer thickness ($x_{H, electrode}$) and Helmholtz dielectric constant at each electrode ($\epsilon_{H, electrode}$) were propagated through the calculation of total capacitance for the device. The results of this give a larger bound on the capacitance uncertainty, and was calculated as follows [Taylor 1997], using the general form for propagation of error in a function with multiple variables:

$$\delta C = \sqrt{\left(\frac{\partial C}{\partial x_{HA}} \delta x_{HA}\right)^2 + \left(\frac{\partial C}{\partial x_{HC}} \delta x_{HC}\right)^2 + \left(\frac{\partial C}{\partial \epsilon_{HA}} \delta \epsilon_{HA}\right)^2 + \left(\frac{\partial C}{\partial \epsilon_{HC}} \delta \epsilon_{HC}\right)^2} \quad (3.33)$$

Where C is the capacitance, x_H is the Helmholtz layer thickness, ϵ_H is the Helmholtz layer dielectric constant, and the subscripts A and C refer to anode and cathode, respectively, and δ refers to the uncertainty of the given quantity. Table 3.2 below lists the input parameters for the double-layer capacitance model curves shown in Figure 3.32. The Ca^{2+} hydration radius is given as 2.4 Å in [Burgess

1999], but because of uncertainty in the true composition of the layer, we assume a cathode Helmholtz layer thickness of 4 ± 2 Å. The SO_4^{2-} ion has a hydration radius of 3.6 Å between the sulfur in the sulfate ion and oxygen in the water molecules in the hydration shell (S-O_w distance) [Vchirawongkwin 2007]. We assume a Helmholtz layer thickness at the anode of 7 ± 2 Å.

Table 3.2: Uncertainty values for input parameters in double layer capacitance model.

Input Parameter	Value	$\delta(\text{Value})$
ϵ_{water}	80	0
$\epsilon_{\text{H,cathode}}$	25	10
$\epsilon_{\text{H,anode}}$	25	10
T	298.15 K	0 K
$x_{\text{H,cathode}}$	4 Å	2 Å
$x_{\text{H,anode}}$	7 Å	2 Å

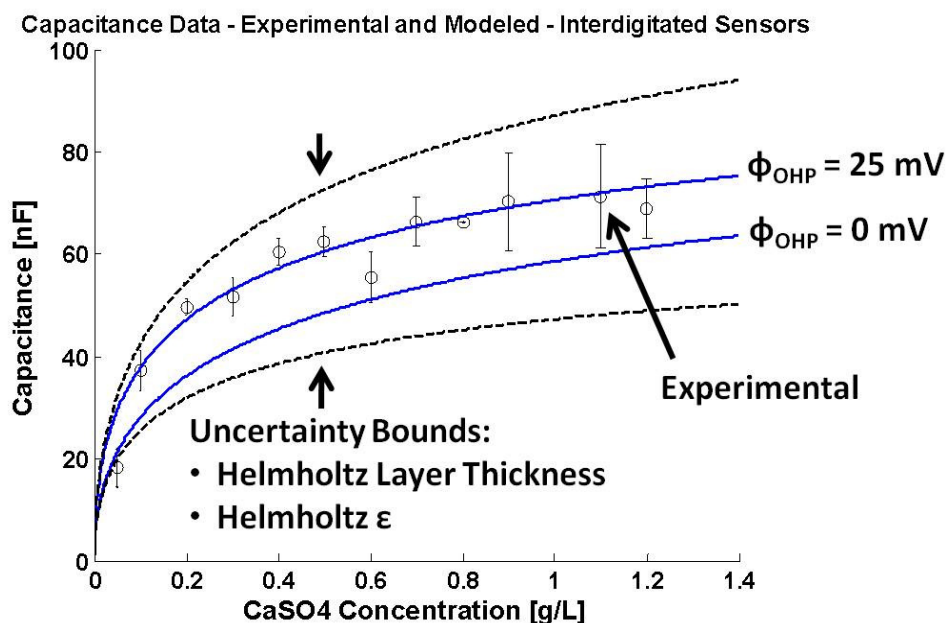


Figure 3.32: Plot of experimental capacitance data from tests with interdigitated electrodes. Modeled capacitance ranges included. The two solid curves are for Outer Helmholtz Plane (OHP) potentials of 0 and 25 mV with $x_{\text{OHP,anode}} = 7$ Å, $x_{\text{OHP,cathode}} = 4$ Å, and $\epsilon_{\text{H,anode}} = \epsilon_{\text{H,cathode}} = 25$. The dashed curves account for propagation of uncertainty in the Helmholtz layer thicknesses and dielectric constants.

The figure shows that the experimental data match the predicted model fairly well, which was developed using reasonable input parameters. Table 3.3 gives the mean and standard deviation on the mean of the capacitance data in each concentration bin.

Table 3.3 Capacitance vs. concentration data shown in Figure 3.32.

Concentration [g/L]	Capacitance [nF]	Concentration [g/L]	Capacitance [nF]
0.05	18.2 ± 3.6	0.7	66.3 ± 4.8
0.1	37.2 ± 3.9	0.8	66.2
0.2	49.7 ± 1.6	0.9	70.3 ± 9.5
0.3	51.6 ± 3.7	1	N/A
0.4	60.4 ± 2.7	1.1	71.3 ± 10
0.5	62.5 ± 2.9	1.2	68.9 ± 5.8
0.6	55.4 ± 4.9		

3.8.5. Analysis of Conductance Responses

In Section 3.2 the concept of the cell constant was introduced, which is used to relate conductance to conductivity. Conductance is an intrinsic property dependent on electrode geometry and conductivity is an extrinsic property of an electrolytic solution. Measurements were taken of multiple electronic properties from the integrated sensors with the introduction of the monolithic electrodes. Previously only capacitance had been recorded, following the methodology presented by Zhang [Zhang 2005, 2006]. In this section we present an analysis of solute conductance measurement demonstrating proof-of-concept sensor verification.

The conductance from all six of the integrated sensors was recorded by the LCR meter at each of the following concentrations: 0.02, 0.06, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g/L. The cell was operated in pure cross-flow mode (permeate valve closed) so that all sensors were sampling the bulk feed stream of known

concentration. The cross flow velocity was 8.2 cm/s ($Re = 188$) and the pressure was 551 kPa (80 psi).

Each of the sensors shows a good linear fit of conductance with solute concentration (Figure 3.33).

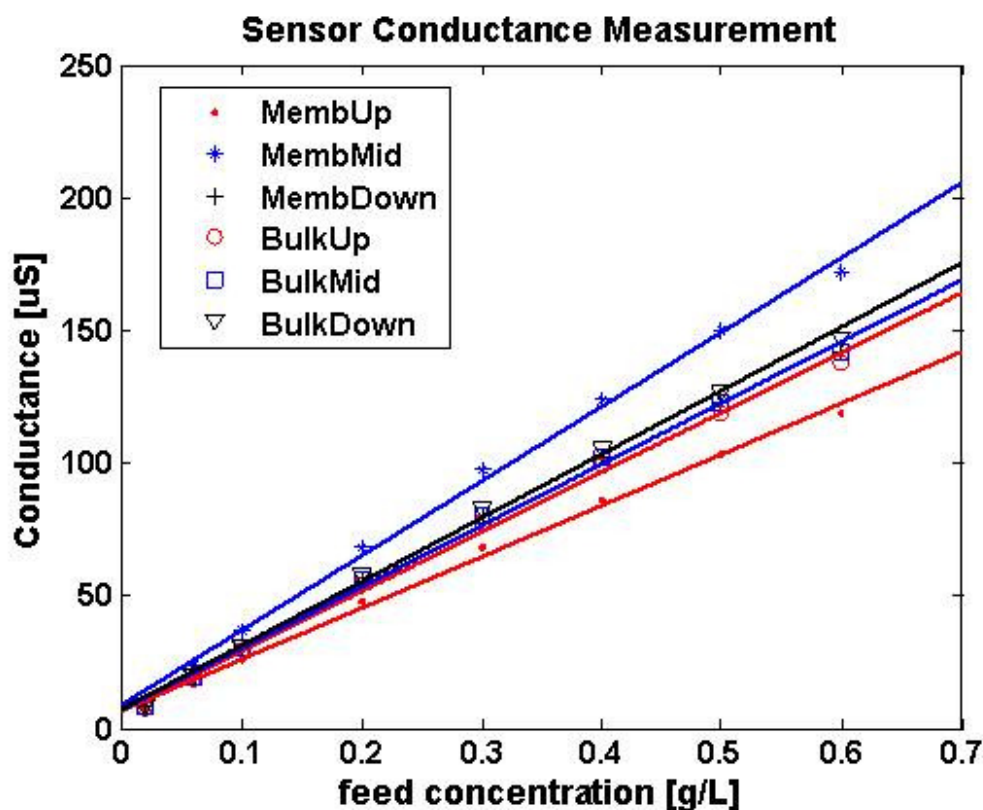


Figure 3.33: Plot of concentration versus conductance for monolithic electrode sensors.

The feed conductivity was also simultaneously recorded by the commercial conductivity probe (CDCN-91 conductivity meter) installed in the feed tank. The cell constant was calculated at each concentration according to the following relation:

$$\kappa = \frac{\sigma}{G} \quad (3.34)$$

Where κ is the cell constant, σ is the conductivity and G is the conductance. These experimentally calculated cell constant values were compared with a theoretical model to verify that the sensors were

functioning as expected. Olthuis [Olthuis 1995] presented a derivation for calculating the cell constant of probes with arbitrary geometry. This derivation starts with Gauss's Law:

$$\oiint_V \epsilon_r \epsilon_0 \vec{E} \cdot d\vec{A} = Q_F \quad (3.35)$$

Where dA is a differential area element of the Gaussian surface, Q_F is the free charge contained in an imaginary Gaussian volume between the electrodes and ϵ_r is the dielectric constant of the medium between the electrodes (80 for water). Ohm's Law, which can be expressed in terms for current flux, J , conductivity, σ , and applied electric field, E , is then applied.

$$\vec{J} = \sigma \vec{E} \quad (3.36)$$

Integration of Ohm's Law over the Gaussian surface gives:

$$I = \oiint_V \sigma \vec{E} \cdot d\vec{A} \quad (3.37)$$

Combining Ohm's Law and Gauss's Law gives:

$$\frac{\oiint_V \epsilon_r \epsilon_0 \vec{E} \cdot d\vec{A}}{\oiint_V \sigma \vec{E} \cdot d\vec{A}} = \frac{Q_F}{I} \quad (3.38)$$

Combining Ohm's Law, $I = V/R$, with the definition of capacitance, $C = Q/V$, and substituting into the right hand side of equation 3.38 gives:

$$\frac{\oiint_V \epsilon_r \epsilon_0 \vec{E} \cdot d\vec{A}}{\oiint_V \sigma \vec{E} \cdot d\vec{A}} = CR = \frac{C}{G} \quad (3.39)$$

If the conductive medium is assumed to be homogeneous, the following relation then applies:

$$\frac{C}{G} = \epsilon_r \epsilon_0 \rho = \frac{\epsilon_r \epsilon_0}{\sigma} \quad (3.40)$$

Based on equation 3.40, and the general definition of cell constant, the constant an arbitrary electrode configuration can be calculated as follows:

$$\kappa = \frac{\epsilon_r \epsilon_0}{C} \quad (3.41)$$

An analytical solution is provided by Olthuis [Olthuis 1995] for rectangular interdigitated planar electrodes. These solutions were obtained by conformal mapping methods. In the current work, however, the two planar monolithic electrodes are of trapezoidal shape. We used electrostatic finite element modeling to determine the capacitance of the given electrode configuration. A model of the system was created in CoventorWare, and the capacitance was then calculated with variable element sizes to ensure acceptable convergence of the solution. The solution was obtained for variable gap width between the nickel electrodes, since this is one of the primary sources of uncertainty in the physical system. The electrodes were mounted by hand, meaning the gap distance ranged from 0.5 to 1.5 mm. The resulting experimentally calculated cell constant values and range of modeled cell constants are given in Figure 3.34. The plot shows that the experimental values match well with the theoretically expected range.

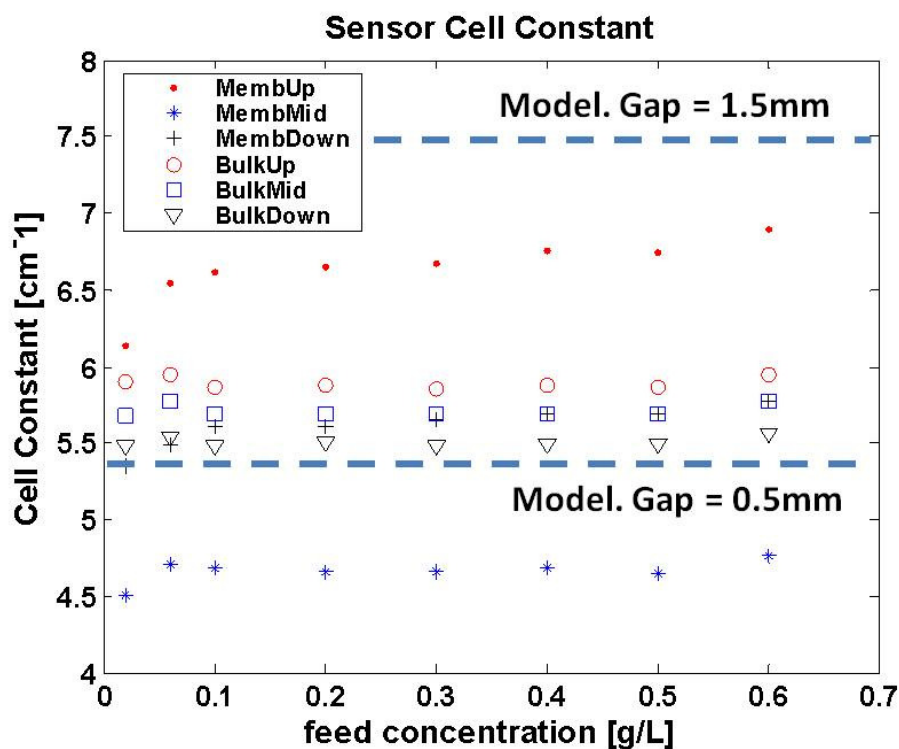


Figure 3.34: Plot of experimentally determined cell constants for integrated sensors. The dashed lines show the range of theoretical cell constant for variable electrode gap width, following the Olthuis model [Olthuis 1995], with input from finite element modeling (CoventorWare).

In the experiments presented in thesis, electronic measurements were taken using an AC test signal from the LCR meter, and therefore the effect of frequency on the conductivity readings is of interest. According to Rieger [Rieger 1994], the ionic atmosphere relaxation time is on the order of $10^{-7}/C$ seconds, where C is the molar concentration [mol/m^3]. At high frequencies, the ions move faster than their ionic atmospheres can rearrange, reducing the retarding effect of the ionic atmospheres and yielding higher measured conductivities. In the experiments we conducted, all tests were performed with a 10 kHz signal, meaning the period of this signal is 10^{-4} s. It can be seen in Figure 3.35 that the test signal period is much greater at all concentrations used (0.02 to 0.7 g/L) than the ionic atmosphere relaxation time. This means that the Onsager conductivity formula (equation 3.7) should apply.

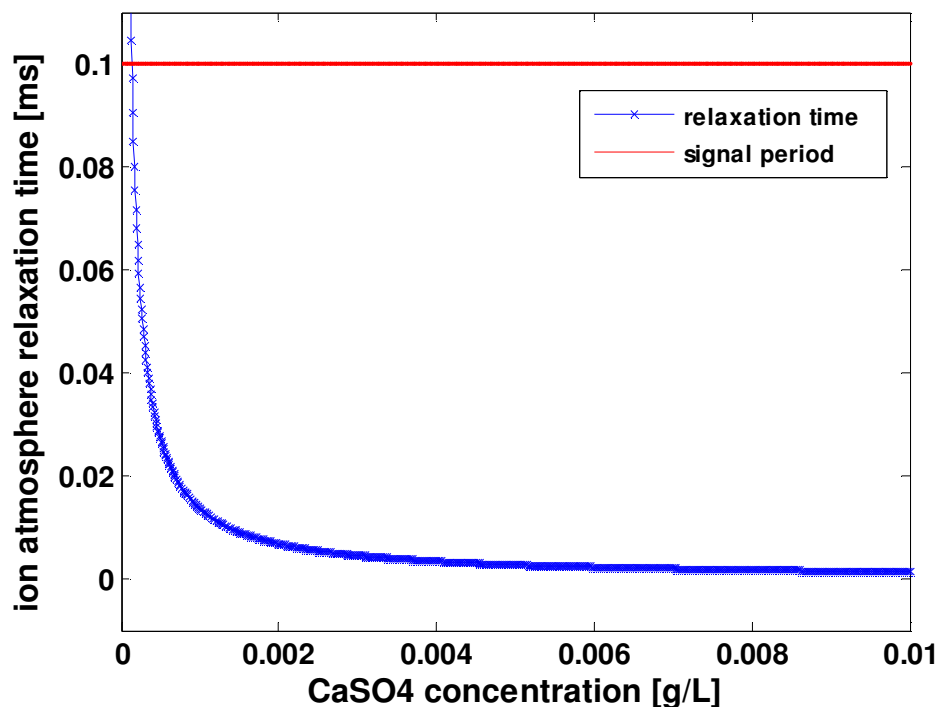


Figure 3.35: Plot of ionic atmosphere relaxation time versus calcium sulfate concentration.

The cell constants shown in Figure 3.34 and the measured conductance data shown in Figure 3.33 were then used to directly calculate the conductivity at each solute concentration. Theoretical conductivity over the concentration range of interest was also calculated following the Onsager relation for dilute solutions. Figure 3.36 shows that the experimental values match the Onsager conductivity well, especially at low concentration. Deviation of experimental data from the theoretical curve increases with increasing concentration. In particular, the fit appears to be best up to ~10% of the saturation concentration. The Onsager formula is intended to work best for very dilute solutions [Rieger 1994], so this behavior is not unexpected. Additionally, conductivity values for aqueous CaSO₄ solutions from the literature [Washburn 2003] are presented in the figure, and show good agreement with the model and integrated sensor results.

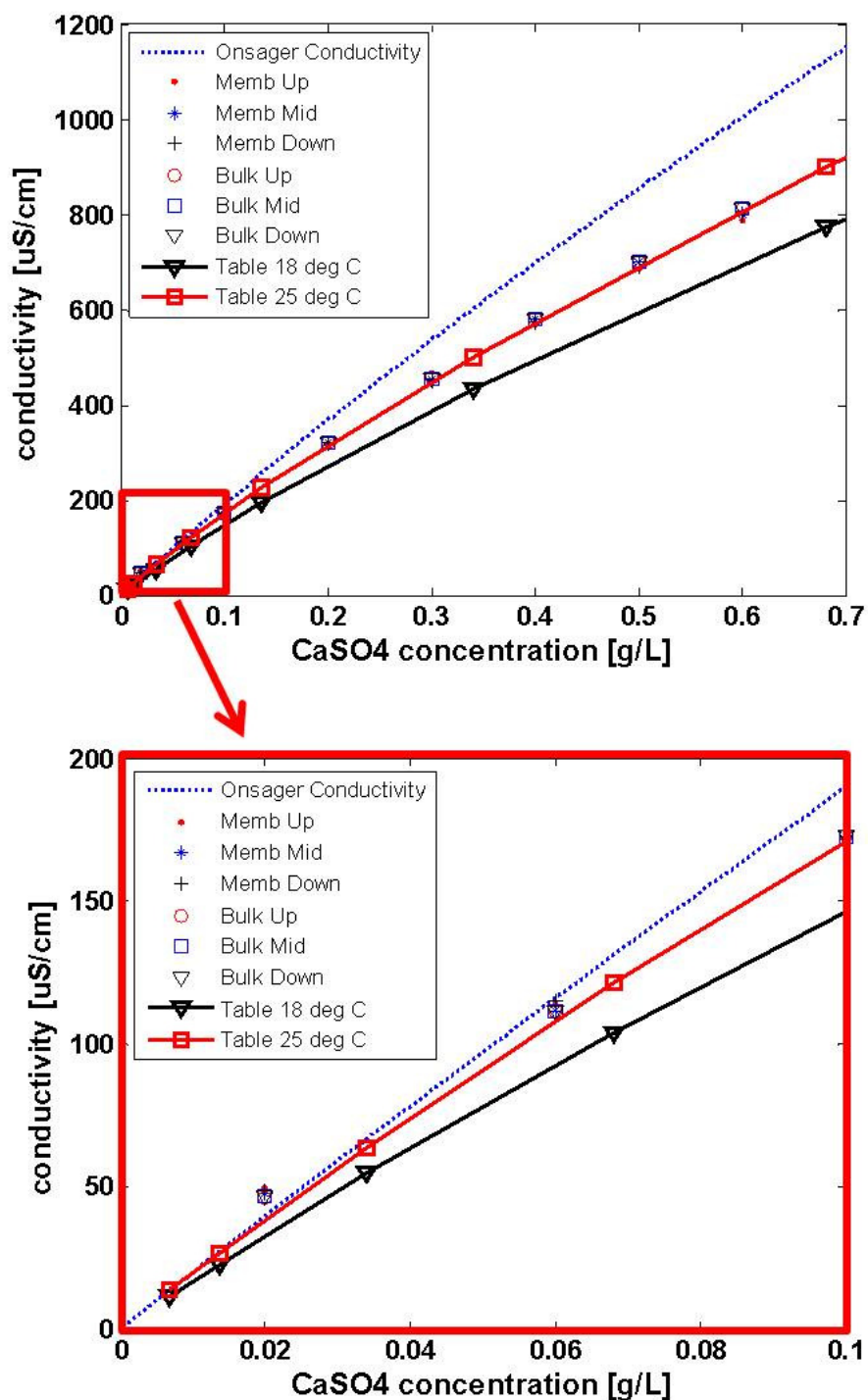


Figure 3.36: Plot of experimentally determined conductivity from the integrated sensors, along with theoretical conductivity following the Onsager relation. Tabulated data from [Washburn 2003] show good agreement with the results of this experiment and the Onsager model. The bottom plot is an inset of data at low concentration

3.8.6. Scaling Monitoring

In order to demonstrate sensor response due to scaling, an experiment was performed with a feed concentration of 0.7 g/L CaSO_4 at a reduced cross-flow velocity (2.2 cm/s, $\text{Re} = 53$). This combination of high concentration and lower cross-flow rates yields much larger supersaturation ratios at the membrane surface, resulting in reduced scaling induction times. The experiment was stopped after the electronic parameters indicated scaling, and the membrane was removed for post-mortem analysis. In this situation, the conductance (G) recorded by the LCR meter demonstrated the greatest response to scaling formation (Figure 3.37). The plot shows the deviation in conductance reading for each sensor over the course of the scaling test. While there is some drift in the bulk sensor readings, the magnitude of the conductance change is much greater for the membrane sensors. It is expected that scaling would occur first at the downstream location followed by midstream followed by upstream, and this appears to be clearly represented in the data. Δt indicates the scaling induction time of each sensor, as indicated by the conductance readings. All of the membrane sensors show a marked decrease in conductance that correlates with scaling. This supports the hypothesis that scaling results in a reduction in local concentration in the CPBL due to precipitation of the supersaturated solute. In addition, as scaling covers the membrane surface, permeation flow is blocked locally. This results in a local reduction of concentration polarization [Gilron 1987, Lyster 2009], which would in turn yield lower conductivity.

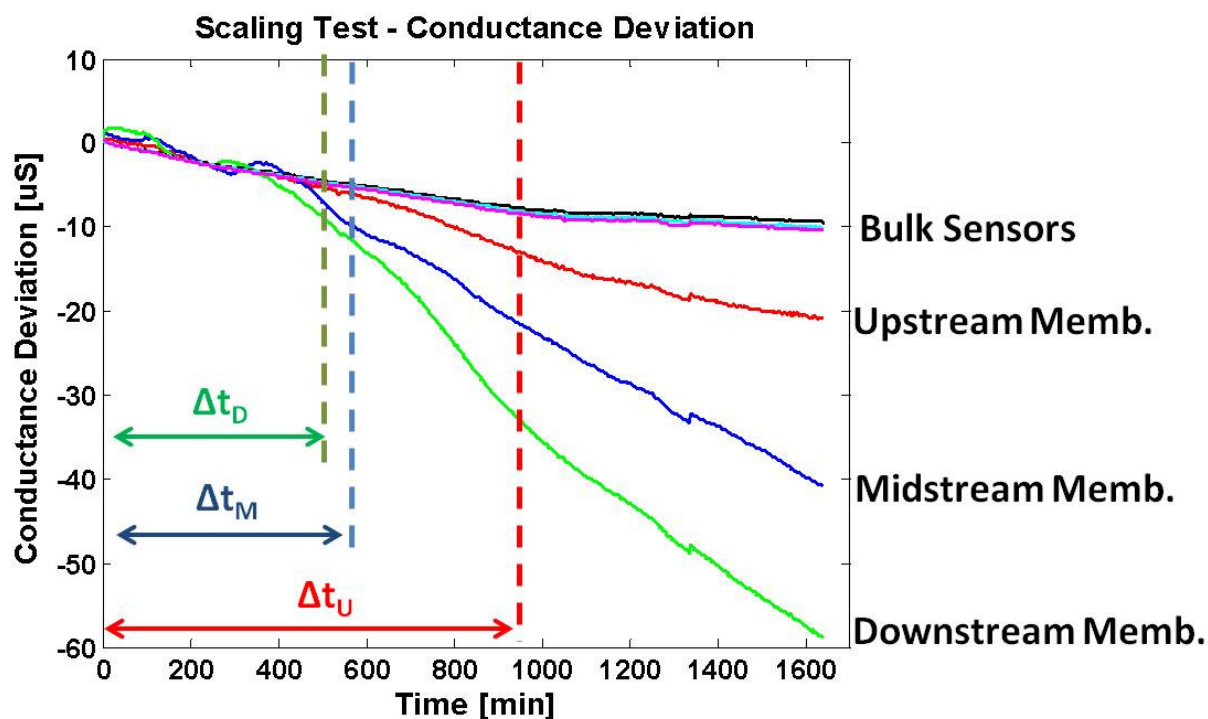


Figure 3.37: Conductance data demonstrating scaling formation on the membrane surface. Δt indicates the scaling induction time of each membrane sensor.

At the completion of this experiment, the membrane was removed from the module and the presence of scaling was analyzed. Photographs of scaling at the sensor locations are shown in Figure 3.38. From the figure it can be seen that heavy scaling has occurred in the membrane surrounding the downstream sensor, while moderate scaling is seen around the upstream sensor. The scaling density increased from upstream to downstream, as expected. These post-mortem results support the conclusion that the measured conductance results provide a good indicator of scaling formation.

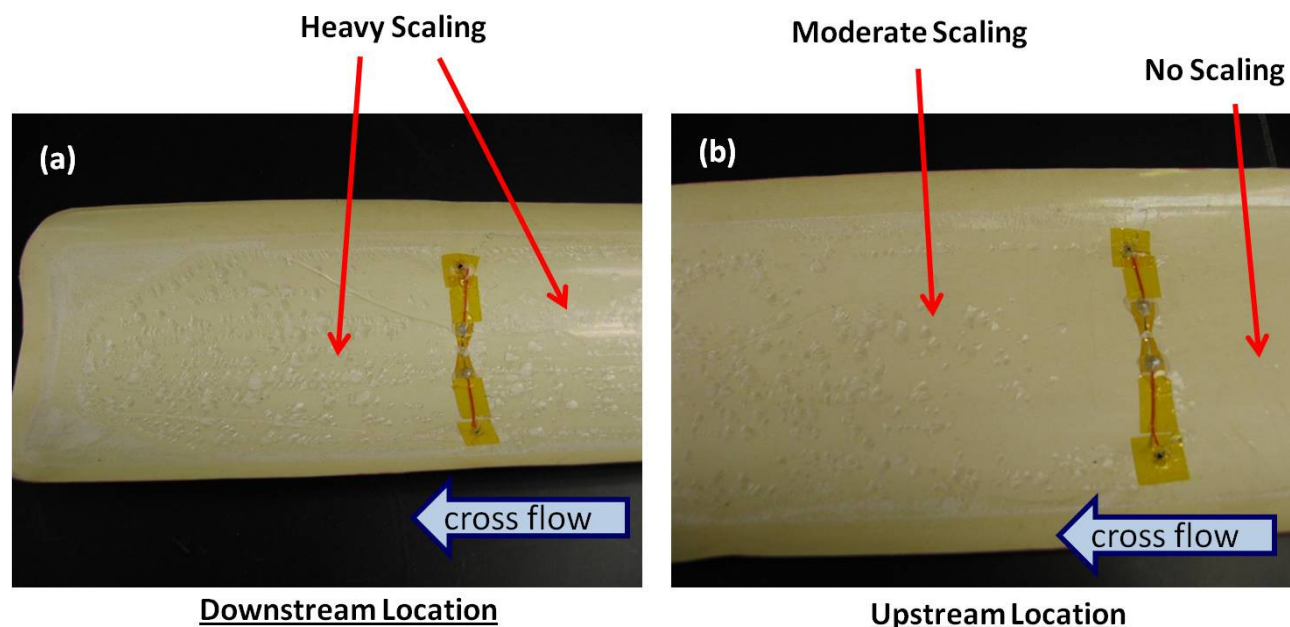


Figure 3.38: Post-mortem photographs of the filtration membrane after the conclusion of the scaling test. (a) shows heavy scaling around the downstream sensor and (b) shows moderate to little scaling around the upstream sensor.

3.9. Significance

The work presented in this chapter has demonstrated the initial application of thin flexible electrolytic sensors, which were integrated into the flow channel of a flat-sheet cross flow desalination module. The sensors represent next-generation devices, building upon the work presented by Zhang et al. [2005, 2006] for the monitoring of concentration of dissolved ions in the CPBL near the membrane surface. This chapter has demonstrated that the integrated sensors were able to sample salt concentrations with reasonable accuracy, as demonstrated by comparison of experimentally measured capacitance and conductance with theoretical models. Based on this knowledge, we were able to develop a calibration procedure so that different sensors could accurately monitor concentration within the concentration polarization boundary layer. While models have been developed to predict concentration values within the CPBL, direct measurement in a system such as ours has thus far not been possible.

The responses of the integrated sensors demonstrated qualitative agreement with concentration and scaling behavior under which concentration polarization was present. This includes detection of highest concentration and earliest onset of scaling at the downstream location in the module. Due to the complex nature of developing appropriate sensors and integration schemes, the data set for this class of sensors is still sparse. Future work will require additional experiments to demonstrate greater statistical repeatability in direct measurements of the axial and velocity dependence of CP. Despite this, the fact that the electronic data recorded matches well with theory, both in terms of predicted electronic measurements and mass transport properties, is quite encouraging.

Chapter 4

Integrated Ultrasonic Sensors for Monitoring of Early-Stage Inorganic Scaling

4.1. Motivation and Components of Work

In Chapter 3 we presented work on integrated electrolytic sensors to monitor the concentration polarization that develops near the membrane surface during reverse osmosis desalination. When the concentration is high enough, solute precipitates out of solution, forming crystal scaling that grows on nucleation sites. Scaling can be costly and time intensive to remove. Ultrasonic time-domain reflectometry (UTDR) is a method for non-destructive membrane monitoring that shows more immediate potential for use with industrial desalination systems. Although UTDR cannot detect concentration polarization (CP), ultrasonic transducers can be used to detect the formation and cleaning of inorganic scaling. Ultrasonic transducers can be manufactured in a wide variety of configurations, and are already incorporated in commercial non-destructive testing (NDT) systems.

The motivation behind the work presented in this chapter is to investigate the viability of miniature, internally integrated ultrasonic sensors as an alternative to, and improvement on methods previously presented in the literature. It has been demonstrated in the literature that ultrasonic transducers mounted externally on flow cell housings can be applied to monitor the formation and cleaning of fouling layers on the separation membrane. Integration of miniature in-situ sensors, which are mounted internally in the filtration module is investigated. This configuration places the transducer closer to the membrane surface where fouling occurs, presenting the potential for improved signal-to-noise ratio, and thus improved detection performance. Such an integration scheme would reduce acoustic losses due to unwanted reflections (from the flow cell housing/feed solution interface), scattering (through module walls and in the flowing feed solution) and beam spread.

Placing a transducer directly in contact with the back side of the membrane could be problematic, since it locally blocks permeation. This may inhibit the local formation of scaling at the transducer location. Convective cross-flow, however, should permit scaling at the transducer location similar to the surrounding unblocked areas. Determining whether the location of the transducer beneath the membrane causes problems in the formation and detection fouling is another major question addressed in this study.

The research conducted on integrated ultrasonic sensors consists of the following primary areas:

- Design and in-house fabrication of a miniature-scale ultrasonic transducers.
- Development of an internal ultrasonic transducer integration scheme in a working reverse osmosis/nanofiltration system with modification of a flat-sheet cross flow module for conducting experiments under realistic operating conditions.
- Development and testing of signal processing methodologies for detection of formation and cleaning of scaling layers.
- Examination of the influence that permeation blocking caused by internal transducers has on local scaling.

4.2. Acoustic Wave Propagation in Media and at Interfaces

Acoustic impedance is a very important factor in the design and application of ultrasonic transducers. The impedance is a material property, physically describing the ratio of pressure to induced particle velocity caused by a sound wave propagating through the medium. The Rayl [$\text{N}\cdot\text{s}/\text{m}^3$] is the primary unit of acoustic impedance. Impedance is a complex property with a real part, analogous to an electrical resistor in an equivalent circuit, and an imaginary part, which is reactive and similar to an electrical capacitor. The imaginary part of the impedance is manifested in a phase relation between the pressure and the particle velocity. The complex nature of the acoustic impedance becomes a factor when considering waves propagating in attenuating or dispersive media, as well as waves with non-normal incidence on an interface between media with differing acoustic properties [Mason 1958]. The characteristic acoustic impedance, Z_0 , is defined according to equation 4.1 as the speed of sound in the

material, c_0 , multiplied by the density of the material, ρ . Table 4.1 lists some common materials and their associated characteristic acoustic impedances:

$$Z_0 = c_0 \rho \quad (4.1)$$

Table 4.1: A list of common materials and associated acoustic impedance [Onda Corp. 2007].

Material	Acoustic Impedance [MRayl]
Oxygen at 20° C	4.33×10^{-4}
Isopropyl Alcohol at 20° C	0.92
Water at 25° C	1.5
Polystyrene	2.42
Aluminum	17.33
Copper	44.6
Tungsten	101

At the interface between two materials of differing acoustic impedance, part of the pressure wave, as well as the energy contained in the wave will be reflected and the remainder will be transmitted. Characterization of these interfacial transmissions and reflections is the fundamental concept on which all acoustic non-destructive testing (NDT) is based. First, we consider a plane longitudinal wave propagating at normal incidence to an interface between two media, travelling from medium 1 to medium 2. The pressure fronts of the incident, reflected and transmitted waves take the following forms [Schmerr 1998]:

$$p_{inc} = P_{inc} \exp(ik_1 x - i\omega t) \quad (4.2)$$

$$p_{refl} = P_{refl} \exp(-ik_1 x - i\omega t) \quad (4.3)$$

$$p_{trans} = P_{trans} \exp(-ik_2 x - i\omega t) \quad (4.4)$$

Where p is the wave pressure, P is the amplitude of the wave, i is the imaginary number, k is the acoustic wavenumber in the medium ($k = \omega/c$), x is the position coordinate, ω is the radial frequency of the sound wave ($\omega = 2\pi/T$), T is the period of the wave and t is time. The incident, reflected and transmitted waves

are expressed as complex functions of position and time. At the interface, the pressure as well as the normal velocity must be continuous, under the assumption that the two media displace but don't separate. The velocity can be taken as a normal derivative of the pressure [Schmerr 1998]. These amplitude boundary conditions are represented in equations 4.5 and 4.6.

$$P_{inc} + P_{refl} = P_{trans} \quad (4.5)$$

$$\left(\frac{ik_1}{v_1}\right)P_{inc} - \left(\frac{ik_1}{v_1}\right)P_{refl} = \left(\frac{ik_2}{v_2}\right)P_{trans} \quad (4.6)$$

Solving these two equations simultaneously yields the following results for the transmission and reflection coefficients, in terms of pressure:

$$T_p = \frac{P_{trans}}{P_{inc}} = \frac{2\rho_2 c_2}{\rho_1 c_1 + \rho_2 c_2} = \frac{2Z_2}{Z_1 + Z_2} \quad (4.7)$$

$$R_p = \frac{P_{refl}}{P_{inc}} = \frac{\rho_2 c_2 - \rho_1 c_1}{\rho_1 c_1 + \rho_2 c_2} = \frac{Z_2 - Z_1}{Z_1 + Z_2} \quad (4.8)$$

This derivation clearly shows that the pressure reflection and transmission behavior of acoustic waves can be expressed in terms of the material properties of media 1 and 2, and do not depend on the amplitude or frequency of the waves themselves. Specifically, this behavior can be expressed in terms of the acoustic impedance, as defined in equation 4.1. It is useful to plot these coefficients as the ratio Z_2/Z_1 , shown by the representative curves in Figure 4.1. $Z_2/Z_1 = 0$ corresponds to an interface between material 1 and a vacuum, T_p is 0, indicating complete reflection, and R_p is -1, indicating that the phase of the reflected wave is opposite that of the incident wave, resulting in destructive interference. $Z_2/Z_1 = 1$ corresponds to transmission between identical media, $T_p = 1$ indicates complete transmission, and $R_p = 0$ indicates no reflection. Above this value of Z_2/Z_1 , R_p takes a positive value, indicating the reflected wave is of the same phase as the incident wave.

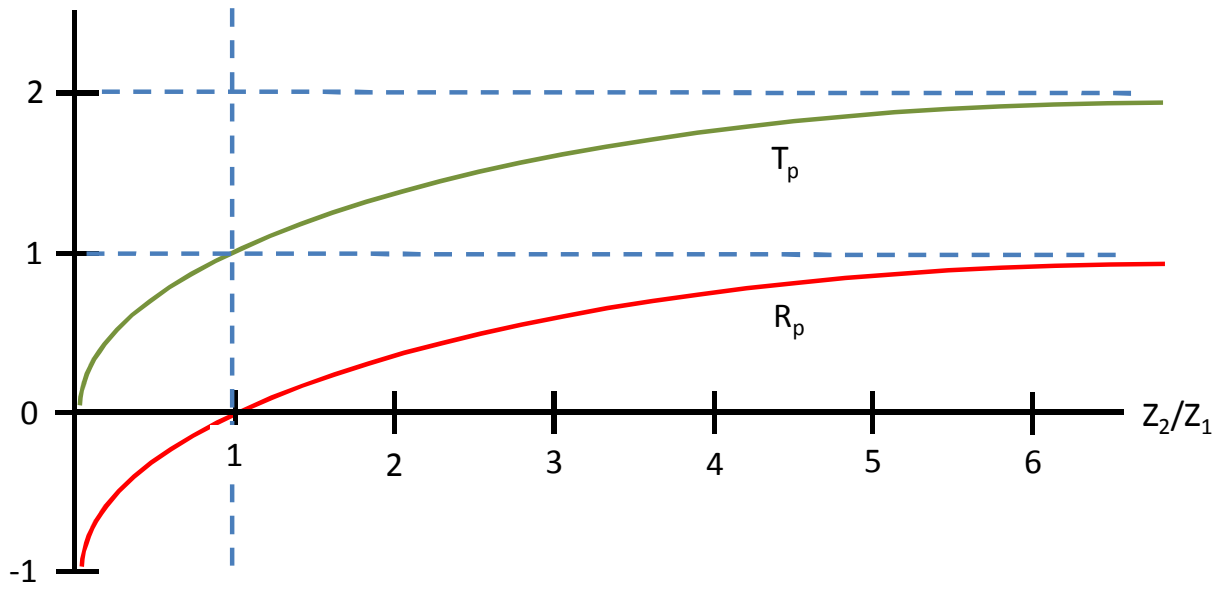


Figure 4.1: Plot of transmission and reflection coefficients as a function of the ratio of acoustic impedances at an interface, Z_2/Z_1 . Following [Schmerr 1998].

It is also useful to express the reflection and transmission coefficients in terms of energy. The intensity, I , is given in units of power per area over the full period of the wave; thus it has units of energy per area. In the case of a wave with normal incidence to the interfacial plane, the intensity is related to the pressure through the following:

$$I = \frac{P^2}{2Z} \quad (4.9)$$

Here I is the intensity, P is the pressure and Z is acoustic impedance. After some mathematical manipulations enforcing conservation of energy for the incident, reflected and transmitted waves, the following relations are obtained [Schmerr 1998], where the sum of the reflection and transmission coefficients must equal 1, following conservation of energy:

$$R_I = R_p^2 \quad (4.10)$$

$$T_I = \frac{Z_1}{Z_2} T_p^2 \quad (4.11)$$

$$R_I + T_I = 1 \quad (4.12)$$

Many applications of ultrasonic NDT employ obliquely incident waves. In this case, additional factors must be considered, which we briefly discuss here. First, one must consider the type of interface. At a fluid-fluid interface, the incident longitudinal plane wave will result in reflected and transmitted longitudinal waves, also called P-waves. P-waves occur where the local displacement of the medium through which the wave travels is in the direction of propagation. At a fluid-solid interface, the reflected wave is again of the longitudinal type (P-wave), but in the solid material, shear waves (S-waves) may also occur. S-waves are transverse waves, where the direction of material displacement is perpendicular to the direction of propagation. These waves are possible because shear displacements can be supported in an elastic solid with a non-zero shear modulus, whereas fluids have a shear modulus of zero. A solid-solid interface with smooth contact is also a common configuration. This type of interface is found when a transducer is coupled to another solid object by a thin liquid couplant. In this configuration, a no-shear boundary condition is applied at the interface. The reflected wave, as well as the transmitted wave, may have shear components. A good mathematical treatment of these effects is presented by Schmerr [Schmerr 1998].

The concept of the critical angle comes into play when considering waves incident on an interface at an oblique angle. Snell's law is used in acoustics to describe refraction of waves passing from one medium to another; the transmission and reflection coefficients can be expressed by incorporating the incident angle. Equations 4.13 and 4.14 describe the coefficients for a simple fluid-fluid interface. This is not the most general case because shear waves are not considered, but is useful in introducing the concept of the critical angle [Schmerr 1998].

$$R_p = \frac{Z_2 \cos(\theta_i) - Z_1 \left(1 - \frac{c_2^2 \sin^2(\theta_i)}{c_1^2} \right)^{1/2}}{Z_2 \cos(\theta_i) + Z_1 \left(1 - \frac{c_2^2 \sin^2(\theta_i)}{c_1^2} \right)^{1/2}} \quad (4.13)$$

$$T_p = \frac{2Z_2 \cos(\theta_i)}{Z_2 \cos(\theta_i) + Z_1 \left(1 - \frac{c_2^2 \sin^2(\theta_i)}{c_1^2} \right)^{1/2}} \quad (4.14)$$

We can thus see that as long as $\sin(\theta_i) \leq c_1/c_2$, both the reflection and transmission coefficients are real. Beyond this, the term is imaginary, and we obtain the following relation (after some mathematical manipulation) for the transmitted pressure wave:

$$p_{trans} = P_t \exp\left(\frac{-\omega \alpha y}{c_2}\right) \exp(ik_x x - i\omega t) \quad (4.15)$$

Where:

$$\alpha = \left(\frac{c_2^2 \sin^2(\theta_i)}{c_1^2} - 1 \right)^{1/2} \quad (4.16)$$

$$k_x = \frac{\omega}{c_x} \quad (4.17)$$

$$c_x = \frac{c_1}{\sin(\theta_i)} \quad (4.18)$$

The result is that a travelling wave propagates along the interface between the media (x-direction), while an inhomogeneous wave is transmitted (y-direction) and quickly expires due to the decay factor in the exponential. Thus, the reflection is 1. There is no violation of conservation of energy since the energy flux crossing the interface averages to 0 over one full cycle. Thus, the presence of an inhomogeneous transmitted pressure wave is shown to be permissible. The expression for the critical angle is:

$$\theta_{cr} = \sin^{-1}\left(\frac{c_1}{c_2}\right) \quad (4.19)$$

The experimental work in this thesis utilizes ultrasonic transducers oriented normally to the interfacial surfaces (membrane, module housing), but normal orientation is merely a specific case of the general oblique wave propagation problem. Many applications of ultrasonic NDT utilize the properties of oblique incident wave to glean additional information, particularly for near surface NDT that would otherwise be in the near-field of a planar transducer [Schmerr 1998, Emsminger 1988].

4.3. Ultrasonic Transducers: Design Concepts

4.3.1. Plane Wave Transducer

Ultrasonic transducers function in much the same way as audio speakers and microphones. Speakers use a membrane or dish mounted on a piston which vibrates in response to electrical signals, reproducing music or speech through the resulting acoustic pressure waves. These vibrations propagate as sound, which we can hear. A microphone, on the other hand, is a membrane that vibrates in response to incident acoustic pressure waves. The membrane is coupled to a magnetic coil which generates electrical currents so that the sound can in turn be electronically recorded or amplified by a speaker dish.

In an ultrasonic transducer, a thin piezoelectric element serves the same purpose as the dish or membrane in speakers or microphones. When excited with a voltage from a power source, the piezoelectric material expands and contracts, displacing the surrounding material, forming a propagating acoustic wave. Similarly, when an acoustic disturbance impacts the element, the element is deformed and a voltage develops across the piezoelectric material. If connected to an appropriate circuit, the resulting current can be recorded. Ultrasonic transducers are designed to operate beyond the range of human hearing, typically greater than 20 kHz [Emsminger 1988]. The transducers used in this work for non-destructive monitoring of membrane-based filtrations resonate at a center frequency of 10 MHz.

The work presented in this thesis utilized commercial plane-wave (flat) transducers. A diagram of such a device is presented in Figure 4.2. The piezoelectric element is typically a thin plate with a thin metal layer on each of the opposing flat faces, and is packaged inside a housing to protect it from the

outside environment. The element is usually mounted between layers of material, such as a loaded epoxy, for the purpose of acoustic impedance matching and damping. A voltage signal applied across the piezoelectric element results in deformation in the thickness mode, and plane, longitudinal acoustic waves (or pulses) travel forward into the matching layer toward target material. The waves generated by displacement on the back-side transmit into the backing layer. The backing layer is usually made of a material that closely matches the acoustic impedance of the piezoelectric element, in order to reduce ringing.

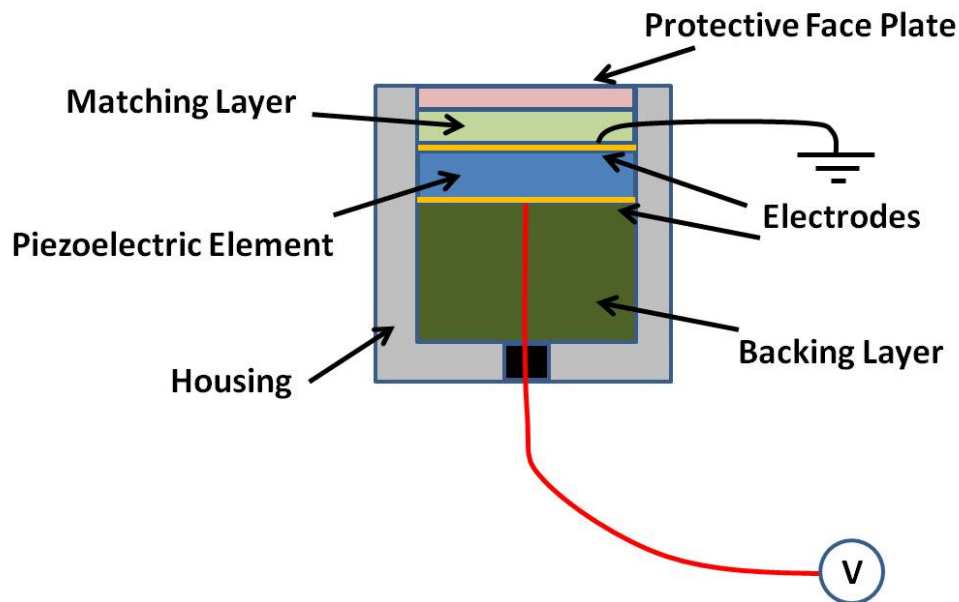


Figure 4.2: Schematic of a typical plane-wave ultrasonic transducer.

In addition to the plane transducer discussed above, focused transducers are used in a variety of applications. There are several ways of focusing the acoustic beam generated by a transducer. The beams are often focused in ultrasonic imaging applications to improve signal-to-noise ratio at a particular plane of interest. Focusing increases the intensity of the ultrasonic beam on the focal plane. Although a detailed discussion of focused transducers is beyond the scope of this thesis, some representative information can be found in Sleva [1994], Li [2002], Fleischman [2003], Ketterling [2005], Toda [2005] and Olympus [2006].

4.3.2. Pulse-Echo and Pitch-Catch Ultrasonic NDT

In contact ultrasonic NDT, the transducer is placed in physical contact with a solid material under test, usually using a couplant (such as petroleum jelly, or even honey) to improve transmission. Immersion NDT is also commonly performed; the transducer is submerged in a fluid (such as water) and directed at the material under test. When the transducer is excited by a pulser-receiver, an ultrasonic pulse is generated which propagates forward through the material. The wave or pulse refracts at and reflects from defects in the material, such as gaps, grains or clusters of non-homogeneous material. These defects present interfaces of material with differing acoustic impedance.

The two test configurations that are most commonly used in ultrasonic NDT are called *pulse-echo* and *pitch-catch*, as shown in Figure 4.3 [Krautkrämer 1990]. Note that this diagram demonstrates immersion NDT, as opposed to contact NDT. In a *pulse-echo* configuration, a single transducer generates an acoustic pulse, which travels through a material with echoes returning to the same transducer. The single transducer works as both the wave generator (like a speaker) as well as the receiver (like a microphone). *Pitch-catch* involves two transducers, one of which generates the wave, and another separate transducer that receives the echo. The receiving transducer may be located directly opposite the sample for through-transmission or obliquely for detecting scattered waves [Krautkrämer 1990].

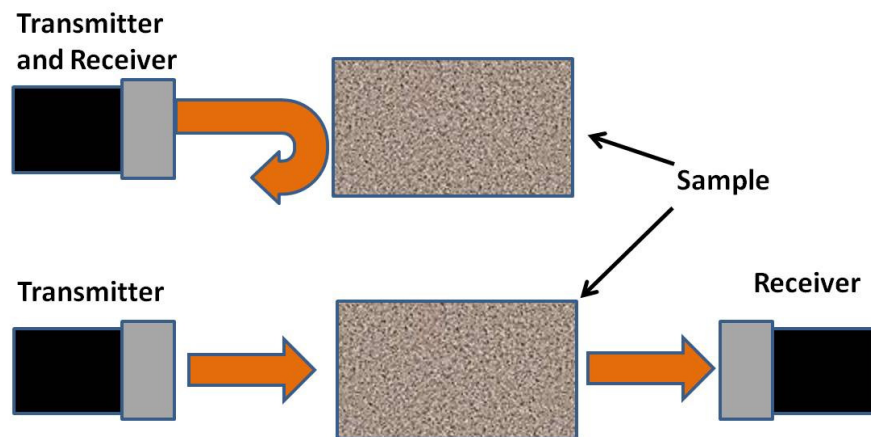


Figure 4.3: Diagram of the pulse-echo (top) and pitch-catch (bottom) configurations commonly employed in ultrasonic non-destructive testing.

4.3.3. Piezoelectricity

The heart of an ultrasonic transducer is the piezoelectric active element. This element can take many shapes and can be made from several different materials, often ceramics and polymers. Most common commercial transducers are plane wave (flat) devices based on a thin plate of lead zirconium titanate (PZT). The opposing faces of the PZT are coated with a thin metal film (i.e., 30 nm nickel [PiezoSystems 2007]). One of the faces is electrically grounded, while the other is excited by a function generator. This excitation most commonly takes the form of a pulse or sinusoidal signal and the piezoelectric disc functions much like a parallel plate capacitor.

Piezoelectricity is a property that certain insulators possess in which the application of an electrical field causes mechanical strains in the material. Conversely, the application of mechanical strains to the material will induce an internal electric field. The *American Institute of Physics Handbook* [AIPH 1957] defines piezoelectricity as “*the phenomena of separation of charge in a crystal by mechanical stresses and the converse.*”

When a piezoelectric material is properly connected to a voltage source through electrodes on the preferred surfaces, the magnitude and rate of expansions and contractions can be controlled as desired. This makes piezoelectrics excellent materials for use in ultrasonic transducers. A sinusoidal signal can be applied, causing a corresponding expansion and contraction in the material. This motion displaces the media in which the device is located (air, water, steel, epoxy...), resulting in a propagating sound wave. Similarly, when external forces such as incoming sound waves create mechanical strain of the piezoelectric material, a voltage will be generated that can be displayed on an oscilloscope. The electromechanical coupling in piezoelectric materials is governed by constitutive equations, which describe how they function as generators of mechanical displacement (by applying a voltage) as well as detectors of mechanical strains.

4.3.4. The KLM Equivalent Circuit and Acoustic Impedance Matching

Equivalent circuits are commonly used to describe and analyze the electromechanical coupling of the piezoelectric elements in ultrasonic transducers. Equivalent circuits can be used to model many different physical and engineering phenomena: electrical, mechanical, fluid, thermal, etc... The circuit was originally developed by Krimholtz, Leedom and Matthei [Krimholtz 1970], and good analyses are presented by Kino [Kino 1987] and Sherrit [Sherrit 1999]. In this formulation, the piezoelectric disc is considered to have full electrodes and differing acoustic loadings at each face. One example of a loading condition is air-backing with epoxy-matching on the front face. The KLM model treats the piezoelectric disc as a three-port black box (Figure 4.4): one electrical port with associated voltage and a current, and two acoustic ports (the front and back faces of the disc) with associated forces and face velocities. In this mathematical model, the forces are treated analogously to voltages and the velocities analogously to currents.

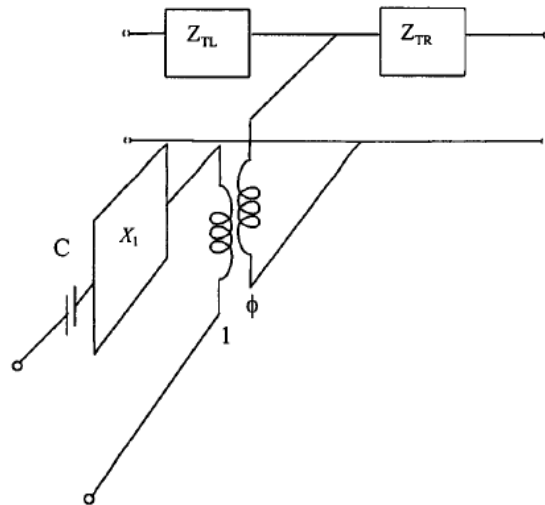


Figure 4.4: KLM equivalent circuit of an ultrasonic transducer [Sherrit 1999].

In Figure 4.4, an equivalent transformer with the ratio $1:\phi$ is used in the circuit to transform between the electrical port (with unstrained capacitance C and a fitting term, X_1) and the acoustic ports, with acoustic impedances Z_{TL} and Z_{TR} . A full development of the equivalent circuit model is beyond the

scope of this thesis; for further details see [Kino 1987]. A system of equations is developed relating the forces and velocities with voltages and currents (equations 4.20):

$$\begin{bmatrix} F_1 \\ F_2 \\ V_3 \end{bmatrix} = -i \begin{bmatrix} Z_{piezo} \cot(\bar{\beta}_a L) & Z_{piezo} \csc(\bar{\beta}_a L) & h/\omega \\ Z_{piezo} \csc(\bar{\beta}_a L) & Z_{piezo} \cot(\bar{\beta}_a L) & h/\omega \\ h/\omega & h/\omega & 1/\omega C_0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ I_3 \end{bmatrix} \quad (4.20)$$

Here, F_1 and F_2 are the forces generated at or imposed upon the transducer faces, V_3 is the voltage across the piezoelectric disc, v_1 and v_2 are the velocities at the faces, I_3 is the current through the electrical circuit, Z_{piezo} is the acoustic impedance of the piezoelectric material, $\bar{\beta}_a$ is the stiffened wave propagation constant for the piezoelectric material (relating frequency and piezoelectric material properties), L is the thickness of the piezoelectric disc, h is the piezoelectric stress constant divided by the unrestrained permittivity, ω is the frequency and C_0 is the capacitance across the unstrained transducer. The load acoustic impedances are handled by the following relation, expressed in terms of the forces and velocities on the element faces [Kino 1987]:

$$Z_i = -\frac{F_i}{v_i} = \frac{AT_i}{v_i} \quad (4.21)$$

Where Z_i is the acoustic impedance at face i of the transducer, F is the force, v is the velocity, A is the area of the face and T is the stress. Further relations for T are developed in [Kino 1987]. In the KLM model, when a voltage is applied across the piezoelectric element causing a mechanical strain, forward and backward propagating waves are assumed to be generated at the center of the element. The relations for stress at the element face and resonance thickness of the element are derived based on this assumption. The element will be cut to an odd-integer-multiple of the acoustic half-wavelength in the piezoelectric material, for operation at a specific desired resonant frequency.

Impedance matching on the element face is used in order to improve energy-transfer efficiency into the material under test. Both forward and backward propagating waves are generated at the center of

the element, so in order to maximize the acoustic energy transmitted through the forward face. A backing with an impedance of nearly zero would result in complete reflection of the backward propagating wave. If the disc thickness is an odd-integer-multiple of the acoustic half-wavelength and the element is actuated with a sinusoidal signal of the appropriate frequency, the back-reflection will constructively interfere with the forward propagating wave (Figure 4.5).

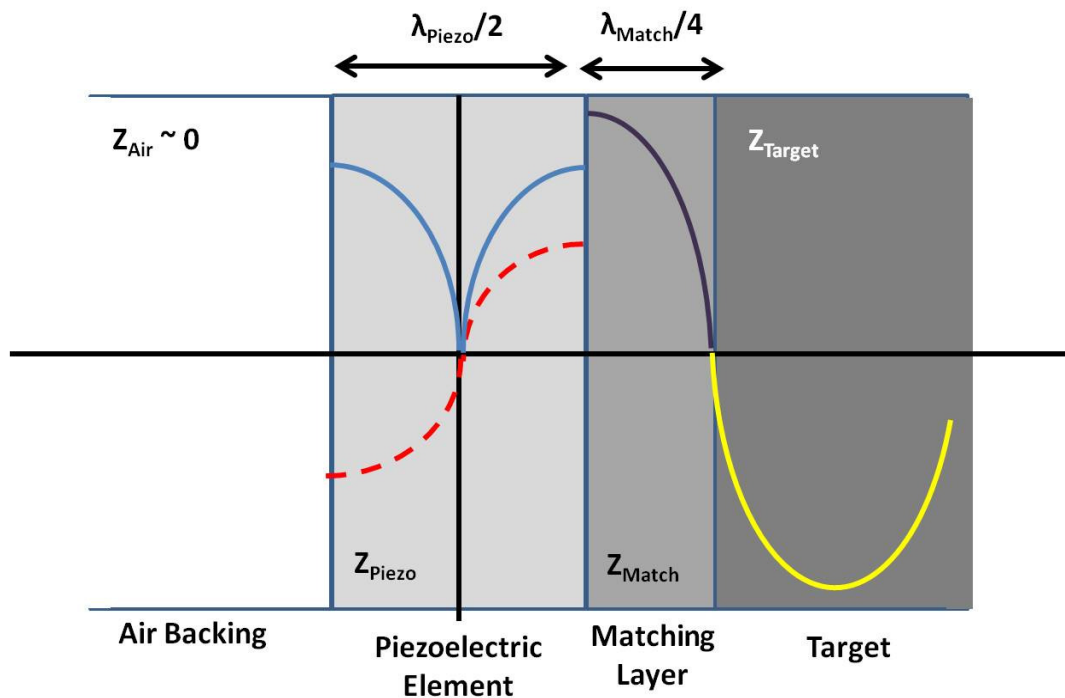


Figure 4.5: Example of wave generation and resonance in a loaded piezoelectric disc. The backing is air, so the backward propagating wave reflects with a 180° phase shift. The piezoelectric element is $\lambda/2$ thick and the matching layer is $\lambda/4$ thick.

In practice, many ultrasonic transducers are excited not by a continuous sinusoidal AC signal, but rather by a very short voltage spike. In this case, a transducer with an air backing (near zero impedance) will ring. It is therefore desirable to place a damping backing layer on the piezoelectric element, in order to absorb the backward traveling wave and reduce ringing. This will yield a short pulse in the time domain, which can be used for pulse-echo NDT. A damping backing will reduce the fraction of total energy traveling in the forward direction, but this usually not a problem.

When the acoustic impedances of the piezoelectric material and the loading medium (target material under test) differ significantly, it is advisable to use a matching layer to enhance forward transmission of acoustic energy. One or more matching layers can be used to form an acoustic gradient which reduces reflections. The matching layer between the piezoelectric disc and the material under test often has a square-root average impedance [Kino 1987].

$$Z_{match} = \sqrt{Z_{piezo} Z_{load}} \quad (4.22)$$

Another parameter of interest is the thickness of the matching layer. A matching layer that is a quarter-wavelength thick is usually used for optimum energy transmission. The complex input impedance between the piezoelectric element and the loading medium, with a thin matching layer in between is given in the following expression [Kino 1987]:

$$Z_{input} = Z_{match} \frac{e^{i\beta L} + R \cdot e^{-i\beta L}}{e^{i\beta L} - R \cdot e^{-i\beta L}} \quad (4.23)$$

Where Z_{input} is the net impedance between the piezoelectric and the loading medium, Z_{match} is the acoustic impedance of the matching material, i is the imaginary number, β is the wave propagation constant, L is the thickness of the piezoelectric and R is the reflection coefficient. This input impedance is minimized when $\beta L = \pi/2$, so $L = \lambda/4$, where λ is the wavelength. Also see Section 4.6.4 for a discussion of wave propagation through layered media.

4.4. Ultrasonic Signal Processing

4.4.1. Review: Membrane Monitoring and Thin Films

One of the most important challenges in this work is determination of the precise time when the echo signals from the membrane indicate the presence of fouling. The initial evidence of scaling, as indicated by the integrated ultrasonic sensors, is referred to as the ultrasonic induction time. The extraction of useful information buried within a raw signal is the basis underlying discrete-time signal processing, which is itself an entire field of study [Oppenheim 1989].

Most of the studies in the literature employing ultrasonic time domain reflectometry (UTDR) for detection of fouling use a configuration similar to that shown in Figure 4.6, which shows the acoustic paths in a flat-sheet cross flow module. The ultrasonic pulse partially reflects off the interface between module housing and the feed solution, and the echo is recorded on an oscilloscope as echo A. The transmitted energy of the acoustic pulse travels to the membrane surface in time, t , reflects and returns to the transducer. The travel time is based on the acoustic velocities of the materials through which it passes, namely, the module housing and the feed solution in the flow channel. In the initial, clean state, an echo will appear on the oscilloscope with a time delay of $2t$ (echo B). When a fouling layer forms, however, the interface is displaced a short distance closer to the transducer, resulting in a return-time shift of the echo to $2t - \Delta t$ (echo C). The amplitude and shape of the reflected signal will also change, because the acoustic impedance, morphology and scattering properties of the scalant differ from the clean membrane. Mairal et al. [Mairal 1999, 2000] were the first to detect the presence of scaling in reverse osmosis desalination by observing this type of time-domain echo shift. It is difficult to truly estimate the thickness of fouling layers, however, because growth patterns and morphologies of fouling layers are often irregular. Biofouling layers consist of hydrogels with dynamic morphology. Scaling layers often grow as scattered clusters.

In this thesis experiments were performed where transducers are mounted in the module so that they are in direct contact with the back-side of the membrane. The motivation behind this type of integration scheme is to reduce acoustic losses and improve signal to noise ratio. Alternative signal processing methodologies must be considered for this configuration because the wavelength of the ultrasonic pulse may be on the order of the membrane thickness. As a very simple example, the longitudinal speed of sound in many common polymers is around about m/s (i.e. polysulfone) [Onda Corp. 2007]. Thus, for a transducer operating at 10 MHz, the wavelength will be: $\lambda = c/f = (2200 \text{ m/s})/(10 \times 10^6 \text{ s}^{-1}) = 0.22 \text{ mm} = 220 \text{ }\mu\text{m}$. Most reverse osmosis or nanofiltration membranes are $\sim 100 - 150 \text{ }\mu\text{m}$ thick.

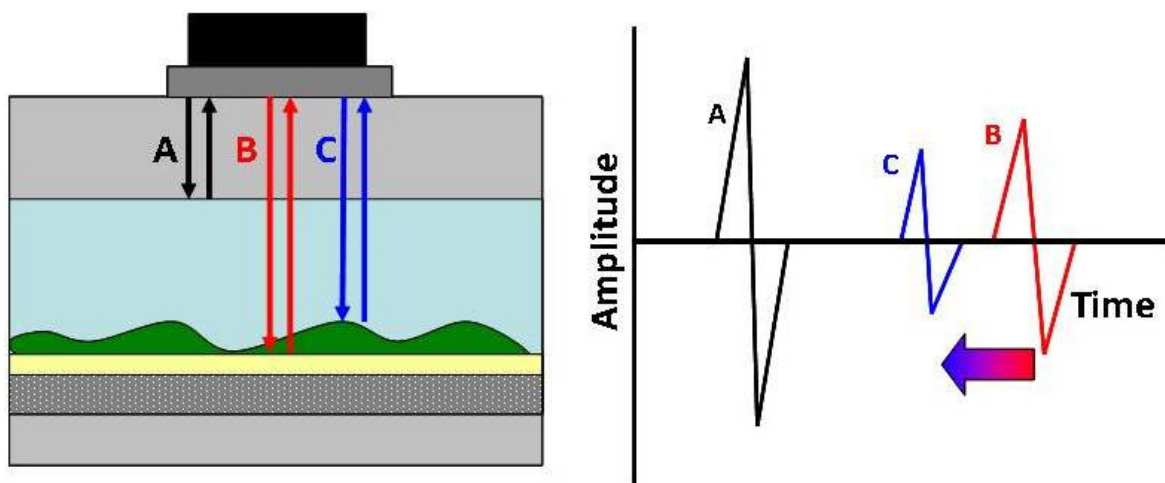


Figure 4.6: Schematic of acoustic paths in monitoring of a flat-sheet cross-flow filtration module with the ultrasonic transducer located above the membrane: echo *A* is the reflection from the solid plate/solution interface; echo *B* is the reflection from the clean membrane/solution interface; echo *C* is the reflection from the fouled membrane/solution interface.

In order to place a transducer in direct contact with a thin membrane, we will need to incorporate a component called a delay line (buffer rod), which consists of a block of material with low acoustic scattering properties that is mounted to the main transducer face. The opposite face of the delay line is then in contact with the sample under test. The delay line delays the return time of echo from the sample, separating the echo of interest from the bang echo, which always occurs off the primary face of the transducer (return time $t = 0$). A reflection from the top of the membrane, which is in contact with the feed solution, would overlap with the reflection from the end of the delay line, which is in contact with the bottom of the membrane. The effect of fouling settling onto the surface of the membrane would be “buried” in the main echo pulse from the end of the delay line by superposition (Figure 4.7). Change in the waveform magnitude and shape may occur because of a change in the reflective properties, but a clear time shift may not be observed. This is the reason why the simple analysis technique shown in Figure 4.6 may not work for this configuration.

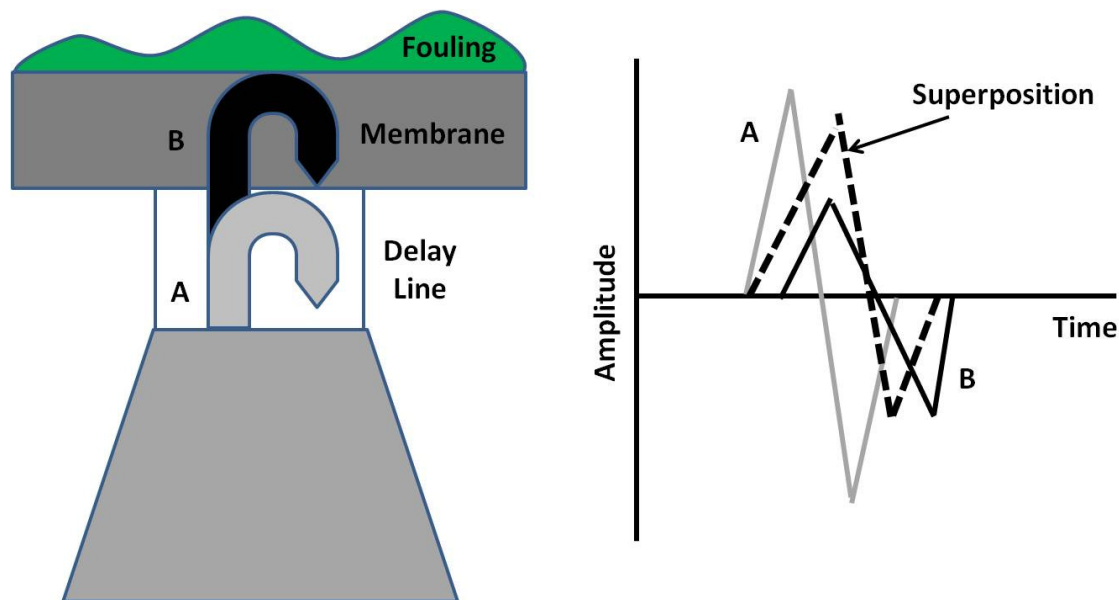


Figure 4.7: Schematic showing acoustic paths for internally integrated transducers used in this work.

A more comprehensive time-domain analysis method was developed by Zhang et al. [Zhang 2003, 2005], in which combined time- and amplitude-shift factors were calculated to determine the onset of scaling during reverse osmosis desalination. This technique was applied to the complex signal reflected from a spiral-wound module. The arrival time and amplitude of the peaks in the echo waveforms were determined at each time the waveform was recorded, and shifts were calculated with comparison to the peaks in a reference signal. Figure 4.8 displays a cross-section of the physical module (left), showing the multiple layers from the windings in a spiral-wound module. The reflected echo pattern is also shown (right). Equation 4.24 is the formula used for calculating the amplitude shift factors and equation 4.25 is the formula for calculating the time shift factors.

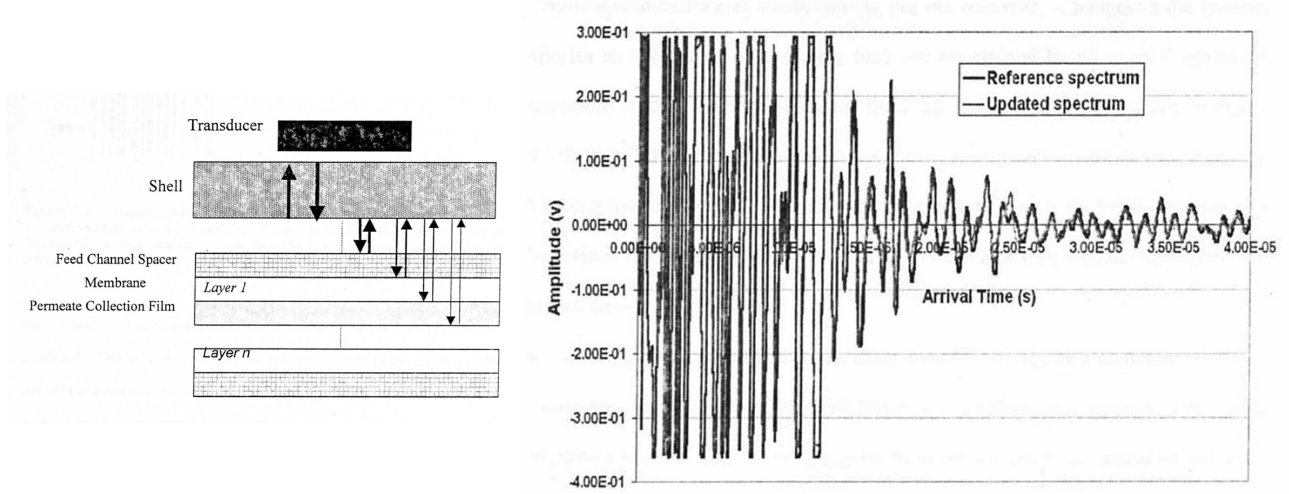


Figure 4.8: Cross-sectional diagram of transducer mounted to spiral-wound module and resulting echo pattern [Zhang 2003, 2005].

$$Q_A = \left[\frac{\sum (V_{iu} - V_{ir})^2}{N} \right]^{1/2} \quad (4.24)$$

$$Q_T = \left[\frac{\sum (T_{iu} - T_{ir})^2}{N} \right]^{1/2} \quad (4.25)$$

Where Q_A is the amplitude-shift factor and Q_T is the time-shift factor. i is a counting variable referring to each peak in the waveform, r refers to the reference spectrum and u refers to the updated, or new, waveform. V is the amplitude of peak i , and T is the time-coordinate of peak i .

The echo waveforms may also be expressed in their frequency domain representations. Kujundzic et al. [Kujundzic 2007, 2008] represented the echoes in terms of total reflected power (TRP) while simultaneously monitoring the permeation flow rate. The arrival time and amplitude of the reflected pulses were recorded and compiled into frequency distributions by Fourier transform methods previously developed and described by Ramaswamy et al. [Ramaswamy 2002, 2004]. The TRP from each acoustic observation was determined by integrating the frequency amplitude spectrum of the reflected sound

waves over the range 0-10 MHz. TRP distributions obtained from fouled membranes were compiled, normalized, and plotted as a function of time. Figure 4.9 demonstrates shifts in the observed TRP values as a function biofoulant mass density [Kujundzic 2008].

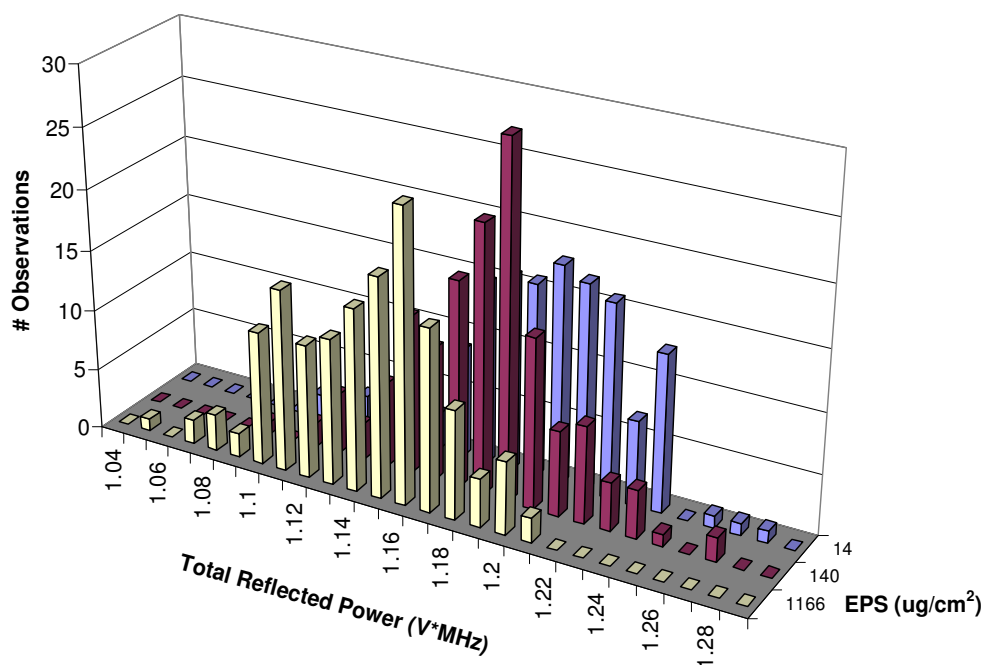


Figure 4.9: Distributions of total reflected power (TRP) showing reflected power reductions in response to increasing biofoulant mass on polyamide membranes [Kujundzic 2008].

Wavelet decomposition techniques have been investigated for non-destructive acoustic characterization of thin films, where the film thickness is of the same order of as the probing acoustic wavelength. The wavelet method has been demonstrated in thickness measurements of thin films using ultrasonic transducers as a means of resolving overlapping echoes from opposite faces of the films [Angrisani 1997]. Wavelets were also used to improve the signal-to-noise ratio of a waveform by processing the different components of the decomposition [Abbate 1997]. The following sections describe the concepts underlying three different signal processing techniques that were explored in this work. These include wavelet decomposition, total reflected power, and a novel technique based on the cross-correlation of waveforms.

4.4.2. Wavelet Decomposition

Wavelet decomposition is similar in concept to a Fourier decomposition; a 1-D signal is separated into a series of higher and lower ‘frequency’ components called ‘details’ and ‘approximations’, respectively. The decompositions are performed using a predefined ‘mother wavelet’ and orthogonal ‘daughter wavelets’ as the bases - as opposed to sines and cosines in a Fourier transform. The decomposition bases are transient wavelet functions having finite value only over a limited window in the time domain, making the method quite useful for analysis of other transient signals [Chui 1992]. The sinusoidal bases in Fourier transforms have finite value over all time. Unlike a Fourier transform, a wavelet analysis can simultaneously provide information in both the time domain and a quasi-frequency domain. A correlation factor between the analyzing wavelets and the signal of interest is calculated at different wavelet scales (stretch) and positions (slide) (Figure 4.10). This results in a surface plot with correlation factors as a function of wavelet scale and position. There are a variety of families of standard basis wavelets, each with a number of orthogonal orders that can be used in decomposing a signal. Examining different decomposition levels using different basis wavelets provides a large variety of ways in which to analyze the signal.

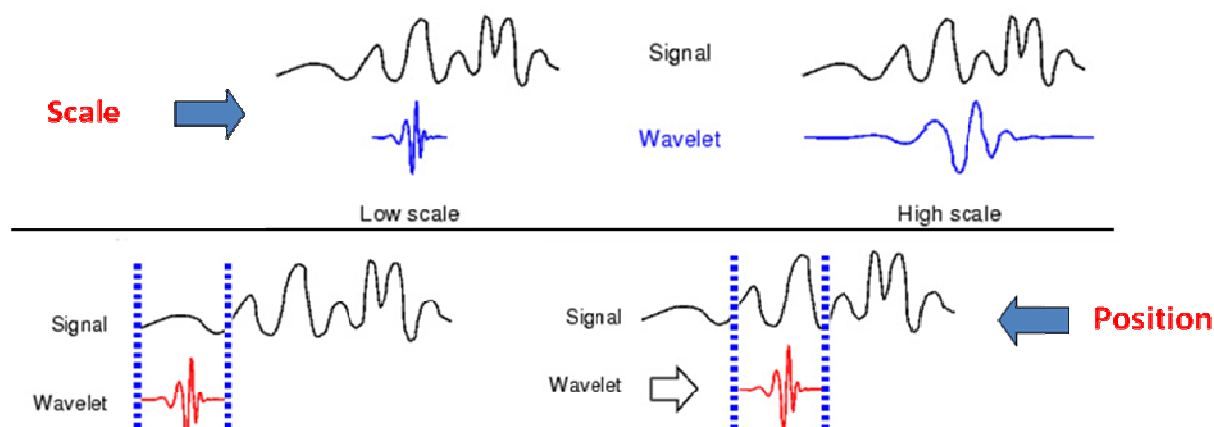


Figure 4.10: Scale and position wavelet decompositions for simultaneous analysis of a signal in the scale and position domains [Mathworks 2007].

Wavelet decomposition is a correlation between the signal and the wavelet basis (equation 4.26):

$$W(a, b) = \int_{-\infty}^{\infty} s(t) \cdot h_{a,b}(t) dt = s(t) \otimes \frac{1}{\sqrt{a}} h * \left(\frac{t}{a} \right) \quad (4.26)$$

Where:

$$h_{a,b}(t) = \frac{1}{\sqrt{a}} h \left(\frac{t-b}{a} \right) \quad (4.27)$$

And a and b refer to the scaling and time-shift factors of the mother wavelet, respectively. Here, W is the wavelet coefficient matrix, s is the time-domain signal and h is the time-domain mother wavelet. The term $a^{-1/2}$ is a normalization constant, similar to the term $(2\pi)^{-1/2}$ seen in the definition of the Fourier Transform.

4.4.3. Total Reflected Power

The power spectrum magnitude is the square of the Fourier transform of the signal, $f(t)$, as expressed in equation 4.28, and displays the contribution of a range of frequency components to the signal. The maximum of this distribution appears at the center resonant frequency of the transducer. The power spectrum is, effectively, an indicator of the overall strength, or *power*, of the signal.

$$P(\omega) = \left| \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \right|^2 \quad (4.28)$$

Echo waveforms from an oscilloscope and computed the power spectrum (frequency vs. power). The area under the power spectrum curve was then calculated. This area was determined by fitting the computed power spectrum points with a shape-preserving cubic spline and integrating (Matlab). The area was then normalized (with respect to a chosen reference value) and plotted versus filtration run-time. The aim was to see trends and relative values of power spectrum area from each transducer, before and after fouling.

4.4.4. Cross-Correlation

We also investigated an analysis technique based on the cross-correlation between waveforms. The cross-correlation is often called the ‘sliding dot product’, and is a common method used in signal processing for finding similarities and differences between signals. Each recorded waveform is a discrete vector of data points, and the discrete cross-correlation between two such vectors is expressed in equation 4.29. This calculation generates the cross-correlation vector, which, if comparing two signals each with N points, becomes a vector of $2N-1$ points.

$$(f * g)[n] = \sum_{m=-\infty}^{\infty} f^*[m] \cdot g[n+m] \quad (4.29)$$

Our signal processing method involved selecting a reference waveform and cross-correlating it with all other waveforms from the same transducer throughout the duration of the filtration run. The root mean square (rms) value of each of these cross-correlation vectors was calculated as a lumped value to account for subtle amplitude and time shifts in all points of waveform. These rms values were then normalized to that of the autocorrelation (cross-correlation of the reference waveform with itself), and plotted versus time. The rms cross-correlation factor was used to quantify changes in the echo over time, before and after fouling.

4.5. Systems Integration

4.5.1. Initial Work: In-House Fabricated Transducers

Initial work focused on the design and fabrication of simple miniaturized ultrasonic transducers using microfabrication facilities on the University of Colorado campus. Prototype plane-wave (flat) ultrasonic transducers were designed and fabricated for preliminary experiments. They were tested stand-alone as well as in a dead-end filtration module. Proof-of-concept data was obtained from these devices, but their use was discontinued because of low yield in the manufacturing process. Results from the in-house fabricated transducers are presented in Section 4.7.1. Work continued with commercial transducers

that proved to be acceptable for internal integration in a flat-sheet cross-flow module. This approach is discussed in the following sections.

4.5.2. Ultrasonic Transducer Integration

Olympus M203-SM delay line ultrasonic transducers with a center frequency of 10 MHz were mounted internally into the bottom plate of the membrane module. Figure 4.11 is a photograph of the transducer model used in this work and Figure 4.12 is a schematic showing how it is mounted into the flat-sheet cross flow module. The delay line on the transducer is also often called a buffer rod, and consists of a cylindrical block of material with low acoustic scattering properties that is mounted to the main transducer face. The opposite face of the delay line is then in contact with the sample under test - in this study, the membrane - hence delaying the return time of echo from the sample. The delay line separates the echo of interest, that from the membrane, from the bang echo which always occurs from the primary face of the transducer (return time $t = 0$). This configuration permits measurement where the transducer is in direct contact with the membrane.

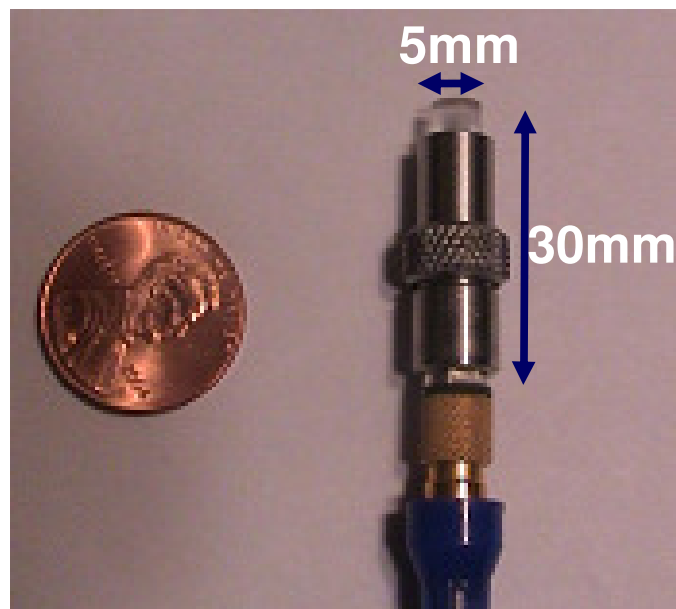


Figure 4.11: Olympus M203-SM delay line ultrasonic transducer with center frequency of 10 MHz.

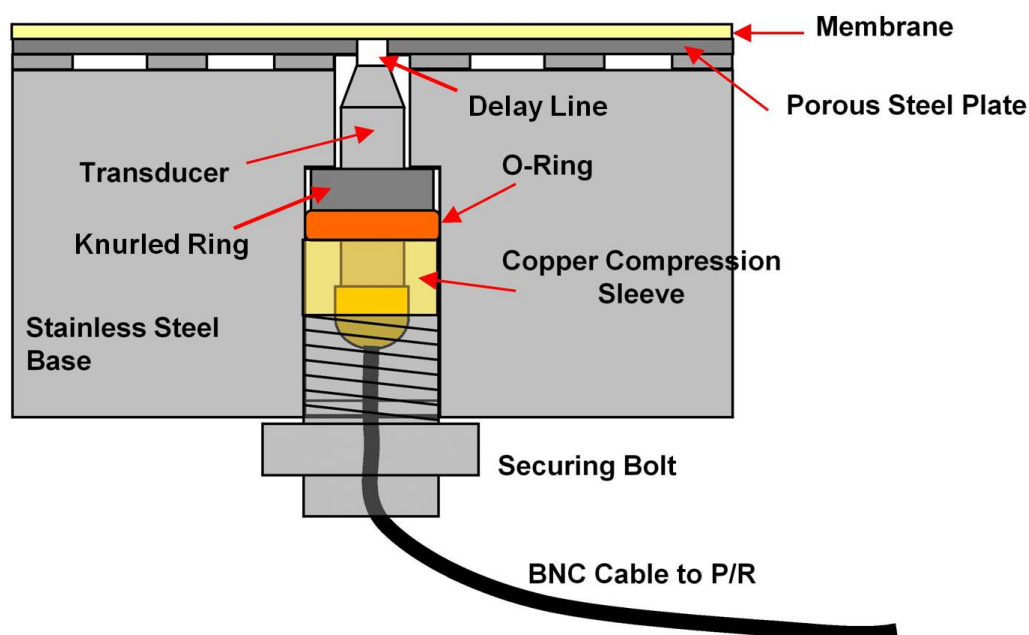


Figure 4.12: Integration of internal ultrasonic sensors into flat-sheet module. A step-change in the diameter of the transducer hole provides a stop against which the knurled ring on the transducer casing rests, ensuring that the delay line is flush with the top of the porous steel support plate.

The flat-sheet cross flow module used for ultrasonic membrane monitoring is the same as that used in experiments with the electrolytic sensors described in Chapter 3 (Section 3.6.1). A hole was drilled through the steel base of the membrane module with a diameter larger than that of the transducer casing. A step-change reduction in the diameter of the hole was located near the top of the base plate to serve as a stop to the transducer. A hole having the same diameter as that of the transducer delay line (5 mm) was machined in the porous steel support plate. The transducer then was inserted into the port in the steel base with the delay line passing through the hole in the porous steel support plate. The top of the delay line was practically flush with the top of the porous steel support plate (slightly above, $\sim 20\ \mu\text{m}$) to ensure good acoustic coupling with the underside of the membrane when the cell was pressurized. This contact with the membrane also ensured that consistent pressure was applied to the transducer face for all experiments, as it was controlled by the known pressure within the flow channel. This factor can be

important for reproducibility of results. An O-ring was placed around the bottom housing of the transducer and rested against a knurled ring. The O-ring was compressed by a copper compression sleeve and a securing bolt to prevent leaking. The BNC signal cable, which connected the transducer and pulser-receiver via a multiplexer, passed through the compression sleeve and securing bolt.

The positioning of the top of the delay line flush with the top of the porous steel support plate and in intimate contact with the underside of the membrane is potentially problematic. The presence of the impermeable surface of the transducer delay line immediately beneath of the membrane can impede or totally block permeation through a small area of the membrane ($\approx 0.20 \text{ cm}^2$). However, the convective mass transfer owing to the cross-flow should establish a concentration profile of the calcium sulfate above this small affected area that can cause precipitation of this sparingly soluble salt much in the same way that it occurs in adjacent unimpeded areas of the membrane. Determining whether the location of the delay line beneath the membrane caused any problems in detecting the fouling was one of the main questions addressed in this study.

Three transducers were mounted internally (M203-SM, Olympus, 10 MHz), at up-, mid- and down-stream locations in the flow channel. Three transducers were mounted externally (V111, Panametrics, 10 MHz) at corresponding locations. The external transducers were mounted to the module housing with consistent pressure by spring-loaded frames installed on the top module plate, and a petroleum jelly couplant was applied to ensure efficient acoustic transmission into the module.

4.5.3. Electronic Control and Data Acquisition

The six ultrasonic transducers were connected to a custom built multiplexer that was interfaced to a pulser-receiver (Panametrics 5072PR). The multiplexer incorporated high-bandwidth signal router modules (PRL-854, Pulse Research Labs), which were necessary to transmit voltage spikes of extremely short length ($\sim 10 \text{ ns}$) generated by the pulser-receiver. A custom LabView program (National Instruments) was used to control the multiplexer and record echo waveforms displayed on an

oscilloscope. Each waveform from each transducer was transmitted from the oscilloscope to a desktop computer via a GPIB cable and GPIB card (National Instruments). The waveforms were recorded as column vectors to a spreadsheet on the computer. After initial experimentation, we decided to use the cross-correlation signal processing protocol described in Section 4.4.4. Real-time signal processing and plotting was performed by a Matlab script, which regularly analyzed the waveform data posted to the spreadsheets. LabView was also used to continuously record permeate and retentate fluxes (S-111 Flo-Meters, McMillan) as well as the module pressure (PX603-550G5V pressure gauge, Omega), which were also plotted by the Matlab script. See Appendix F for the LabView code and Appendix G for the Matlab code. The integrated electronic and hydraulic systems are shown in Figure 4.13.

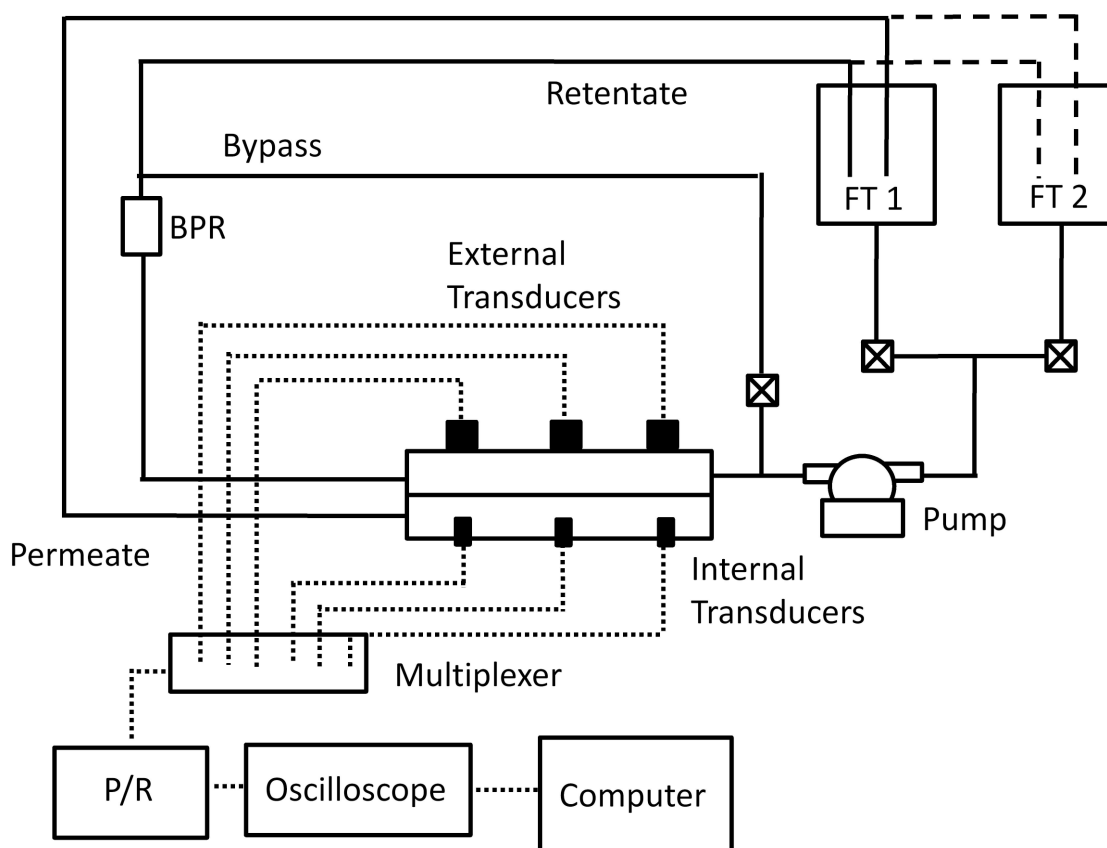


Figure 4.13: Schematic of flow system and electronics for data acquisition. Solid lines are hydraulic paths and short-dash lines are electronic connections. P/R is the pulsar/receiver, BPR is the back-pressure regulator, FT1 and FT2 are feed tanks 1 and 2, the small boxes with 'x' are valves.

4.6. Multiple Integrated Transducers: Experimental Design

4.6.1. Experimental Design and Protocol

A robust factorial-with-replication design was employed in which two feed concentrations and two axial velocities were used as the experimental variables. A combination of real-time UTDR measurements and post-mortem analyses served as the response variables. All experiments were performed at a feed pressure of 0.55 ± 0.013 MPa (80 psi) with NF membranes (NF-90, Dow FilmTec), using calcium sulfate (CaSO_4) as a model inorganic scalant. The concentrations used were 0.47 and 1.19 g/L CaSO_4 and the axial velocities used were 0.9 cm/s ($\text{Re} = 23$) and 8.2 cm/s ($\text{Re} = 188$). Ultrasonic reflectometry and permeate flux comprised the real-time responses and post-mortem measurements included the mass and surface coverage of the scaling deposits.

In each experiment the system was operated for at least 16 hours with deionized water (DI) to allow membrane compaction and steady-state operation. After this period, the feed stream was switched from the DI water tank to the CaSO_4 solution. During each experiment, ultrasonic responses were obtained from each transducer at 10 minute intervals and permeate flux was measured every 2 minutes.

At the conclusion of each experiment, the membrane was removed from the module and allowed to dry. Membrane sample coupons ($2.5 \text{ cm} \times 2.5 \text{ cm}$) were cut from each of the internal transducer locations and weighed on a precision balance to determine the area mass-density of the scale deposited at that location. The location on the membrane sampled by the external transducers was axially offset from the corresponding internal transducer locations by approximately 2.5 cm. Since the total flow-channel length is 55 cm, the sample coupons, centered about the internal transducer location, are quite representative for the external transducers as well. Scanning electron microscopy (SEM) and optical micrographs were taken at each of the locations, both at the exact location of the internal transducers (physical imprint on the membrane, 5 mm diameter), and on the surrounding areas. The SEM and optical micrographs indicated the presence and area coverage (%) of the crystallized scalant on the membrane

surface. In addition, energy-dispersive x-ray spectroscopy (EDS) was performed on selected samples to determine the composition of the scaling layer. The study consisted of two types of experiments, referred to as *extended scaling experiments* and *interval experiments*.

Extended Scaling Experiments

The goal of these experiments was to observe the effect of variable cross-flow velocity on the ultrasonic response of the six transducers under otherwise constant conditions. The cross-flow velocity influences the nature of the concentration polarization boundary layer and thus affects the scaling induction time, i.e., the time between the introduction of the salt solution and the initial occurrence of scaling on the membrane surface. These experiments used 1.19 g/L of CaSO_4 (1.5 g/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with cross flow velocities of 0.9 cm/s ($\text{Re} = 23$) and 8.2 cm/s ($\text{Re} = 188$), and allowed an experiment to continue until significant fouling had occurred on the membrane surface.

Interval Experiments

The purpose of these experiments was to correlate the responses from the ultrasonic transducers with the corresponding membrane surface condition during early-stage scaling. Post-mortem analyses were conducted at up-, mid- and downstream locations and used to correlate acoustic responses with different stages of scaling layer development. These experiments used a constant feed-solution concentration of 0.47 g/L CaSO_4 (0.6 g/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with a cross flow velocity of 0.9 cm/s ($\text{Re} = 23$), and were terminated at pre-determined intervals of 60, 120 and 150 minutes after the switch from DI water to the calcium sulfate feed solution.

4.6.2. Concentration Polarization Model

The design of experiments using the integrated ultrasonic transducers was based on numerical modeling of the concentration polarization profile, just as it was for the electrolytic sensors presented in Chapter 3. The concentration profile is calculated as a function of axial position. Mass-transport properties are numerically calculated at discrete points along the length of the flow channel axis. Initial

conditions at the channel entrance assume no concentration polarization, i.e., the concentration at the membrane surface equals that of the bulk feed. The cross-flow velocity and hence the Reynolds number are then appropriately adjusted over the axial length of the flow channel by subtracting the flux removed by permeation at the previous axial location.

The model calculations were based on the geometry of the flow channel, the flow conditions and the feed concentrations used in the experiments presented in this study. As described in the preceding section, filtration experiments were performed under the following conditions: 1.19 g/L CaSO_4 solution (equivalent to 1.5 g/L of powdered $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in water) at cross-flow velocities of 0.9 cm/s ($\text{Re} = 23$) and 8.2 cm/s ($\text{Re} = 188$), as well as 0.47 g/L CaSO_4 solution (0.6 g/L dissolved $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at a cross-flow velocity of 0.9 cm/s ($\text{Re} = 23$). Model predictions for the membrane-surface supersaturation ratio ($SR = C_{\text{wall}}/C_{\text{sat}}$) as a function of axial position are presented in Figure 4.14 (a). The expected permeate flux is also displayed as a function of axial position (Figure 4.14 (b)). The utility of the model was verified by comparison with experimental permeate flow rates - the average rate over the entire permeable area. The computed flux rate, when averaged over the permeable area, matched the experimental rate within 10%. The predictions, which reflect steady state conditions before the onset of fouling, indicate SR profiles in which supersaturated concentration levels are present under each set of experiment parameters. These profiles were needed in the experiment design to ensure that membrane scaling developed over a relatively short time period over much of the membrane. The highest concentration levels, and thus the shortest fouling induction times, are found at the downstream end.

3.6.3. Ultrasonic Signal Processing and Interpretation

This study significantly extends the acoustic signature methodology advanced by Zhang et al. [Zhang 2003, 2005] to provide a sensitive indicator of scaling layer formation. Zhang et al. utilized only select points from waveform peaks for their acoustic signature analysis. The procedure employed in this study involves cross-correlation of the entire acoustic waveform with a reference waveform. The mathematical development of this method was described in Section 4.4.4. The reference waveform is

from a clean membrane, immediately before the switch from deionized water feed to calcium sulfate solution. This procedure is used to obtain a similarity value for the waveforms, to track how they change over time with exposure to the calcium sulfate solution. The signal processing technique accounts for changes in waveform shape over the entire time domain signal, not just a few select points. The cross-correlation similarity values were computed and plotted at regular intervals during the experiment. This time-domain approach was used, in contrast to the simple time-shift method [Mairal 1999], because of geometric concerns for the internally integrated transducers (Figure 4.7). A representative baseline ultrasonic response value is selected shortly before the switch from DI water to CaSO_4 feed; the onset of scaling is then determined when the ultrasonic similarity value passes outside of a 'breakout threshold' that is chosen to minimize the occurrence of false-positive responses.

The ultimate goal of utilizing ultrasonic reflectometry is to determine the onset of scaling before any measureable decrease in the permeate flux occurs. Figure 4.15 shows the idealized relationship between the ultrasonic signals and permeate flux values during an experiment. Immediately after a switch from DI water to a salt solution, the flux decreases due to osmotic effects and then remains relatively constant until sufficient scaling has developed. The flux then decreases further due to membrane surface blockage.

The time between the switch from DI water to the salt feed, and the decrease in permeate flux due to membrane fouling is referred to as the permeate induction time (Δt_p). Similarly, the ultrasonic induction time is defined as the time between the switch to salt feed and a change in the UR signal owing to membrane fouling (Δt_u). Because the ultrasonic transducers provide a point response, the ultrasonic induction time should be less than the permeate induction time, particularly at the downstream location. The permeate induction time is based on a measurement averaged over the entire membrane area.

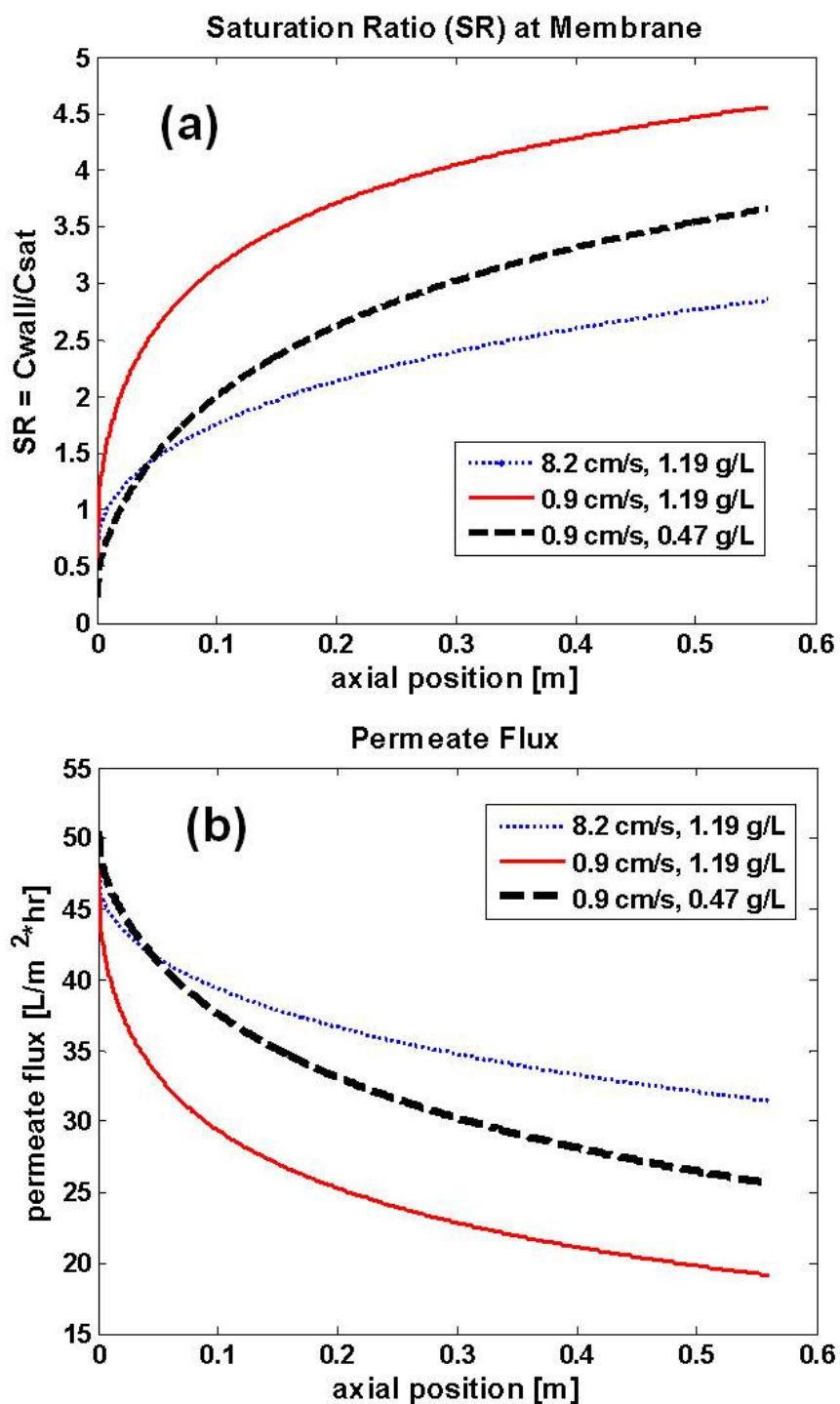


Figure 4.14: (a) Numerical modeling predictions for membrane supersaturation ratio (SR) and (b) permeate flux at the membrane surface as a function of axial position in flow channel. Values are based on the film-theory transport model with complete solute rejection of $CaSO_4$ for the flow channel geometry used in this study.

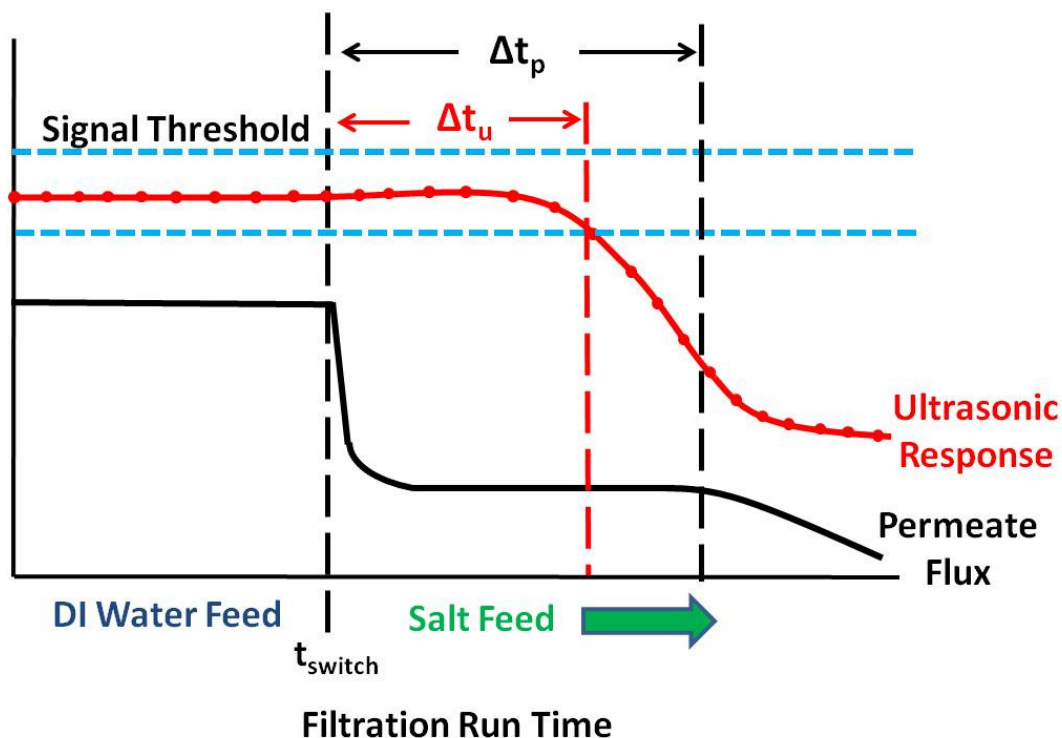


Figure 4.15: Idealized cross-correlation acoustic response values and permeate flux profile. Δt_u is the ultrasonic induction time, where the transducer detects scaling. Δt_p is the permeate induction time, where the total module flux observably decreases due to scaling. Note that the idealized ultrasonic response deviates from the baseline before the observable flux decrease.

4.6.4. Model of Acoustic Reflection from Layered Media

In this section we consider a mathematical treatment of the acoustic reflection from a stack of thin layers. This configuration roughly corresponds with the situation encountered in the current work. We are interested in the reflection coefficient from the membrane surface, either in the geometry encountered using externally mounted transducers (Figure 4.6) or that using internally mounted transducers (Figure 4.12). For the externally mounted transducers, the stack thus consists of the water in the flow channel (considered to be the top semi-infinite layer in the model), the membrane, the porous steel support plate under the membrane, the permeate flow channel under the plate, the bottom wall of the module, and the air beneath. For the internally mounted transducers, which are in contact with the back side of the membrane, we are interested in the stack consisting of the membrane, the water in the flow channel, the

top plate of the module, and the air above. The purpose of this model is to compare the reflection coefficients from the surface of interest at normal incidence, for the case of a varying membrane thickness. This accounts for the possibility that slight variations in membrane thickness may occur due to compression from changing osmotic pressure under varying salt concentrations in the feed.

We follow the analytical model for calculating the reflection coefficient from a stack of layered media presented by Brekhovskikh [Brekhovskikh 1980]. The simplest configuration is that of a thin layer between two arbitrary semi-infinite media (Figure 4.16). First, we consider the general input impedance of the layer as a whole. The total reflection coefficient is given by:

$$R = \frac{Z_{in} - Z_3}{Z_{in} + Z_3} \quad (4.30)$$

Where Z_{in} is the equivalent combined acoustic impedance of the thin layer (medium 2) and the underlying layer (medium 1) and Z_3 is the impedance of the medium above the thin layer where the incident wave propagates (medium 3). We now determine the input impedance through the thin layer, Z_{in} , which is given in equation 4.31.

$$Z_{in} = \left[\frac{Z_1 - iZ_2 \tan(k_2 d)}{Z_2 - iZ_1 \tan(k_2 d)} \right] Z_2 \quad (4.31)$$

Here Z_1 is the acoustic impedance of the bottom layer, Z_2 is the acoustic impedance of the thin layer, k_2 is the wavenumber of the acoustic wave in the thin layer ($k_2 = \omega/c_2$), and d is the thickness of the thin layer. The imaginary component in this equation occurs to account for phase of the acoustic wave in the thin medium. Substituting equation 4.31 into equation 4.30 gives the following relation for the reflection coefficient from the layer:

$$R_{ThinLayer} = \frac{(Z_1 + Z_2)(Z_2 - Z_3)\exp(-ik_{2z}d) + (Z_1 - Z_2)(Z_2 + Z_3)\exp(ik_{2z}d)}{(Z_1 + Z_2)(Z_2 + Z_3)\exp(-ik_{2z}d) + (Z_1 - Z_2)(Z_2 - Z_3)\exp(ik_{2z}d)} \quad (4.32)$$

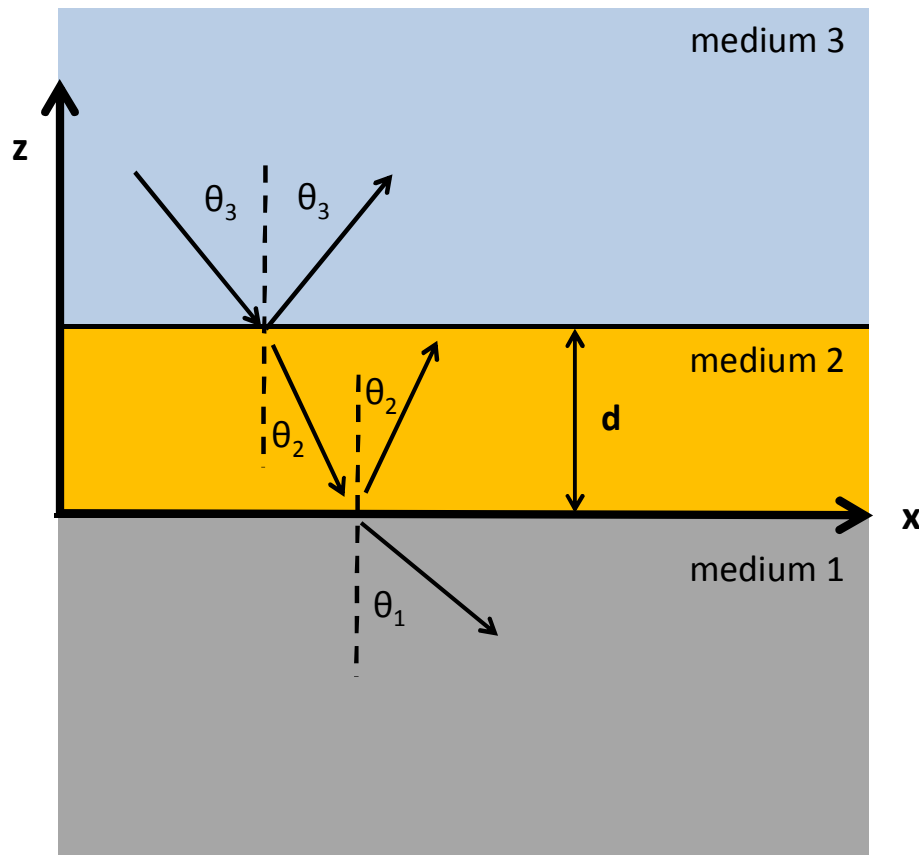


Figure 4.16: Schematic of acoustic paths across a thin layer between semi-infinite media. Following [Brekhovskikh 1980].

The concepts demonstrated for the single thin layer can then be applied to a stack of thin layers “sandwiched” between two semi-infinite media (Figure 4.17). Here it is assumed that there are $n-1$ layers between semi-infinite media. In the case with the single thin layer, we merely determine the input impedance of the thin layer plus the semi-infinite medium below in calculating the overall reflection coefficient. Now we need to find the input impedance of the entire stack. This can be done by recursively solving for the input impedance starting at the bottom, using the form of equation 4.32. This was done computationally to model the particular layers in the membrane filtration system discussed here.

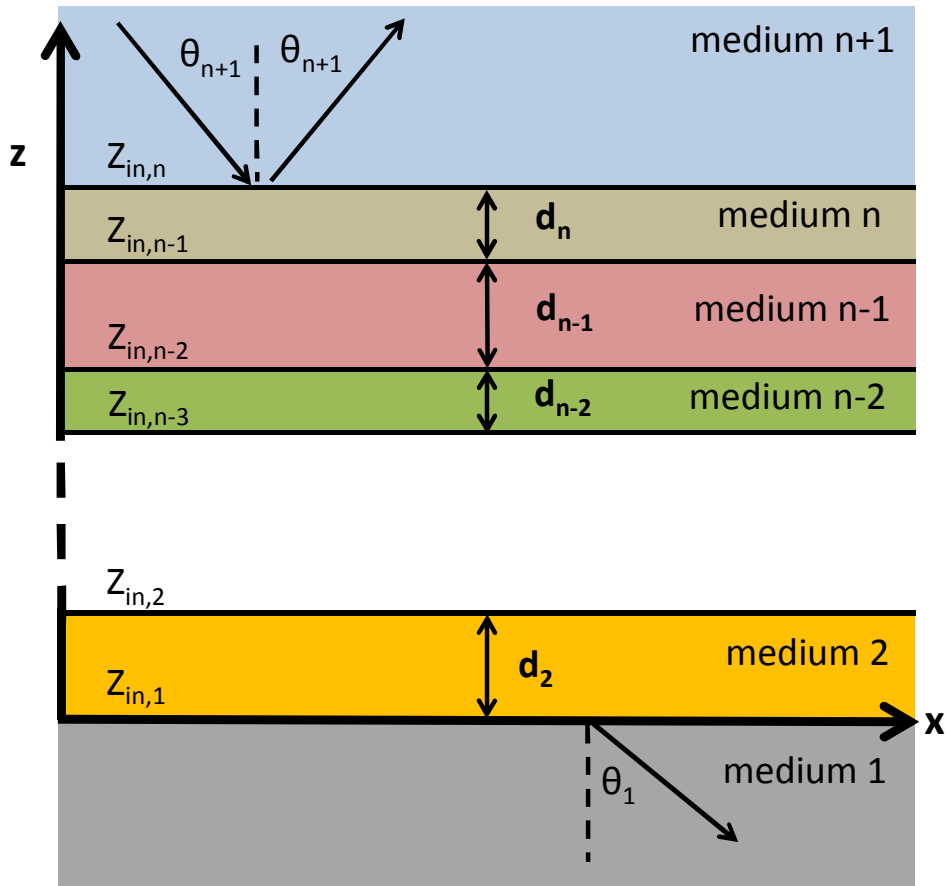


Figure 4.17: Schematic of acoustic paths across a stack of thin layer between semi-infinite media, including conventions for input impedances. Following [Brekhovskikh 1980].

This model was utilized for computations for the stacks described at the beginning of this section, for each of the transducer types.

Table 4.2 lists the input parameters used for the external transducer stack, and Table 4.3 lists the input parameters for the internal transducer stack. The input parameters for the porous layers (polymer membrane and steel support plate) were calculated as a weighted average of the bulk material and water, based on the porosity. Polysulfone was selected as the representative polymer for the membrane and transducer delay line.

Table 4.2: Table of input parameters for analytical multi-layer reflection model using external transducers [OndaCorp. 2007]. Porous parameters are weighted averages and the polymer is polysulfone.

	Material	Porosity	density [kg/m ³]	Acoustic Velocity [m/s]	Layer Thickness [mm]
Layer 1	Air	N/A	1.2	344	semi-inf.
Layer 2	Steel	N/A	7890	5790	20
Layer 3	Water	N/A	1000	1480	2
Layer 4	Porous Steel	0.3	5823	4497	2
Layer 5	Porous Polymer	0.3	1168	2012	0.11 - 0.13
Layer 6	Water	N/A	1000	1480	semi-inf.

Table 4.3: Table of input parameters for analytical multi-layer reflection model for internal transducers [OndaCorp. 2007]. Porous parameters are weighted averages and the polymer is polysulfone.

	Material	Porosity	density [kg/m ³]	Acoustic Velocity [m/s]	Layer Thickness [mm]
Layer 1	Air	N/A	1.2	344	semi-inf.
Layer 2	Steel	N/A	7890	5790	20
Layer 3	Water	N/A	1000	1480	2
Layer 4	Porous Polymer	0.3	1168	2012	0.11 - 0.13
Layer 5	Polymer	N/A	1240	2240	semi-inf.

Figure 4.18 shows that the maximum change in reflection coefficient for a 20 μm range of membrane thickness is 0.09. This analysis is highly idealized since the layers are assumed to be ideal isotropic materials with constant properties. In reality, scattering and energy loss would play an important role. This model, therefore, places an upper bound on variation of the reflection coefficient that could possibly be detected by the experimental system.

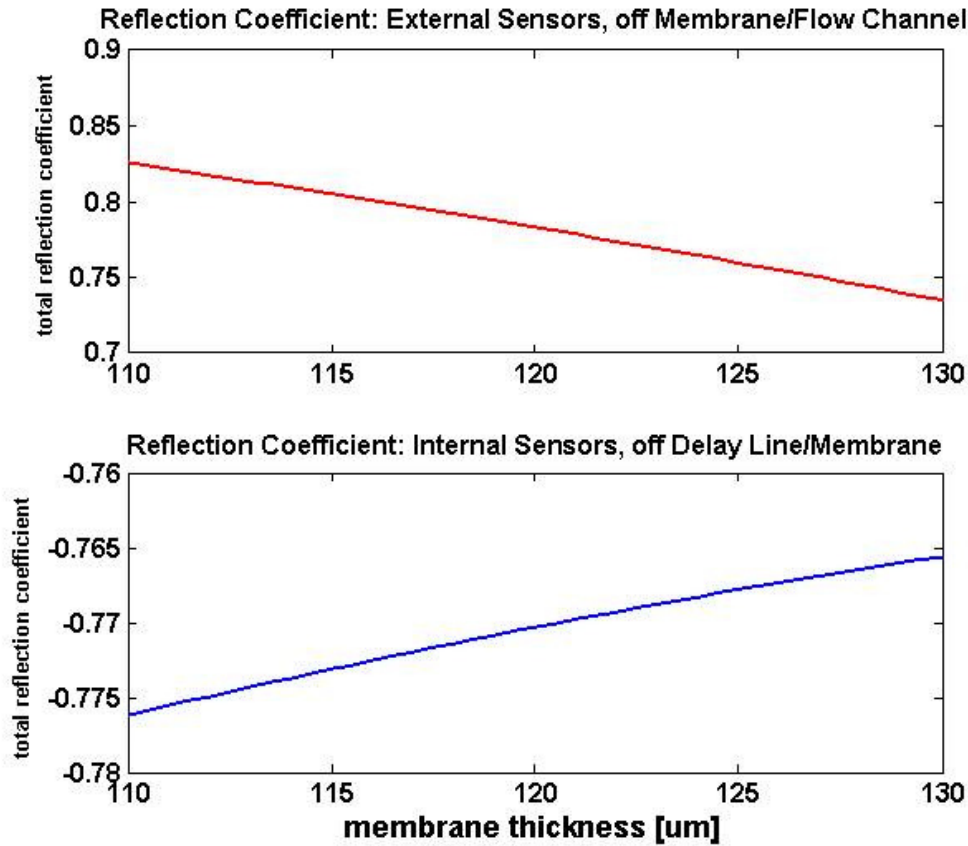


Figure 4.18: Plot showing reflection coefficients from membrane for variable membrane thickness. Top, external sensor stack. Bottom, internal sensor stack.

The reflection model accounts only for the magnitude of the reflection coefficient and therefore of the reflected acoustic wave or pulse. It does not assume any distortion in the shape of the wave or pulse. The cross-correlation signal processing protocol presented in Section 4.4.4 was used in this work to analyze the waveforms reflected from the membrane surface. A reference echo waveform was selected and then all other waveforms were compared with that by means of the cross-correlation. The cross-correlation vectors are then calculated, and the rms-value of this vector is taken as the bulk similarity metric between the two waveforms. These are all referenced to the rms-value of the auto-correlation as a means of detecting significant differences between waveforms recorded from the same transducer at different times.

An example is given below to show the effect of the signal processing protocol on the cross-correlation between waveforms, which differ only in their magnitudes such that there is no distortion. An example waveform was selected from one of the data sets generated in this thesis. It was multiplied by 1.25 and 1.5, far greater than the maximum variation in reflection coefficient shown in Figure 4.18. The three waveforms were then analyzed by the cross-correlation program in Matlab. Figure 4.19 shows the waveforms (a) and the point-wise difference between the cross-correlation vectors and the autocorrelation vector.

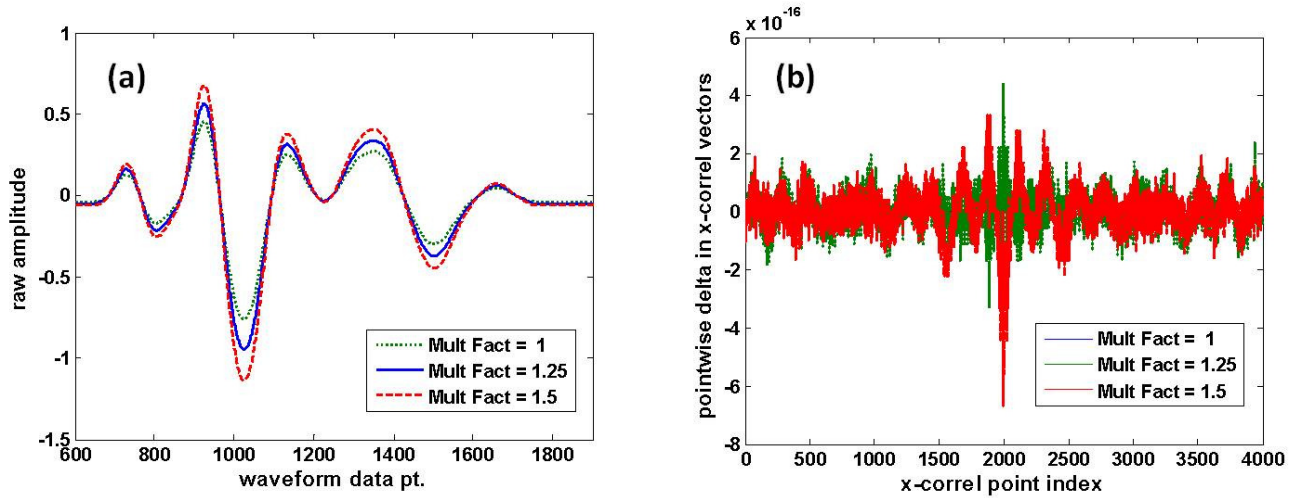


Figure 4.19: (a) Example waveform multiplied by 1.25 and 1.5. (b) Plots of difference between autocorrelation and cross-correlation vectors.

This simple test of the Matlab algorithm shows that the difference in the cross-correlation vectors is effectively zero. The data shown in Figure 4.19 (b) is practically at the machine precision limit. This shows that the changes in rms cross correlation factors obtained in the experiments are due to real changes in the shapes of the recorded waveforms, but not their magnitude.

4.7. Results and Discussion

4.7.1. Fabrication and Test of Miniature Ultrasonic Transducers

Initial work focused on the design and fabrication of simple miniaturized ultrasonic transducers using microfabrication facilities on the University of Colorado campus. A prototype plane-wave (flat) ultrasonic transducer was designed and fabricated for preliminary testing to detect scaling layers. The piezoelectric element of this transducer operated in the thickness-mode, and could be mounted into the support plate of a prototype dead-end filtration module. This placement put it in direct contact with the membrane from the back side.

The transducers that we designed and built consisted of a thin piezoelectric disc (PZT 5A - lead zirconium titanate, Piezo Systems Inc.) which served as the active element. The element had a 30 nm coating of nickel on each flat surface. When excited with a voltage spike (duration of a few nanoseconds) from a pulser-receiver (Model 5072PR, Panametrics), the disc expands and contracts in the thickness mode. The devices included a tungsten-filled epoxy acoustic matching layer between the piezoelectric disc and a Pyrex rod, which serves as an acoustic transmission delay line.

The fabrication process for the transducers is given below (See Appendix H for a fabrication flow diagram):

1. Spin-coat SU-8 photoresist epoxy (Microchem) on a Pyrex wafer and process by photolithography to form an array of standoff ring structures. These rings serve as reservoirs/spacers for the acoustic matching layer between the PZT disc and Pyrex delay line.
2. Dice the standoff structures from the wafer by dicing saw (to produce square Pyrex die) or by coring tool (to produce Pyrex discs).
3. Coat the Pyrex die with a thin layer of gold by sputtering or thermal evaporation. This provides an electrical ground for the downward facing electrode of the piezoelectric disc when it is mounted.
4. Attach a thin wire to the downward facing electrode of the piezoelectric disc with conductive epoxy. This will provide electrical contact between this electrode and ground.
5. Deposit tungsten-filled epoxy for acoustic matching into the standoff ring reservoir with pneumatic epoxy dispensing system or by hand.
6. Carefully mount piezoelectric disc onto epoxy filled standoff ring structure using a flip-chip bonder. Allow epoxy to cure at room temperature.

7. Ground the front electrode of the piezoelectric disc to the gold-coated Pyrex rod by epoxying the wire to the die with conducting epoxy. Attach another wire to the back electrode. This electrode will receive the actuation signal from the pulser-receiver.
8. Lower a steel housing tube over piezoelectric disc and bond it to the Pyrex die with epoxy. Back-fill the housing tube with tungsten-filled epoxy to damp the piezoelectric disc in order to reduce time domain ringing.

A small number of prototype devices were successfully fabricated and tests were performed to demonstrate basic functionality. Figure 4.20 shows one of the prototype devices alongside a Panametrics V111 transducer, which is typical of transducers used in the literature to monitor membrane fouling.

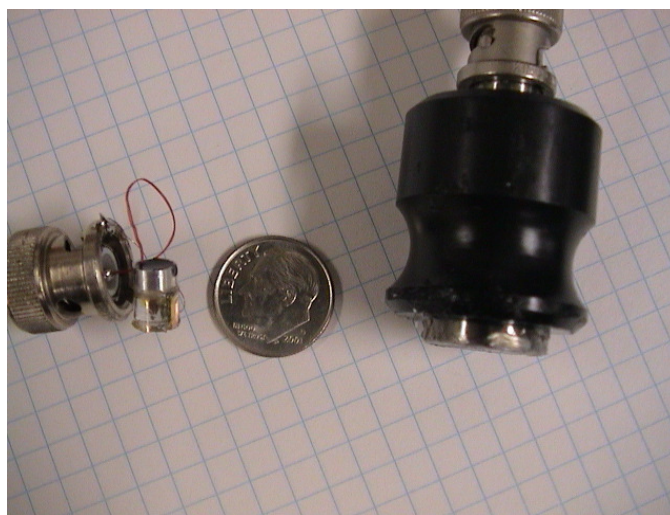


Figure 4.20: In-house fabricated ultrasonic transducer (left) attached to BNC cable for initial testing. Panametrics V111 ultrasonic transducer (right) representative of those used in previous studies for monitoring of membrane fouling.

Figure 4.21 shows the bang signal from two transducers; one with air backing on the piezoelectric element and the other with a tungsten-filled epoxy backing. The figure demonstrates that the epoxy backing significantly reduces the ring-down time of the transducer, as expected. This allows for shorter pulses in the time-domain, which yield greater spatial resolution. According to these waveform data, the center frequency of the devices is 14 MHz.

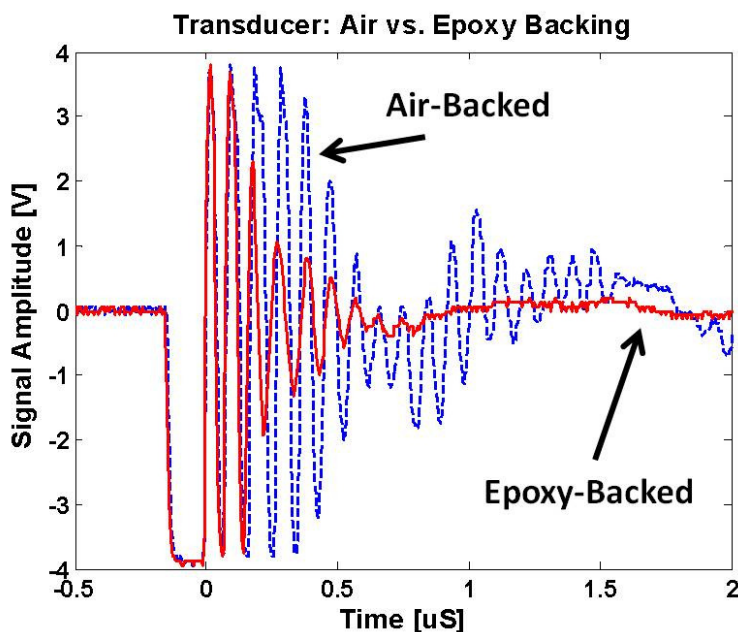


Figure 4.21: Bang signal from in-house fabricated transducer demonstrating improvement in ring-down time by using a tungsten-filled epoxy backing on the piezoelectric element.

Figure 4.22 shows the signal demonstrating echoes from the end of the Pyrex delay line. The arrival time correctly matched that expected based on calculations using the speed of sound in Pyrex. The sensor also showed secondary and even tertiary echoes from the end of the delay line, which also occur at the correct times. A microscope slide was then applied to the end of the delay line, and the ultrasonic signals were compared (Figure 4.23). Primary and secondary echoes are observed from the surface of the microscope slide.

A further test showed that the transducer, internally mounted in a dead-end pressure cell (Amicon), was sensitive enough to detect changes of pressure in the cell, as well as the settling of a relatively thick layer (~ 1 mm) of calcium sulfate on a nanofiltration membrane surface. Figure 4.24 is photograph of the pressure cell with the transducer installed. Table 4.4 provides normalized total reflected power responses (TRP, Section 4.4.3) with and without settled calcium sulfate at two different pressures. One test was performed at 103 kPa (15 psi) and three separate tests were performed at 206 kPa (30 psi). The same transducer was used in all tests.

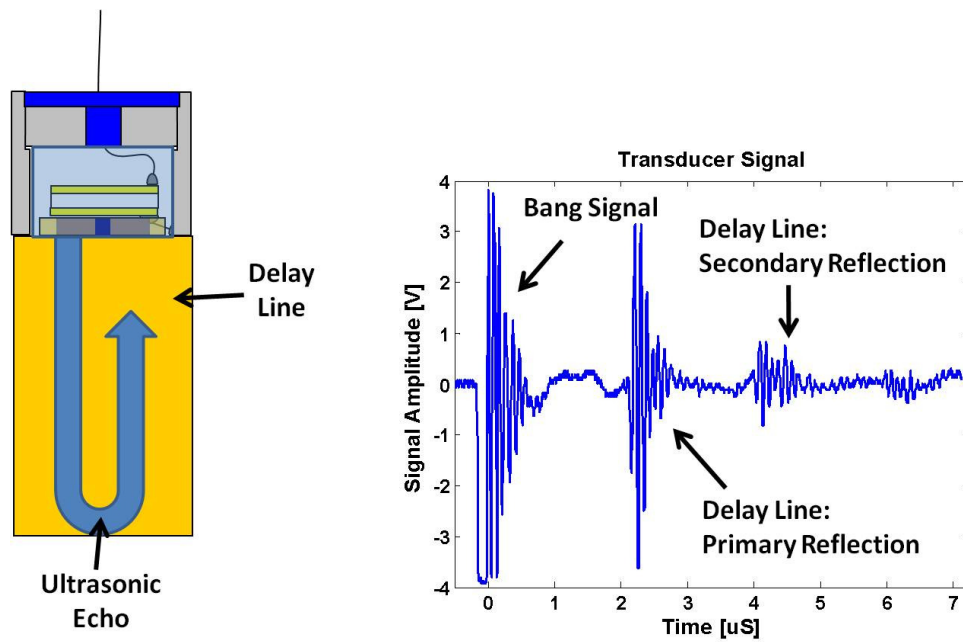


Figure 4.22: Signal from in-house fabricated transducer demonstrating primary and secondary echoes from the end of the delay line.

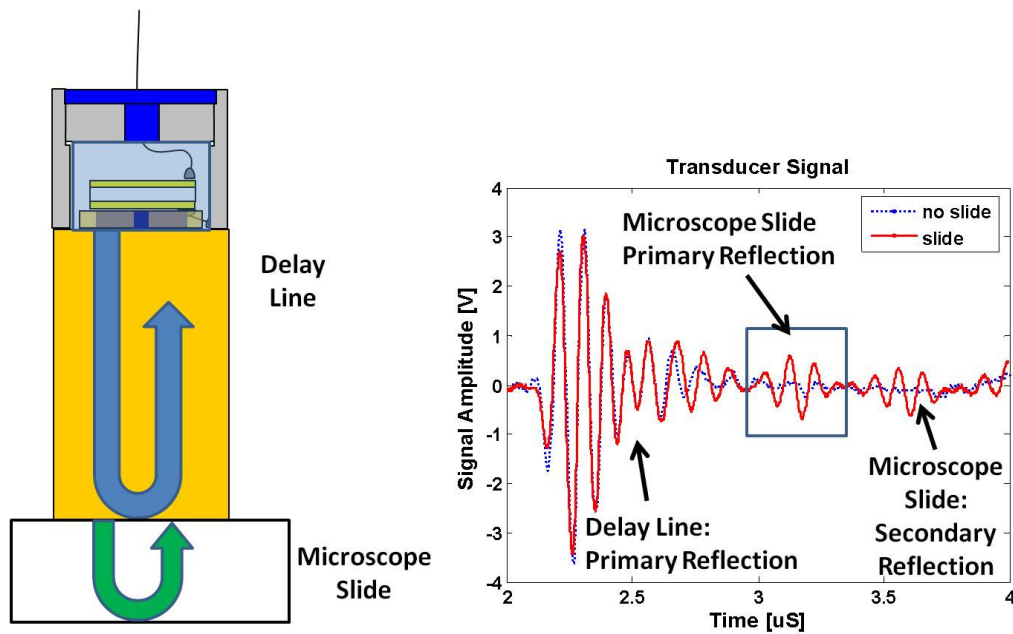


Figure 4.23: Signal from in-house fabricated transducer demonstrating echoes from the end of the delay line and coupled glass microscope slide.

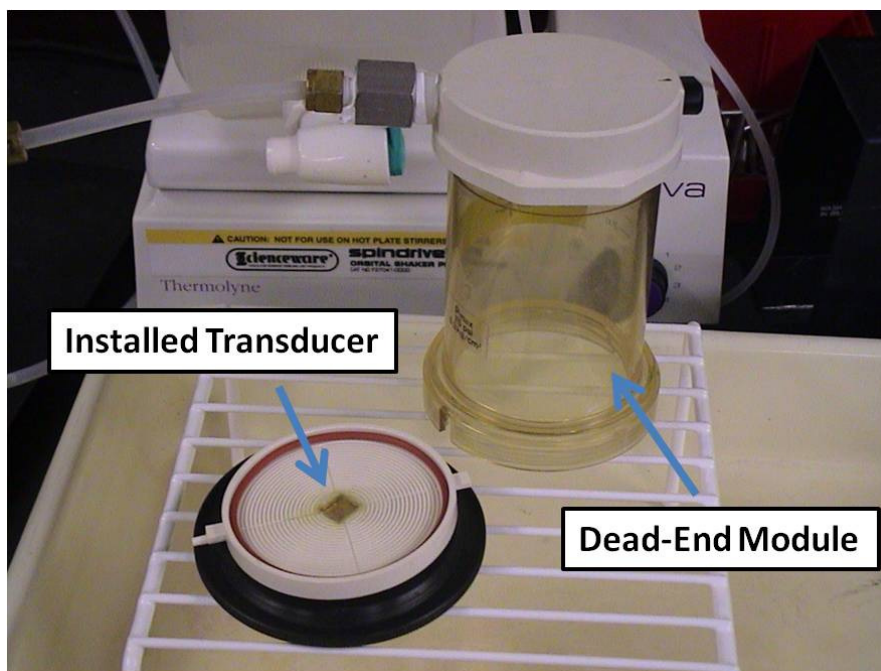


Figure 4.24: Dead-end filtration cell with in-house fabricated transducer installed.

Table 4.4: Normalized total reflected power (TRP) responses from integrated transducer with and without settled CaSO_4 under variable pressure.

	DI Water	Settled CaSO_4
103 kPa (15 psi)	1	0.87
206 kPa (30 psi)	1 ± 0.03	0.79 ± 0.06

The power responses show a clear decrease when the settled calcium sulfate layer is present. This may be due to absorption and/or dissipation of acoustic energy within the calcium sulfate slurry. Further testing with the in-house fabricated ultrasonic transducers was discontinued because of low yield in the fabrication process. These devices were replaced with a commercial transducer (Olympus M203-SM) for use in a flat-sheet cross flow module.

4.7.2. Analysis of Ultrasonic Signal Threshold

In the experiments reported here, the cross-correlation signal processing methodology was deemed best for determining the onset of scaling after switching from DI water feed to calcium sulfate

feed. The size of the ultrasonic response threshold window is the key parameter that determines whether the operator is to be notified that scaling has occurred and remediation measures should be carried out. (Figure 4.15). If the threshold window is too small, the signal noise will incorrectly indicate scaling. If the window is too large, ultrasonic responses due to true scaling will be ignored.

Post-mortem analysis of scaling area coverage on the membrane coupons was used as the verification metric in this work. Each post-mortem analysis corresponded to the area sampled by a particular transducer (internal as well as external) from a particular experiment. Observed area coverage greater than 0% was taken to be a positive indicator of scaling. The circular imprint left by the internal transducer on the membrane was visually analyzed and compared with the ultrasonic response from the respective internal transducer. The representative surrounding area on the coupon was visually analyzed and compared with the ultrasonic response from the respective external transducer. The cross-correlation ultrasonic responses from each of the transducers for a given experiment were then analyzed to determine positive or negative signal response under the following threshold values: 0.1%, 0.2%, 0.3%, 0.4% and 0.5% of the reference pre-switch value. The ultrasonic indicator is defined to be positive if a single point breaks the given threshold.

There are four possible response metrics: positive-ultrasonic/positive-coverage (+/+), negative-ultrasonic/negative-coverage (-/-), negative-ultrasonic/positive-coverage (-/+, false-negative), and positive-ultrasonic/negative-coverage (+/-, false-positive). The first two cases indicate that in the given experiment, the transducer correctly indicated the physical result. The false-negative (-/+) case must be considered more carefully. It is reasonable to assume that a very small amount of scaling might not be detected by the transducer since all physical sensors have sensitivity limits. Another consideration is that the limited sampling area of the sensors may not detect scaling present in the immediate vicinity. The estimated spot size diameters for the internal and external sensors are 5 mm and 3 mm, respectively; therefore, they each effectively provide point measurements. Since the scaling does not grow as a uniform film, but rather as discrete rosette clusters, the sensor may be sampling an area of clean membrane, even

if there are clusters in the vicinity. This condition could result in a negative acoustic response if the sampling area did not reflect surrounding area scaling.

In this work, 14 separate filtration experiments were completed (6 of the *extended scaling* type and 8 of the *interval* type). Each experiment employed 3 internal transducers and 3 external transducers. This yields 3 distinct data sets from internal transducers and 3 distinct data sets from external transducers, for every experiment performed. The 14 separate experiments yield a total of 42 data sets for each transducer type. The ultrasonic response from each data set was correlated against the corresponding area coverage values (%) from the appropriate membrane coupon, and the comparison results were used as a basis for selecting an appropriate signal threshold window. Table 4.5 presents the results for the internal sensors, and Table 4.6 presents the results for the external sensors:

Table 4.5: Ultrasonic signal threshold level and (ultrasonic/coverage) response counts for all internal transducer data sets (42 total); ultrasonic response is + if a single datum passes the threshold, and coverage is + if greater than 0% area is scaled.

Threshold	Count (+/+)	Count (-/-)	Count (+/-) "false positive"	Count (-/+) "false negative"	Sum(+/, -/-) "Success Rate"
0.10%	23/42	6/42	12/42	1/42	29/42 = 69%
0.20%	18/42	15/42	3/42	6/42	33/42 = 79%
0.30%	16/42	15/42	3/42	8/42	31/42 = 74%
0.40%	16/42	17/42	1/42	8/42	33/42 = 79%
0.50%	15/42	18/42	0/42	9/42	33/42 = 79%

Table 4.6: Ultrasonic signal threshold level and (ultrasonic/coverage) response counts for all external transducer data sets (42 total); ultrasonic response is + if a single datum passes the threshold, and coverage is + if greater than 0% area is scaled.

Threshold	Count (+/+)	Count (-/-)	Count (+/-)	Count (-/+)	Sum(+/, -/-)
0.10%	21/42	11/42	6/42	4/42	32/42 = 76%
0.20%	17/42	14/42	3/42	8/42	31/42 = 74%
0.30%	15/42	15/42	2/42	10/42	30/42 = 71%
0.40%	15/42	16/42	1/42	10/42	31/42 = 74%
0.50%	15/42	16/42	1/42	10/42	31/42 = 74%

Table 4.5 and Table 4.6 indicate that there is not a large difference in the total sum of “successful” responses, i.e. (+/+) and (-/-), as the threshold changes. The percent of (+/+) and (-/-) readings is over 69% for both transducer types at all thresholds. We now need to examine the cases where the ultrasonic response did not match the observed post-mortem scaling, starting with the false-negative (-/+) case. Here, an acoustic response outside the threshold was not recorded, but scaling area coverage of greater than 0% was observed. Table 4.7 and Table 4.8 summarize the instances where the area coverage values were either below or above 5% for the internal and external transducer locations, respectively.

Table 4.7: Counts of instances for internal sensors where undetected scaling area coverage (AC) (-/+ case) was either above or below 5%. Means and standard deviations are calculated for instances where scaling was below 5% coverage. Undetected instances greater than 5% coverage are considered outliers.

Threshold	Count Areas > 5%	Count Areas < 5%	Mean Area [%] (<5% AC)
0.10%	0/42	1/42	1.7
0.20%	0/42	6/42	1.7 ± 0.6
0.30%	1/42	7/42	1.5 ± 0.6
0.40%	1/42	7/42	1.5 ± 0.6
0.50%	2/42	7/42	1.5 ± 0.6

Table 4.8: Counts of instances for external sensors where undetected scaling area coverage (-/+ case) was either above or below 5%. Means and standard deviations are calculated for instances where scaling was below 5% coverage. Undetected instances greater than 5% coverage are considered outliers.

Threshold	Count Areas > 5%	Count Areas < 5%	Mean Area (<5% AC)
0.10%	1/42	3/42	1.7 ± 0.8
0.20%	3/42	5/42	1.4 ± 0.5
0.30%	4/42	6/42	1.9 ± 0.7
0.40%	4/42	6/42	1.9 ± 0.7
0.50%	4/42	6/42	1.9 ± 0.7

From these tables we see that as the threshold value increases, more false-negatives (-/+) occur, as expected. It is interesting to note that external sensors demonstrated a higher count of false-negatives where the area coverage was above 5% for which an ultrasonic response might have been expected.

We also consider cases of false-positive responses from the transducers (+/-). We see from Table 4.5 and Table 4.6 that as the threshold increases, the count of false-positives decreases. In particular, there is a much lower count in false-positives for a 0.2% window than a 0.1% window for both transducer types. This indicates that the false-positive count is unacceptably high with a 0.1% window. The false-positive counts are similar for the 0.2% - 0.5% threshold windows for both transducer types. It should be noted that the false-positives with the 0.2% - 0.5% windows occurred only during *extended scaling experiments*. Additionally, these false-positives occurred only at the upstream locations where no scaling was observed post-mortem. The most likely explanation is that the false-positives are the result of longer-term drift in the acoustic response. During several experiments, the acoustic response did not always become level to a long-term baseline over the course of the DI water compaction phase (at least 16 hours). This indicates that in future work, a more sophisticated signal processing protocol should be developed to provide greater reliability over longer-term filtrations.

Based on the analysis presented in this section, we chose an ultrasonic signal threshold window of 0.4%. This decision is based on minimization of the number of aberrant readings. These are defined as the sum of the count of false-negatives (-/+) with greater than 5% area coverage and the total count of false positives (+/-). At this threshold, there were 2 aberrant points for the internal sensors (out of 42 total instances = 4.8%) and for the external sensors there were 5 (11.9% of total). It is important to note that a few of the outlying points are false-positives that occur due to the acoustic drift discussed above, which occurs at long times after the feed switch. If these points are removed from consideration since they can be explained, then the total count of outlying points becomes 1 for the internal transducers (2.4% of total) and 4 for the external transducers (9.5% of total). In this respect, the internal transducers appear to be more reliable, although future work should focus on further improving the signal processing methodology.

4.7.3. Extended Scaling Experiments

4.7.3.1. Ultrasonic Results: Extended Scaling Experiments

In this section we examine the *extended scaling experiments* more closely. These experiments were performed to analyze scaling induction time as determined by the ultrasonic transducers with variable cross flow velocity. The experiments were conducted under conditions that enabled significant scaling to form over much of the membrane surface within a relatively short period of time following the feed switch.

All of the experiments conducted under the two flow-rate conditions (0.9 and 8.2 cm/s, $Re = 23$ and 188 respectively) demonstrated large ultrasonic response deviations from the pre-switch baseline at the downstream and midstream locations. This occurred for both types of transducers. Scaling was shown to be greatest downstream and gradually decreased in density toward the upstream direction, as expected following the mass-transport model (Figure 4.14). The assumption that these positive ultrasonic responses represent scaling is supported by the post-mortem analyses discussed in the following section.

Figure 4.25 shows representative plots of the ultrasonic responses from internal transducers for experiments at both cross-flow rates. Figure 4.26 shows representative plots of the ultrasonic responses from external transducers for experiments at both cross-flow rates. Ultrasonic induction times as well as post-mortem characterization parameters are listed in Table 4.9, where the experiments with low and high cross-flow rates are considered separately. The ultrasonic induction time is defined as the time between the feed stream switch and that at which the cross-correlation ultrasonic response passed outside the 0.4% breakout threshold. There is too much uncertainty in the data to determine a specific induction time as a function of the particular operating conditions. The statistical analysis does show, however, that the ultrasonic induction times at the downstream and midstream transducers do increase with increasing cross-flow velocity. Note that the only instance of positive acoustic response at an upstream transducer

was a false-positive (+/-), and the induction time occurs on a time scale similar to the drift that was often observed during the pre-switch DI water phase.

In both experiments shown in Figure 4.25 and Figure 4.26, we see that the respective downstream and midstream external transducer responses show similar induction times. The internal transducers, however, both clearly show that the induction time of the midstream sensor is significantly delayed from the downstream sensor. The likely reason for the difference in response is that the presence of the internal sensor locally blocks permeation, thereby impeding the development of scaling. The external sensor, meanwhile, samples the surrounding area where permeation is not blocked and the rapid development of heavy scaling is not hindered.

The ultrasonic responses for these data sets confirm the expected scaling behavior dependence on the cross-flow velocity. Higher cross-flow velocities result in lower concentration indices at the membrane surface and corresponding lower nucleation rates and crystal growth.

4.7.3.2. Post-Mortem Results: Extended Scaling Experiments

Images of membrane coupon samples were taken with an optical microscope and gravimetric analyses were performed after conclusion of the filtration experiments. The 2.5 cm × 2.5 cm coupon samples were taken from locations centered about the internal ultrasonic transducers. Thus, gravimetric measurements are representative of the entire coupon rather than just the internal transducer location, which has only a 5 mm diameter. The area of the internal transducer imprint is small with respect to the area of the entire coupon (~3%). Since the imprint area represents such a small percentage of the total coupon area, the impact of scaling density differences is negligible.

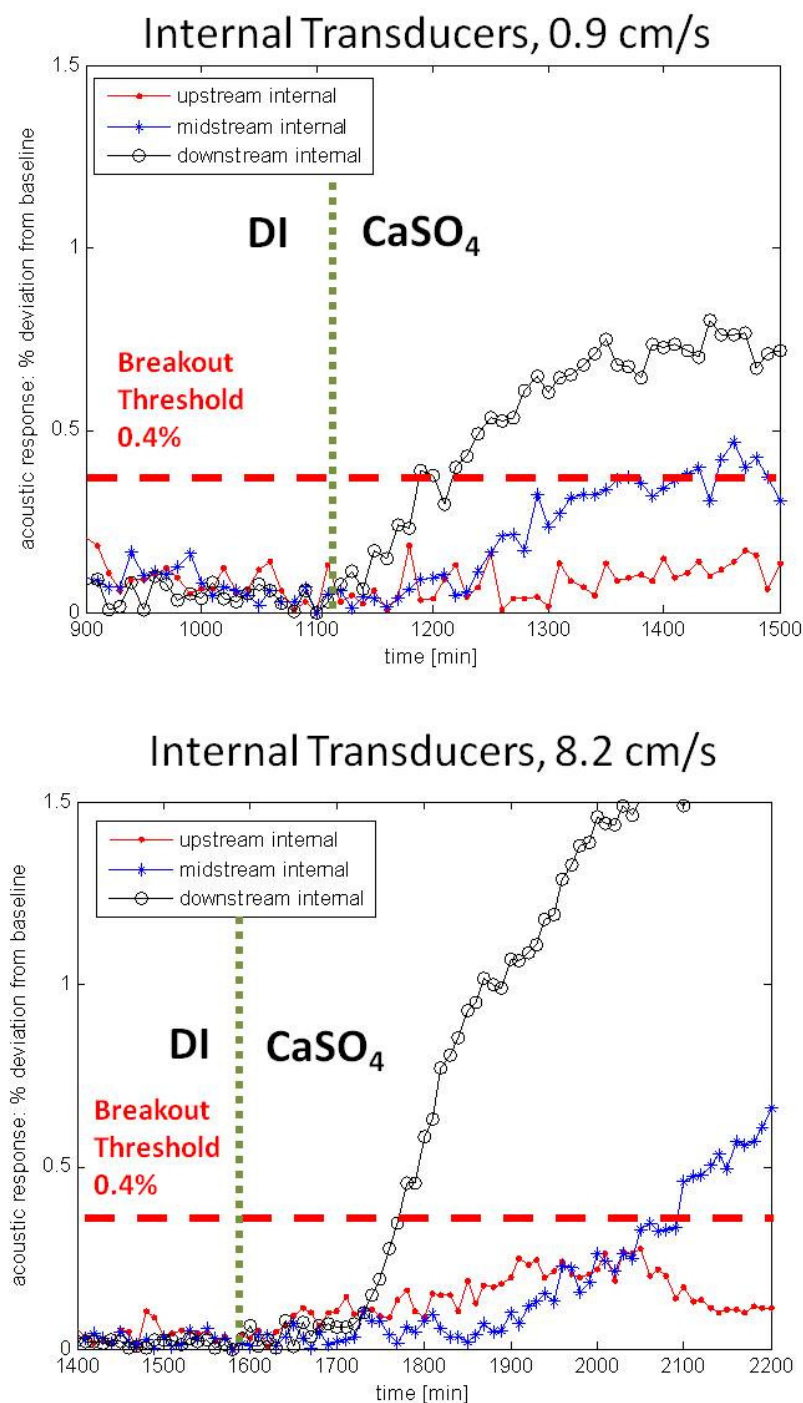


Figure 4.25: Representative plots of the normalized cross-correlation acoustic responses and permeate flux rates from the *extended scaling experiments*. Internal sensors. Dots → upstream transducer, stars → midstream transducer, circles → downstream transducer. Results are for (top) 1.19 g/L CaSO₄ with 0.9 cm/s cross flow velocity ($Re = 23$) and (bottom) 1.19 g/L CaSO₄ with 8.2 cm/s cross flow velocity ($Re = 188$).

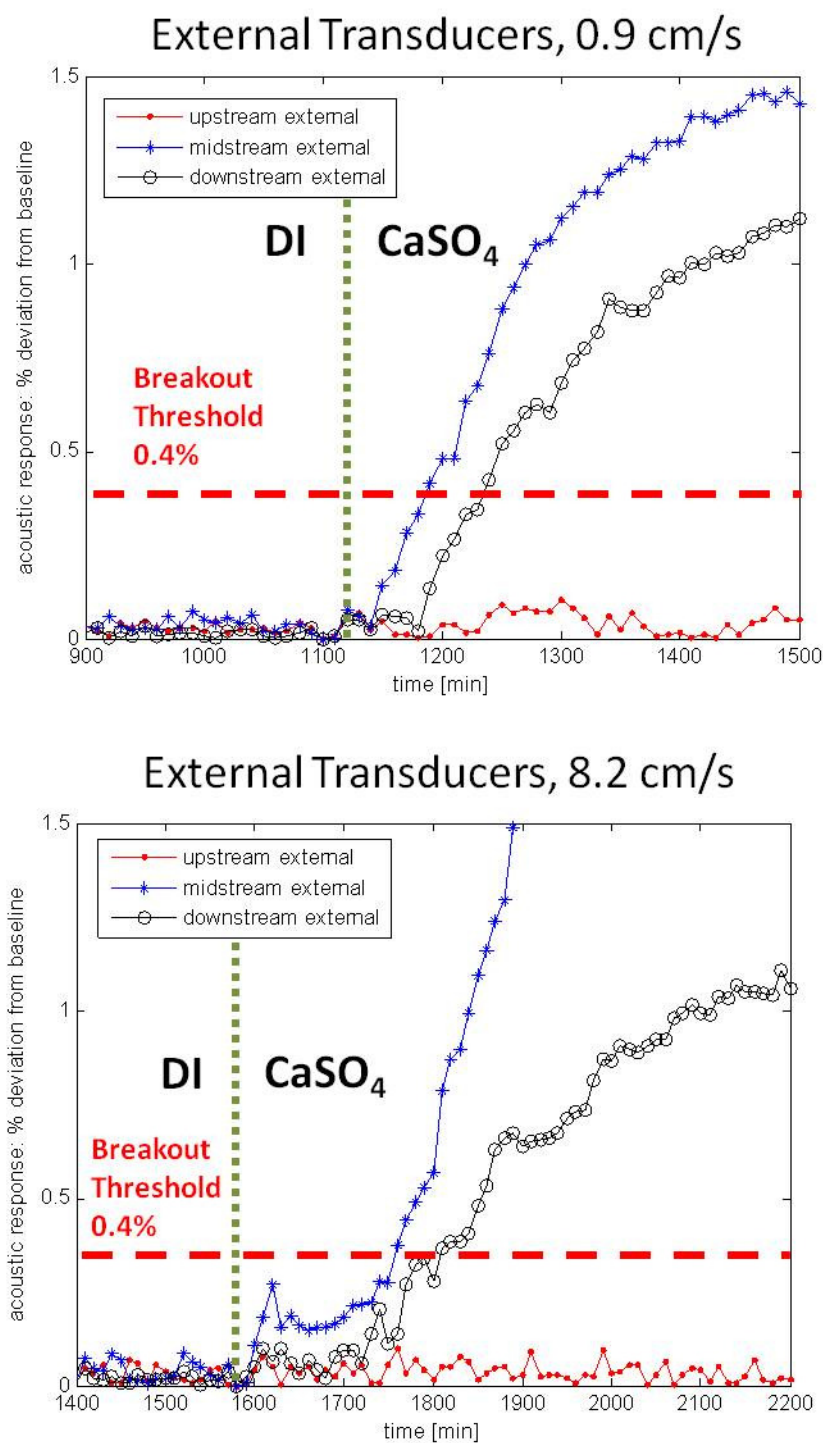


Figure 4.26: Representative plots of the normalized cross-correlation acoustic responses and permeate flux rates from the *extended scaling experiments*. External sensors. Dots → upstream transducer, stars → midstream transducer, circles → downstream transducer. Results are for (top) 1.19 g/L CaSO_4 with 0.9 cm/s cross flow velocity ($\text{Re} = 23$) and (bottom) 1.19 g/L CaSO_4 with 8.2 cm/s cross flow velocity ($\text{Re} = 188$).

Table 4.9 provides the post-mortem parameters for the experiments conducted under each operating condition, including percent gravimetric mass change due to scalant deposition (with respect to a clean coupon), and percent area coverage for the internal transducer imprint as well as the surrounding area sampled by the external transducer. The ImageJ software package was used to analyze area coverage. The micrographs (Figure 4.27 and Figure 4.28) correspond to the representative data sets shown in Figure 4.25 and Figure 4.26. These clearly show the presence of scaling, both on the internal transducer location as well as on the surrounding areas. The mass deposition as well as area coverage clearly increases from upstream to downstream. The coverage and mass deposition also has an inverse relation to the cross-flow rate, as expected. The area coverage downstream on the internal transducer is very similar to the immediately adjacent unblocked areas. This coverage comparison is somewhat more variable at the midstream location.

Table 4.9: Real-time and post-mortem results from *extended scaling experiments* with a 1.19 g/L CaSO₄ feed solution.

Cross-flow velocity [cm/s]	Number of Experiments	Location	Average Gravimetric Measurement [% Δm]	Average Area Coverage [%]		Number of Experiments with UR Response [0.4 % Threshold]		Induction Time [min]	
				Internal	External	Internal	External	Internal	External
0.9	2	Upstream	5.7 ± 4.7	10.7 ± 10.2	22.4 ± 18.0	0	0	N/A	N/A
		Midstream	23.1 ± 2.4	71.9 ± 8.2	77.0 ± 1.9	2	2	190 ± 145	95 ± 20
		Downstream	28.0 ± 2.8	79.6 ± 1.4	79.7 ± 0.4	2	2	75 ± 30	90 ± 35
8.2	4	Upstream	0.8 ± 0.9	0.0 ± 0.0	0.0 ± 0.0	1	1	1180	1090
		Midstream	22.5 ± 2.4	28.5 ± 8.2	74.5 ± 4.4	3	3	553 ± 29	353 ± 101
		Downstream	28.6 ± 1.8	70.5 ± 5.8	79.9 ± 3.4	4	4	145 ± 20	278 ± 36

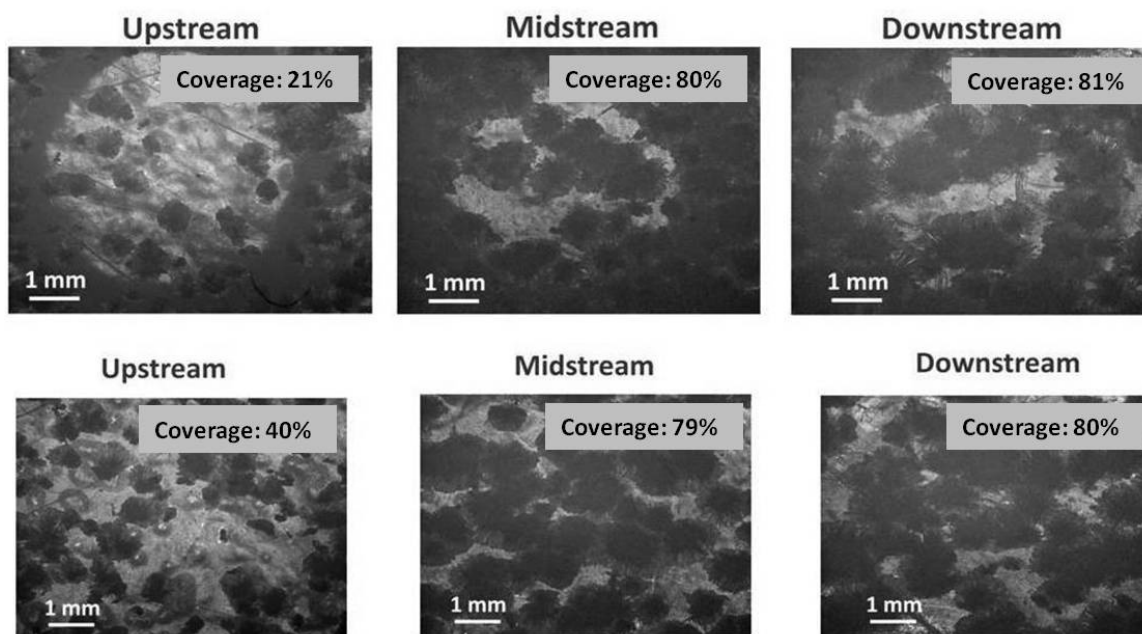


Figure 4.27: Representative optical micrographs of membrane coupons from up-, mid- and downstream transducer locations. *Extended scaling experiments*, 0.9 cm/s cross-flow rate ($Re = 23$). The top row shows the internal transducer locations (circular imprint) and the bottom row shows external transducer location (surrounding areas).

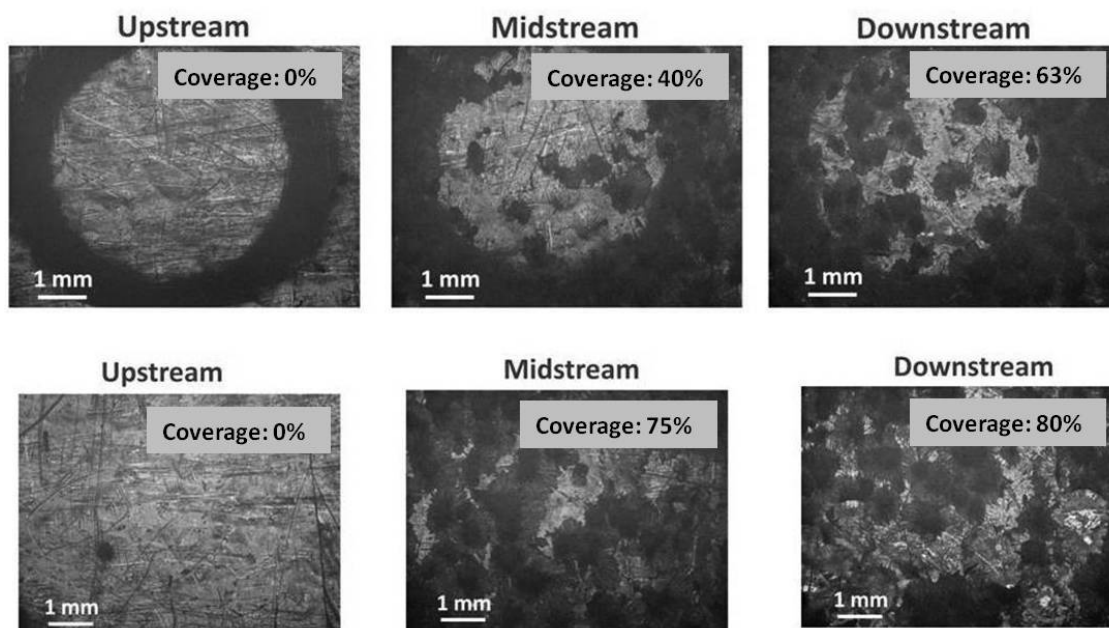


Figure 4.28: Representative optical micrographs of membrane coupons from up-, mid- and downstream transducer locations. *Extended scaling experiments*, 8.2 cm/s cross-flow rate ($Re = 188$). The top row shows the internal transducer locations (circular imprint) and the bottom row shows the external transducer locations (surrounding areas).

In general, the areal scaling density is lower directly over the internal transducer locations than in the surrounding areas. This effect is observed in all experiments, and is due to local blockage of permeation by the transducer itself. Two mechanisms could be responsible for the crystal growth on the blocked internal transducer areas: convective mass transfer that causes concentration polarization over the transducer location, thereby facilitating some degree of scaling; and lateral expansion of scaling clusters initiated in the surrounding unblocked areas.

Scaling was observed upstream directly on the internal transducer location as well as the surrounding area in one of the experiments with the 0.9 cm/s cross-flow rate ($Re = 23$), but none was observed at this location after any of the 8.2 cm/s experiments ($Re = 188$). The salt growth is very similar in both experiments at the mid- and downstream locations, as shown by visual inspection and gravimetric measurement. As surface fouling coverage increases, scalant rosette clusters grow together resulting in asymptotic scale deposition.

The idealized relationship between ultrasonic response and the permeate flux was shown Figure 4.15. Following the switch from DI water to calcium sulfate feed, there is an immediate drop in permeate flux due to osmotic effects. At this point, however, the permeate flux should maintain a steady-state value until sufficient scaling has developed to observably reduce the average permeation flux rate further. This occurs over an interval referred to as the permeate induction time (Δt_p). This phenomenon was observed in several experiments, with the flux induction time evidencing significant variation. Figure 4.29 shows a representative example from an experiment conducted with the 0.9 cm/s cross flow rate ($Re = 23$) where the ultrasonic induction time occurs very close to the observed permeate induction time. This indicates that if a module with an even longer flow channel were used, the ultrasonic induction could very likely precede the permeate induction. Spiral-wound module trains constituting much longer flow channels are common in large-scale desalination systems. At the same time if a lower threshold were chosen ($\sim 0.2\%$) then ultrasonic induction times would be noticeably lower than those of permeate induction times. Given

that for external transducers the false positives represented <10% of the runs, this option may be preferable for a conservative warning device.

4.7.4. Interval Experiments

4.7.4.1. Ultrasonic Results: Interval Experiments

The aim of the *interval experiments* was to correlate responses from the ultrasonic transducers with post-mortem metrics in order to demonstrate a chronological development of early-stage scaling and the ability to detect it. The experiments were performed under constant operating conditions: pressure of 5.5 bar (80 psi), cross-flow velocity of 0.9 cm/s ($Re = 23$) and a feed concentration of 0.47 g/L $CaSO_4$. These identical experiments were terminated at predetermined times (60, 120, 150 minutes) after the switch from DI water to calcium sulfate feed. Table 4.10 shows that ultrasonic responses outside the 0.4% breakout threshold were likely to be observed at the downstream location by both internal and external transducers by the end of the 150 minute experiments, occasionally by the end of the 120 minute experiments and not at all by the end of the 60 minute experiments. This correlated well with observed scaling on the membrane. Figure 4.30 shows representative plots of the normalized ultrasonic responses for each of the cutoff intervals. These plots show instances where scaling was correctly detected by both the internal and external transducers at the downstream location during the 120 and 150 minute intervals. No scaling was ultrasonically detected nor visually observed post-mortem at the other locations in these experiments, and no scaling whatsoever was observed post-mortem for the 60 minute experiments.

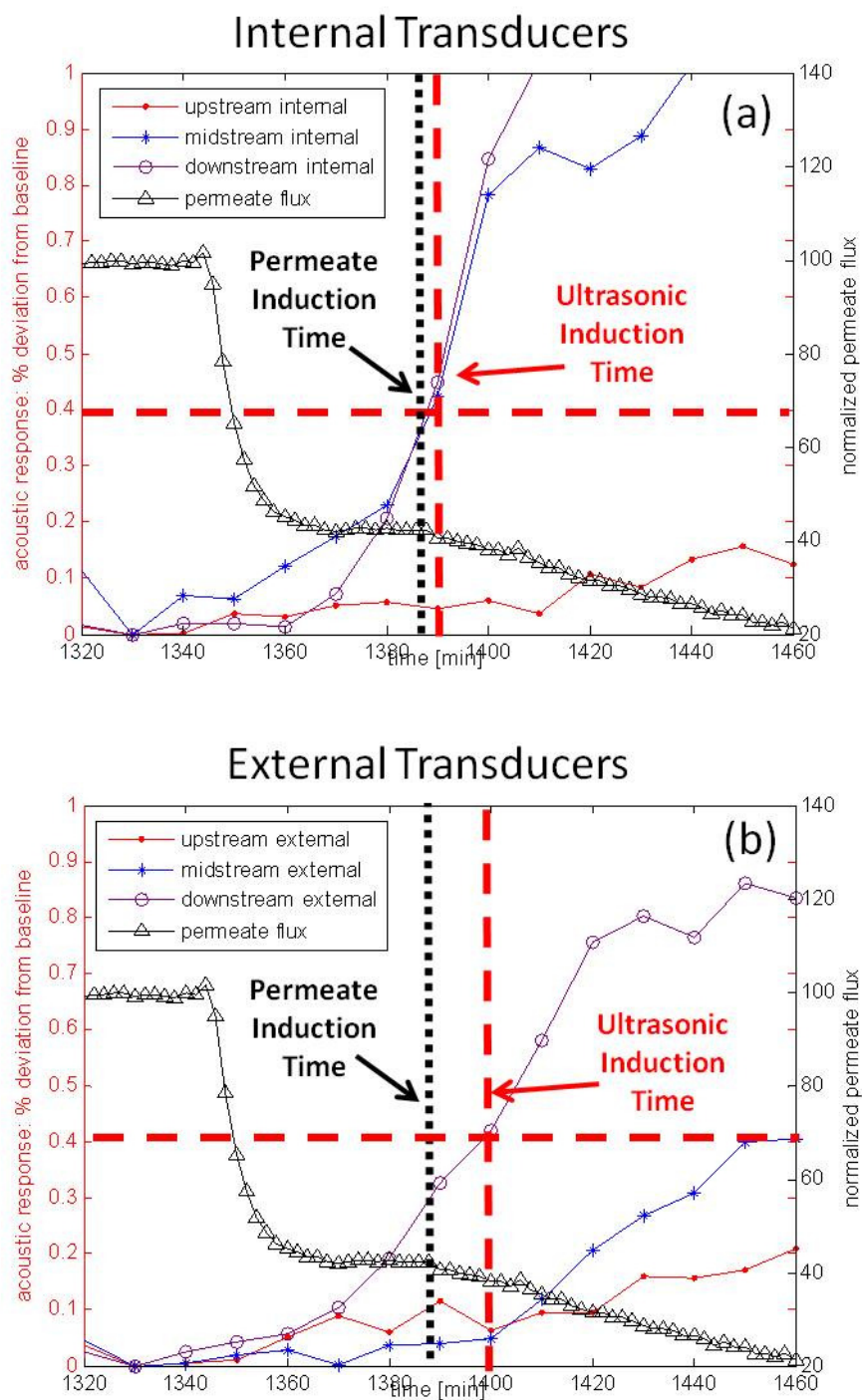


Figure 4.29: Data from a representative extended scaling experiment. (a) internal transducers. (b) external transducers. 0.9 cm/s cross-flow rate ($Re = 23$), 1.19 g/L $CaSO_4$. These plots demonstrate ultrasonic induction time occurring very close to the flux induction time. The 0.4% breakout thresholds are the horizontal dashed lines. The ultrasonic and flux induction times are the vertical dashed lines.

Table 4.10: Real-time and post-mortem results from *interval experiments*. All experiments conducted with a cross-flow velocity of 0.9 cm/s and a feed concentration of 0.47 g/L CaSO₄.

Cutoff Interval [min]	Number of Experiments	Location	Average Gravimetric Measurement [% Δm]	Average Area Coverage [%]		Number of Experiments with UR Response [0.4 % Threshold]		Induction Time [min]	
				Internal	External	Internal	External	Internal	External
60	2	Upstream	-0.1 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0	0	N/A	N/A
		Midstream	0.3 ± 0.6	0.0 ± 0.0	0.0 ± 0.0	0	0	N/A	N/A
		Downstream	-0.5 ± 0.6	0.0 ± 0.0	0.2 ± 0.1	0	0	N/A	N/A
120	3	Upstream	0.4 ± 0.8	0.0 ± 0.0	0.0 ± 0.0	0	0	N/A	N/A
		Midstream	0.6 ± 0.6	0.2 ± 0.2	0.2 ± 0.1	0	0	N/A	N/A
		Downstream	3.2 ± 0.9	9.2 ± 4.4	9.7 ± 3.5	2	1	110 ± 10	110
150	3	Upstream	-0.1 ± 0.3	0.0 ± 0.0	0.0 ± 0.0	0	0	N/A	N/A
		Midstream	0.3 ± 0.5	1.1 ± 0.5	2.8 ± 1.0	0	1	N/A	130
		Downstream	9.4 ± 1.2	23.4 ± 5.6	41.4 ± 4.2	3	2	117 ± 23	130 ± 30

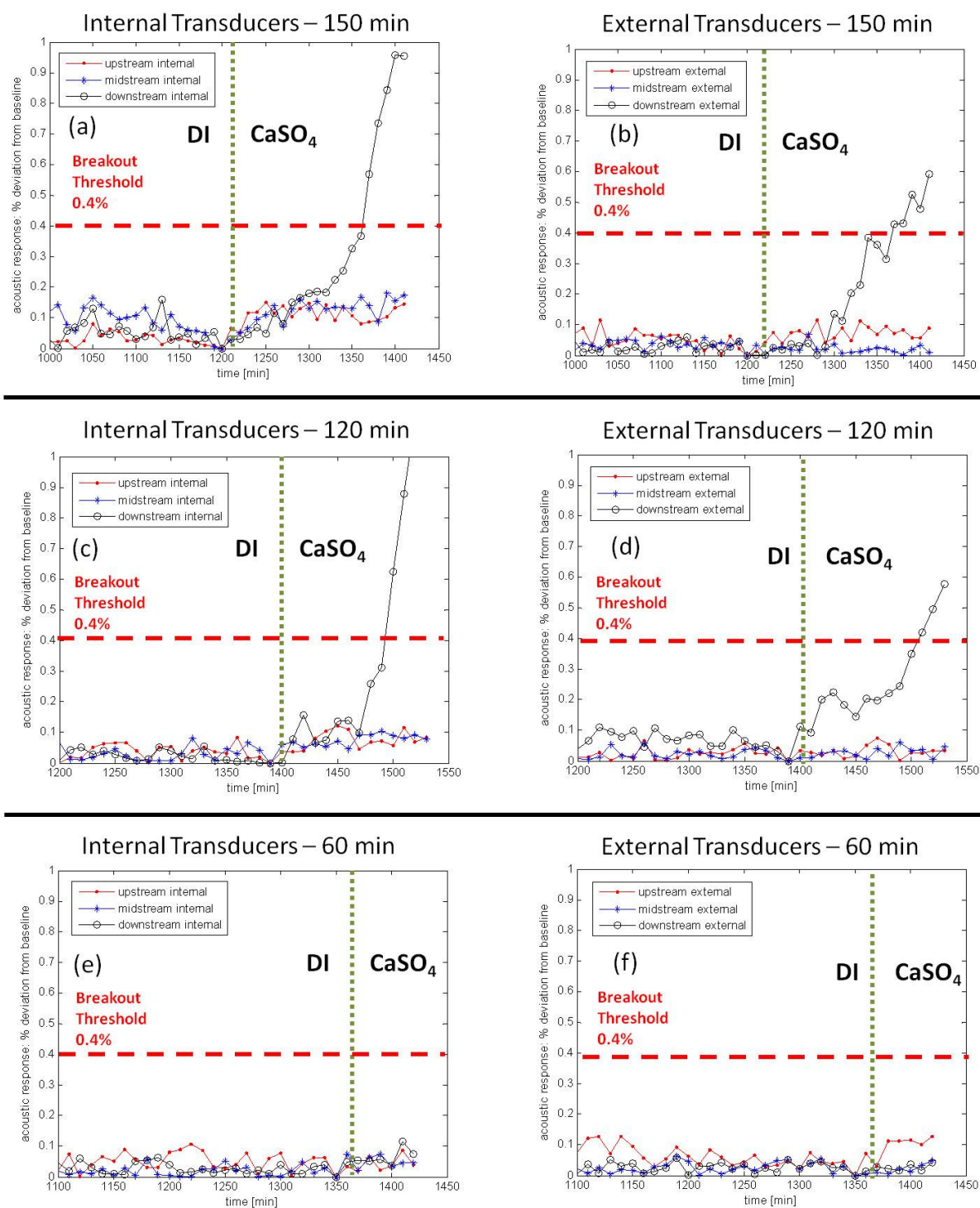


Figure 4.30: Representative plots of the normalized cross-correlation ultrasonic responses from the *interval experiments*. (a,b) 150 minute cutoff interval. (c,d) 120 minute cutoff interval. (e,f) 60 minute cutoff interval. Dots → upstream transducer, stars → midstream transducer, circles → downstream transducers.

4.7.4.2. Post-Mortem Results: Interval Experiments

The area coverage and gravimetric analyses of membrane samples from the *interval experiments* are consistent with the acoustic results obtained from the internal and the external ultrasonic sensors, although there is significant variability in the exact magnitude of these values across replicate experiments. In none of the *interval experiments* was any fouling visually or gravimetrically observed at the upstream or midstream locations. However, scaling was observed on the downstream internal transducer as well as surrounding areas during both the 120 and 150 minute experiments, and only once was extremely sparse rosette growth observed in a 60 minute experiment at the downstream location. See Figure 4.31 for images from the membrane coupons. In considering responses from the external transducers, note that the scaling in the unblocked areas sampled is much sparser than that seen in the *extended scaling experiments*. This supports the contention that the small sampling area of the transducers may be responsible for false-negatives (-/+) in some instances, and delayed ultrasonic induction times in others. As mentioned previously, the transducers essentially represent point measurements. Nucleation sites for rosette crystal growth are randomly dispersed, meaning the transducer may not sample the growth of an early-stage cluster, or a certain amount of time might be required before an existing cluster grows to a sufficient extent to encroach on the sampling area. This could be addressed in a practical system by increasing the transducer diameter or using an array of transducers to increase the probability of detecting local scale formation.

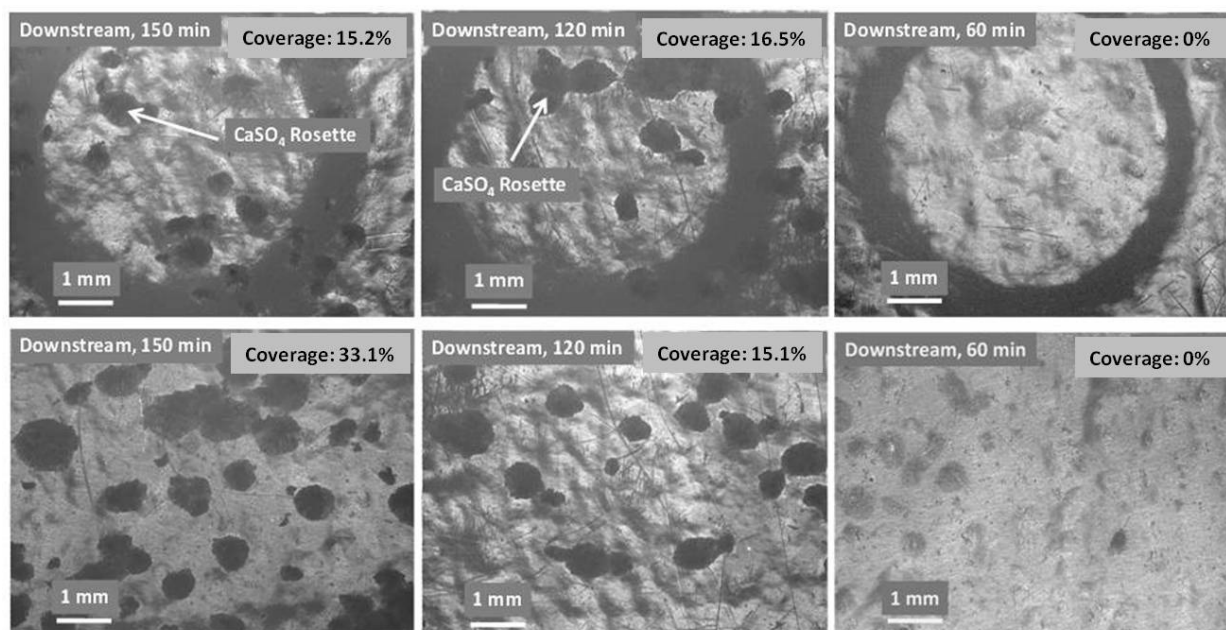


Figure 4.31: Images of downstream membrane coupon samples from *interval experiments*. Internal transducer areas in the top row (circular imprints), external transducer areas in bottom row (surrounding areas).

4.7.5. SEM Imaging and EDS Spectrum

Supplementary post mortem examinations included imaging of select samples by scanning electron microscopy (SEM), and determination of scalant composition by energy-dispersive x-ray spectroscopy (EDS). SEM images confirmed the typical calcium sulfate rosette structure geometry on the membrane surface (Figure 4.32). This substantiates that the calcium sulfate scaling forms by local nucleation and growth that continues until the clusters coalesce to cover the entire local surface [Gilron 1987]. The rosette structure would serve as a good scatterer of incident ultrasonic waves. Under different growth conditions, it has been noted in the literature that CaSO_4 scaling may also assume a plate-like structure that could serve as a better reflector of acoustic waves [Mairal 1999, 2000]. Further investigation of signal processing methodologies could provide insight into the structure and growth mechanisms of inorganic scaling layers. Several locations on membrane coupons from different filtration

experiments were sampled by EDS. The EDS spectra confirmed that the scaling is indeed uncontaminated calcium sulfate (Figure 4.33).

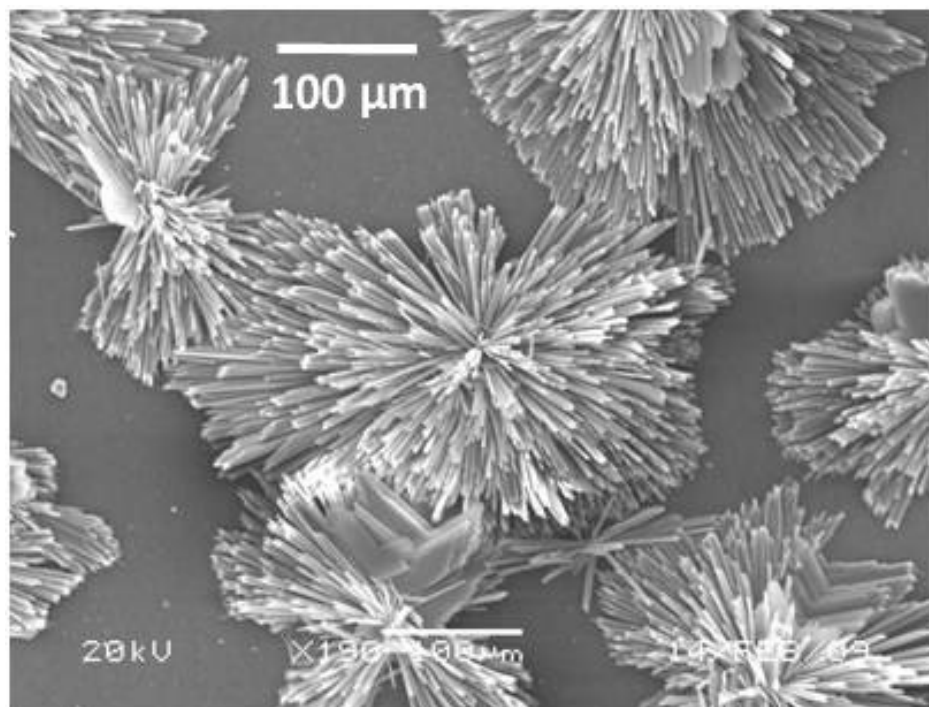


Figure 4.32: SEM micrograph showing calcium sulfate rosette growth on the nanofiltration membrane surface. EDS analysis confirmed the composition of the crystal structures.

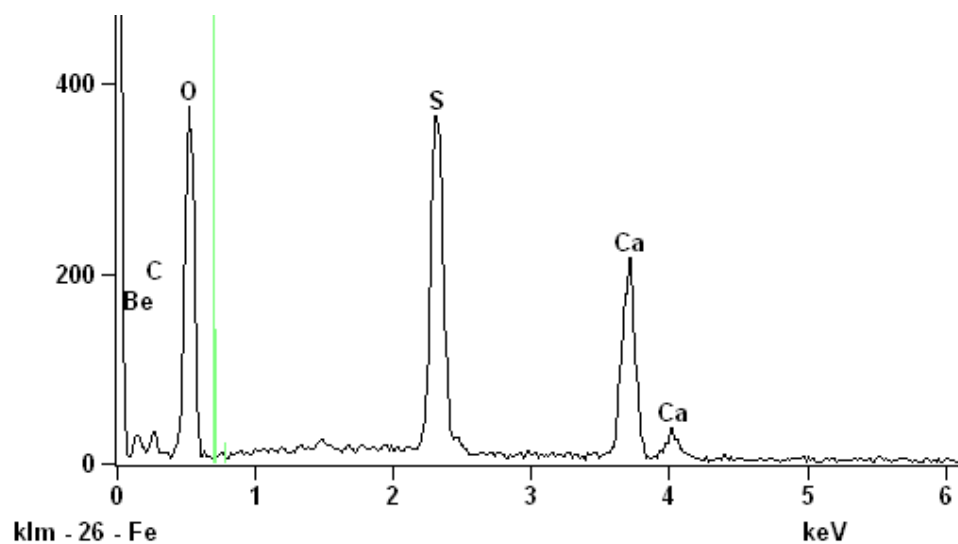


Figure 4.33: Representative EDS spectrum from scaling rosette.

4.8. Significance

The work presented in this chapter demonstrates the use of internally integrated ultrasonic transducers and a novel signal processing algorithm that significantly extends upon the acoustic signature method presented by Zhang et al. [2003, 2005]. This scheme was based on cross-correlation of waveforms to indicate changes in shape with the onset of scaling, followed by an analysis to determine the appropriate signal threshold window that minimizes false-positive readings. The results showed that one could obtain a very high rate of reliability for both internally as well as externally mounted transducers. This demonstrates that externally mounted transducers could be put to good use on larger-scale systems.

The ultrasonic results were verified by post-mortem analysis of the membrane after completion of the filtration runs. The combination of ultrasonic response and observed area scaling was used in determining the optimal threshold window to use in the signal analysis scheme. While the internally integrated sensors demonstrated slightly higher sensitivity and reliability than the externally mounted sensors, it was shown that the local permeate blockage did indeed hinder scaling growth. Therefore, we see a balance between sensitivity and detectable scaling growth rate. On balance, this shows that externally mounted transducers should be adequate for use with practical systems in future work.

Chapter 5

Conclusions and Recommendations

5.1. Electrolytic Monitoring of Concentration Polarization and Scaling

Chapter 3 presented the development and testing of integrated electrolytic sensors for monitoring concentration polarization during cross flow nanofiltration of calcium sulfate feed solutions. The motivation of this work was to design, fabricate and test sensors that improve upon the work presented by Zhang et al. [2005, 2006], by allowing for testing in an environment that more closely resembles that found in industrial desalination systems. The experiments reported by Zhang et al. were performed to demonstrate proof-of-concept CPBL monitoring in a short flat-sheet cross flow module where the system and experiments were intentionally designed to produce boundary layers much thicker than those found in industrial systems. The work presented here focused on the development of thin, flexible electrolytic sensors for use under greater cross flow rates with thinner concentration polarization boundary layers (CPBL). Thin sensors mounted to the membrane surface can be directly immersed within the boundary layer while the flexibility of the sensors allows for potential future use in spiral-wound modules, which are the industry standard. This represents a significantly more sophisticated approach than that presented in [Zhang 2005, 2006].

All experiments were performed in flat-sheet cross flow filtration modules. Initial testing was performed in a module similar to that used by Zhang et al., in order to develop device design and integration schemes for the new sensor concept. Experiments were subsequently carried out in a flat-sheet module with a much longer and thinner flow channel; this enabled testing of sensor response as a function of axial position within the flow channel under greater cross-flow velocities and thinner CPBLs. Over the course of the work, many electronic feed-through schemes and sensor electrode designs were tested for reliability and sensitivity to changing solute concentration in the feed stream and in the CPBL.

The majority of testing was performed with sensors having an interdigitated electrode configuration similar to that used by Zhang et al. We, however, used nickel electrodes fabricated on a polyimide (Kapton) substrate, as opposed to polysilicon electrodes on a silicon nitride/silicon substrate. Capacitance measurements were recorded from multiple sensors of this design in multiple separate experiments at multiple concentrations. Capacitance values recorded under pure cross flow conditions with known bulk feed concentrations. The results of this series of experiments matched well with a theoretical model of capacitance versus concentration, following the Stern-Gouy-Chapman double layer capacitance formulation. Reasonable input values were used in the model, however uncertainties in the calculation were accounted for; these tests were never intended to be extremely well controlled electrochemical experiments, but rather a proof-of-concept demonstration in a realistic operating environment.

Despite the good correlation of experimental and theoretical capacitance values under known concentrations, the interdigitated sensors did not demonstrate clear evidence of the change in concentration as a function of axial position when permeation was allowed. This was one of the major goals of the work, and prompted modification of the electrode design from interdigitated (Figure 3.7) to monolithic (Figure 3.8). The Kapton substrate of the interdigitated sensors presented a significant blockage to local permeation. One of the hypotheses of this study was that convective cross flow would be sufficient to produce concentration conditions directly over the sensor that were similar to the neighboring unimpeded areas. Experimental results, however, showed that this was not the case. Further discussion regarding local blockage due to the presence of internally integrated ultrasonic transducers related to this specific topic was presented in Chapter 4. It is likely that the presence of the sensors perturbed the local CPBL sufficiently so that they were no longer sensitive enough to detect the difference in concentration between the upstream and downstream locations within the module.

The monolithic sensor electrodes were mounted to the nanofiltration membrane so that a permeable gap was present between the two electrodes. This allowed concentration polarization to form directly in the region of fluid being sampled. Experimental results showed that these sensors were able to detect a clear difference in concentration between upstream and downstream. Concentration was determined following a calibration procedure with the measured electronic parameters (i.e., capacitance, resistance, impedance, phase angle, conductance) as inputs. In addition, the work also showed a clear dependence of concentration on axial cross-flow velocity. The membrane sensors at all three locations showed a decrease in concentration with increasing velocity. Indeed, the concentration difference between the downstream sensor and the upstream sensor was most pronounced at low cross flow velocity.

The resulting concentration values were significantly less than the expected membrane surface concentrations predicted by the numerical CP model. This can be explained by the fact that the sensors are not truly on the membrane surface (transfer tape + substrate stack: $\sim 75\text{ }\mu\text{m}$ thick), and that the sensor substrate still generates a perturbation to the boundary layer. We must also consider the specific electronic parameters that are analyzed. Capacitance is an electrode surface effect, largely caused by the ionic double layer that forms when the test signal voltage is applied. This parameter is thus under the influence of perturbation due to permeate blockage. Resistance is a function of the solution between the electrodes. Given the electrode geometry, the electric field lines between the electrodes pass through regions of CP as well as regions of bulk feed (Figure 3.16). The resulting reading is therefore an average of the fluid through which the field lines pass. Experimentally, a thorough analysis of the capacitance and complex impedance magnitude were shown to perform similarly. The data presented are from one test, and further study should be performed to demonstrate replication and provide a better statistical analysis of the behavior of differing electronic parameters under different conditions.

The monolithic electrode sensors also showed a good match between measured and expected conductivity. Cell constants were calculated for each sensor based on the measured conductance (pure-

cross flow, bulk feed) and the known conductivity, which was measured by a commercial conductivity probe installed in the feed tank. These cell constants matched well with the theoretical cell constant, calculated following the methodology of Olthuis [1995], using finite-element input for the trapezoidal shaped electrodes. The cell constants were then used to experimentally compare measured conductivity with theoretical conductivity, as a function of calcium sulfate concentration. The theoretical conductivity was calculated following the Onsager formula [1932], which has consistently been shown to be reliable in describing low concentration aqueous solutions [Rieger 1994]. The experimental conductivity matched well with the theoretical curve. Somewhat greater deviation in the experimental values from the theoretical curve occurred at higher concentrations, which is not unexpected.

Finally, the integrated electrolytic sensors were successfully used to detect the formation of scaling on the membrane (monolithic electrode design). This was best shown through measurement of the conductance, where the deviation in the conductance readings of the membrane-mounted sensors was plotted versus filtration run time. A slower cross-flow velocity and higher feed concentration were used to expedite the onset of scaling. The deviation in conductance of the membrane-mounted sensors was much greater than that from the sensors mounted on the top wall of the flow channel. These deviations occurred first at the downstream location, followed by the midstream and finally the upstream location, as expected. Post-mortem inspection of the membrane showed significant calcium sulfate crystal deposits, with scaling density increasing from upstream to downstream. Future work, again, should focus on interpretation of results during scaling experiments according to the different electronic parameters that can be measured by an LCR meter. In addition, more comprehensive study should consider why one parameter may be more sensitive than another under the conditions imposed by a practical filtration system.

This work has provided significant proof-of-concept evidence that flexible integrated electrolytic sensors can be employed in cross-flow desalination to monitor concentration polarization and scaling at

the membrane surface. The next step is to directly fabricate sensors on the membrane surface. This will significantly reduce the perturbation of the CPBL caused by a (relatively) thick sensor substrate. Although the sensors reported in this work were a significant improvement over those presented by Zhang et al., permeate flow is still somewhat hindered and the total thickness; $\sim 75\ \mu\text{m}$ (transfer tape + Kapton substrate) in a CPBL with estimated thickness on the order of $\sim 200 - 300\ \mu\text{m}$, is still somewhat problematic. As a result, the true conditions at the membrane surface most likely could not be measured with as much accuracy as desired. In addition to a reduction in sensor thickness, direct fabrication on the membrane will allow permeation to occur between the electrodes, significantly reducing perturbation of the CPBL and allowing monitoring much closer to the membrane surface (Figure 5.1). Implementation of this fabrication process may allow the use of interdigitated sensors with much greater sensitivity. This design allows for a large electrode area in a small footprint with the electrodes much closer to each other than in the monolithic electrode design.

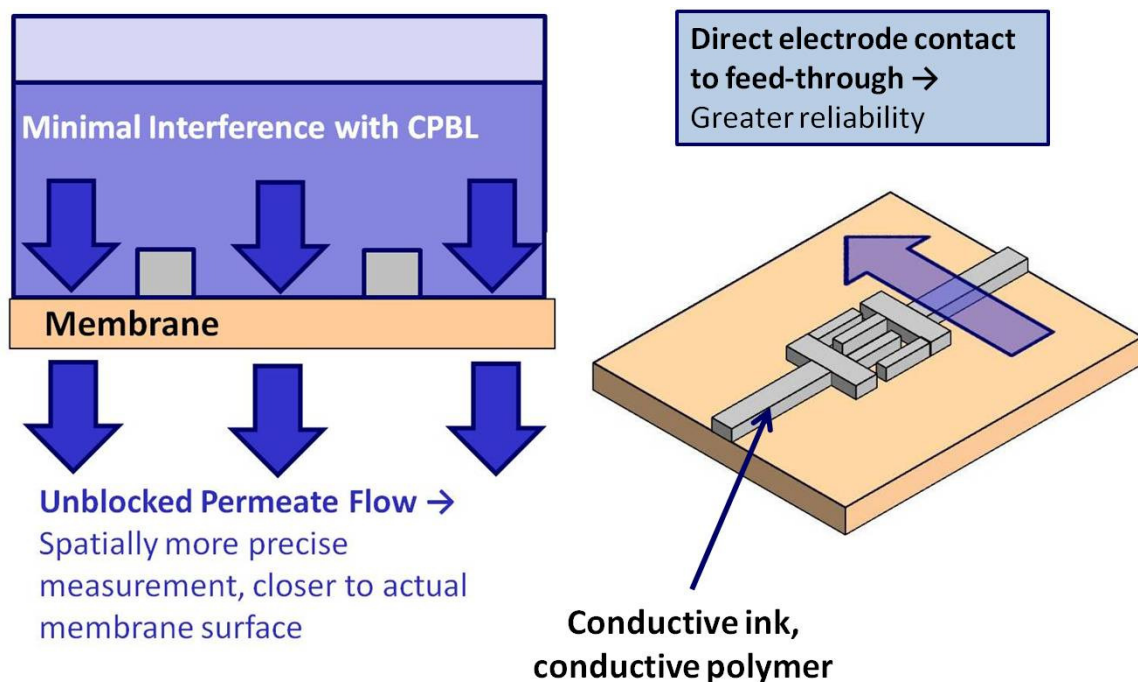


Figure 5.1: Schematic of electrolytic sensor fabricated directly on filtration membrane.

Direct fabrication of sensors on the membrane will require creative choices of materials and manufacturing techniques. Standard reverse osmosis and nanofiltration membranes used in industrial desalination [Dow Water Solutions 2007] are not sufficiently robust with respect to the temperatures, solvents and etchants commonly used in MEMS fabrication processes. Some possibilities include screen printing or ink-jet printing of conductive polymers or low-temperature evaporation of electrode structures on the membrane. The conductive polymers can be cured either at room temperature or by UV exposure [Allied 2010]. Membrane properties should be investigated for degradation of the thin separation layer (usually polyamide, ~200 nm) after significant UV exposure. A UV curing procedure may require the use of an appropriate photomask to protect the membrane. For low temperature evaporation, tests will have to be performed to evaluate metal adhesion to the membrane, before, during and after this fabrication step. Nickel, gold, platinum and palladium are metals that could potentially be used in such a process, as they show good resistance to corrosion.

5.2. Ultrasonic Monitoring of Early-Stage Scaling

This study builds upon the methods and results reported previously in the literature on ultrasonic detection of membrane fouling during desalination processes. A primary novel aspect of this study was the investigation of using internally mounted ultrasonic transducers for improving the detection sensitivity of early-stage scaling. Additionally, a cross-correlation signal processing protocol was developed to analyze the waveforms reflected from the membrane surface. This was shown to provide a sensitive metric for detecting inorganic fouling both for externally as well as internally mounted ultrasonic transducers. The method significantly extends the acoustic signature approach reported by Zhang [2003, 2005]. A detailed analysis of the cross-correlation ultrasonic response values was performed to provide a reliable indicator of the formation of scaling while minimizing false-positives and false-negatives. This procedure involved determining an optimal threshold window for tracking changes in the ultrasonic response variable over the course of the filtration experiments. Similar thresholding

procedures could be applied to alternate forms of waveform signal analysis (i.e. total reflected power, peak-magnitude, peak-shift, wavelet analysis).

The internally mounted ultrasound transducers tended to be somewhat more reliable than the externally mounted transducers in terms of reducing false-positive or false-negative readings. No clear conclusion can be drawn at this time, however, on the relative efficacy of the two transducer integration modes (internal/external). Both modes had similarly high success rates. Post-mortem analysis showed that scalant growth on the permeate-blocked internal transducer locations was noticeably lower than that in the immediately surrounding unblocked areas. This possibly could reduce the overall utility of internal transducers in flat-sheet NF or RO membrane modules, despite the slightly higher reliability. It could, however, prove useful for detecting scaling on the inner windings of spiral-wound modules. An appropriate integration scheme could be developed in which a miniaturized transducer is installed in the central product tube.

Since both the external as well as the internal ultrasonic transducers essentially provide point measurements, crystal rosette formation might not occur directly in the acoustically sampled area. This results in some variability in the false-negative readings (-/+) and in the ultrasonic induction time. A solution to this issue is simply to employ arrays of transducers at given locations. Given the high success rate demonstrated in this thesis with single-point measurements at each axial location in the filtration module, an array of transducers, or a single transducer consisting of multiple linear elements (i.e. B-scan) should prove quite reliable in future detection of early-stage scaling. Overall the ultrasonic responses matched quite well with the post-mortem SEM and optical microscopy analyses. This establishes that both the external and the internal ultrasonic sensors are capable of detecting the scaling layers. In particular, both types of sensors consistently detected scaling layers forming downstream where the convective mass-transport model predicts that concentration polarization will be greatest.

Work that builds on some of the concepts developed in this thesis is currently underway with respect to pilot-scale testing in a desalination facility of modules with integrated ultrasonic transducers for optimized performance (Figure 5.2). This work utilizes externally mounted sensors for detecting scaling on the outer layers of spiral-wound modules. This should provide acceptable sensitivity because industrial desalination systems typically operate with a train of modules that evidence a much greater permeable area than the module used in this thesis. Ultrasonic and permeate induction times were similar during filtration in our module (Figure 4.29). Therefore, even if significant scaling formed near the very end of an industrial module train, it would not likely be detected in the net permeate flux rate of the entire system.



Figure 5.2: Ashkelon Seawater Reverse Osmosis Plant, Israel [Ministry of National Infrastructures 2010].

In addition to use for monitoring of scaling during industrial desalination, ultrasonic transducers could be used in fundamental studies of fouling growth mechanisms. Scalants can grow as either good reflectors (plates) or scatterers (rosette clusters), depending on conditions within the flow channel [Mairal 1999]. Analysis of growth morphology could be tested in real-time by analysis of different signal processing methodologies. These concepts can further be applied to a more fundamental understanding of fouling layer material properties in a variety of filtration systems. Such study requires only an appropriate experimental design and selection of signal analysis protocols.

5.3. Conclusions

The work performed in this thesis has demonstrated that different sensing schemes can be effectively utilized in monitoring process phenomena at the surface of a membrane during liquid separation techniques. Although this work focused specifically on the filtration of sparingly soluble salt (calcium sulfate) during nanofiltration, many of the concepts developed can be applied to a wide variety of filtration processes. Indeed, a review of the literature has shown increasing application of ultrasonic time-domain reflectometry for monitoring many types of fouling layers in different filtration module configurations. The work with electrolytic sensors is currently in an early stage of development, owing to a greater level of fabrication and integration complexity. With further research, however, and the employment of industrial-scale fabrication, smart reverse osmosis membranes could be manufactured with electrolytic sensors directly fabricated on the membrane. The MEMS industry has already clearly demonstrated that the electronic devices that drive our society can be manufactured at extremely low cost when done on a mass-scale.

There seems little doubt that a new generation of smart membranes and modules will contain integrated sensing technologies that serve as control elements in automatically implementing remediation measures, which improve process efficiency in large-scale desalination units. They will reduce the cost of desalination, opening up current brackish water sources that are currently underutilized due to economic

or environmental concerns. With the ever-increasing demand for fresh water in the coming years, use of these sources will become increasingly important so it is critical that the membrane field be ready for the challenge.

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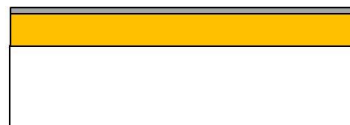
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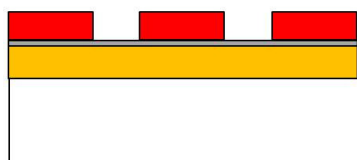
Appendix A: Fabrication Process for Electrolytic Sensors



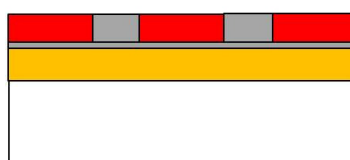
(1) Adhere Kapton to glass slide with WaferGrip.



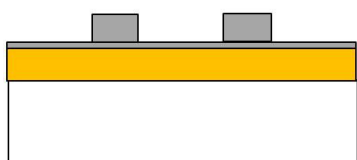
(2) Thermally evaporate Ti/Ni seed layer.



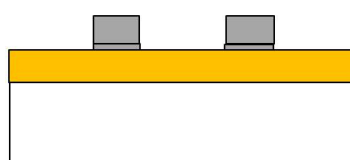
(3) Deposit and pattern photoresist.



(4) Electroplate nickel electrode structure.



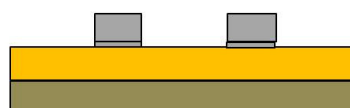
(5) Remove photoresist.



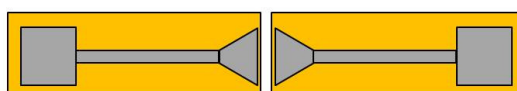
(6) Etch seed layer.



(7) Remove Kapton with nickel structures from glass slide. (8) Clean WaferGrip residue.

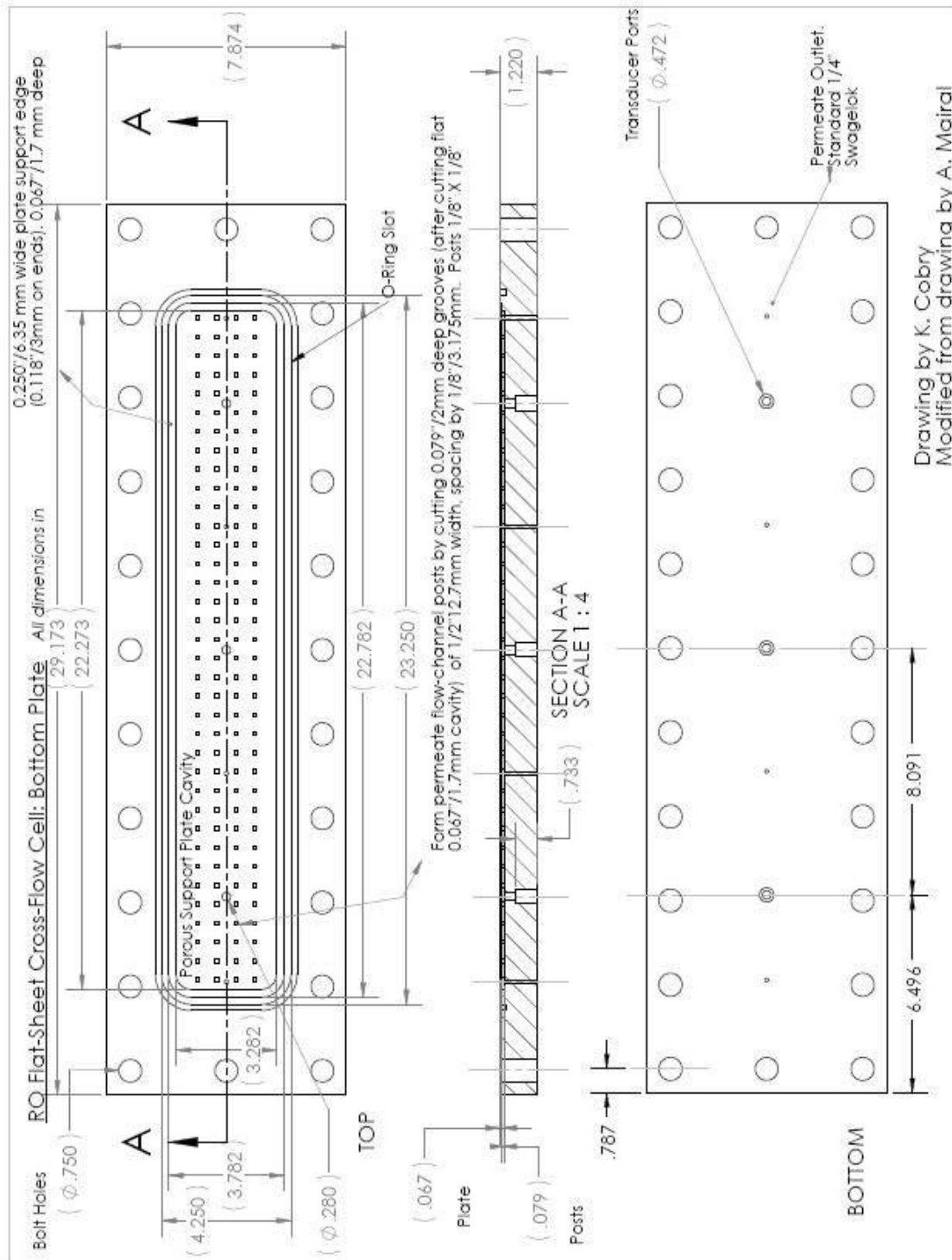


(9) Adhere double-sided transfer tape.

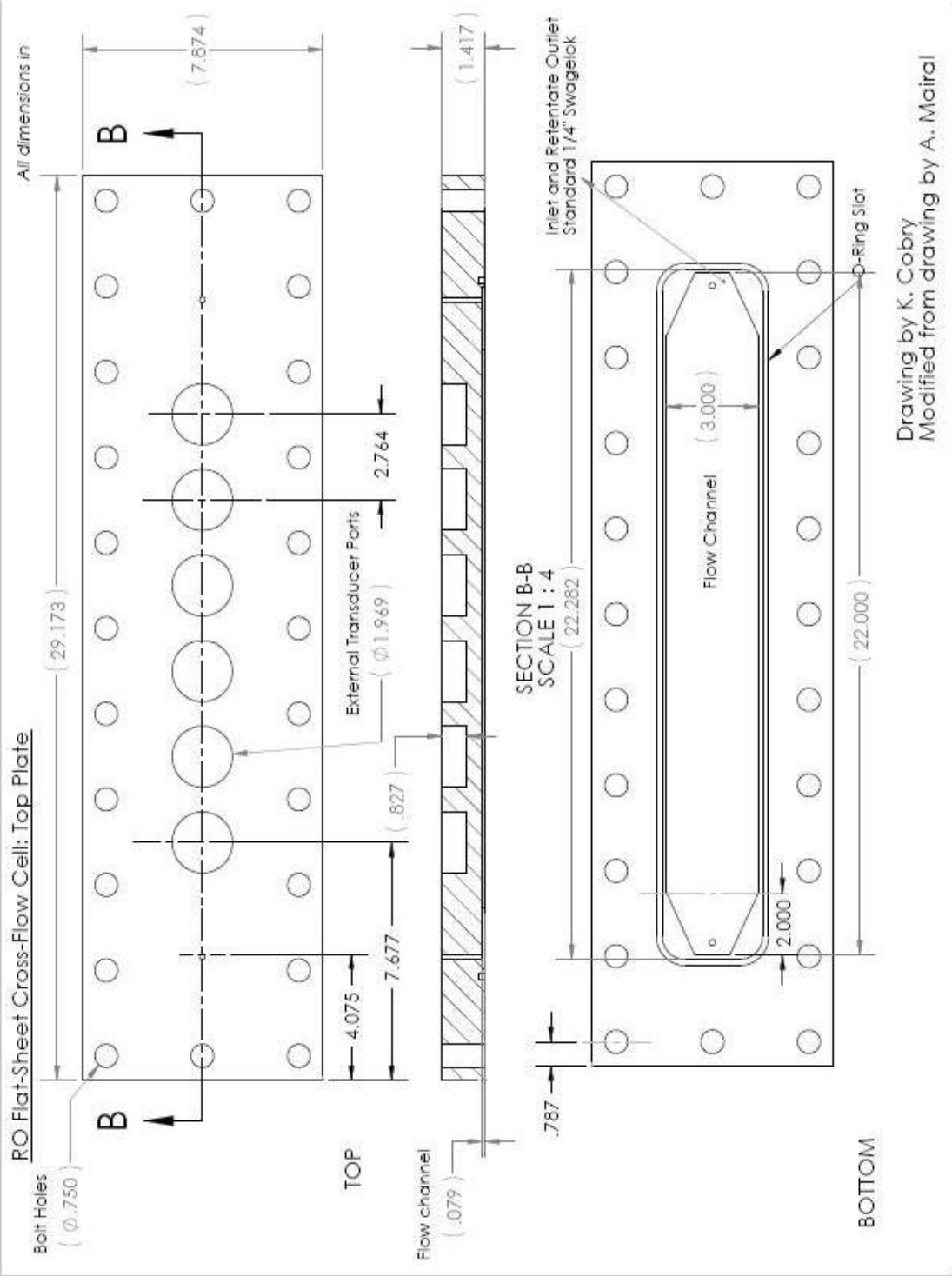


(10) Cut electrodes from 1" Kapton square.

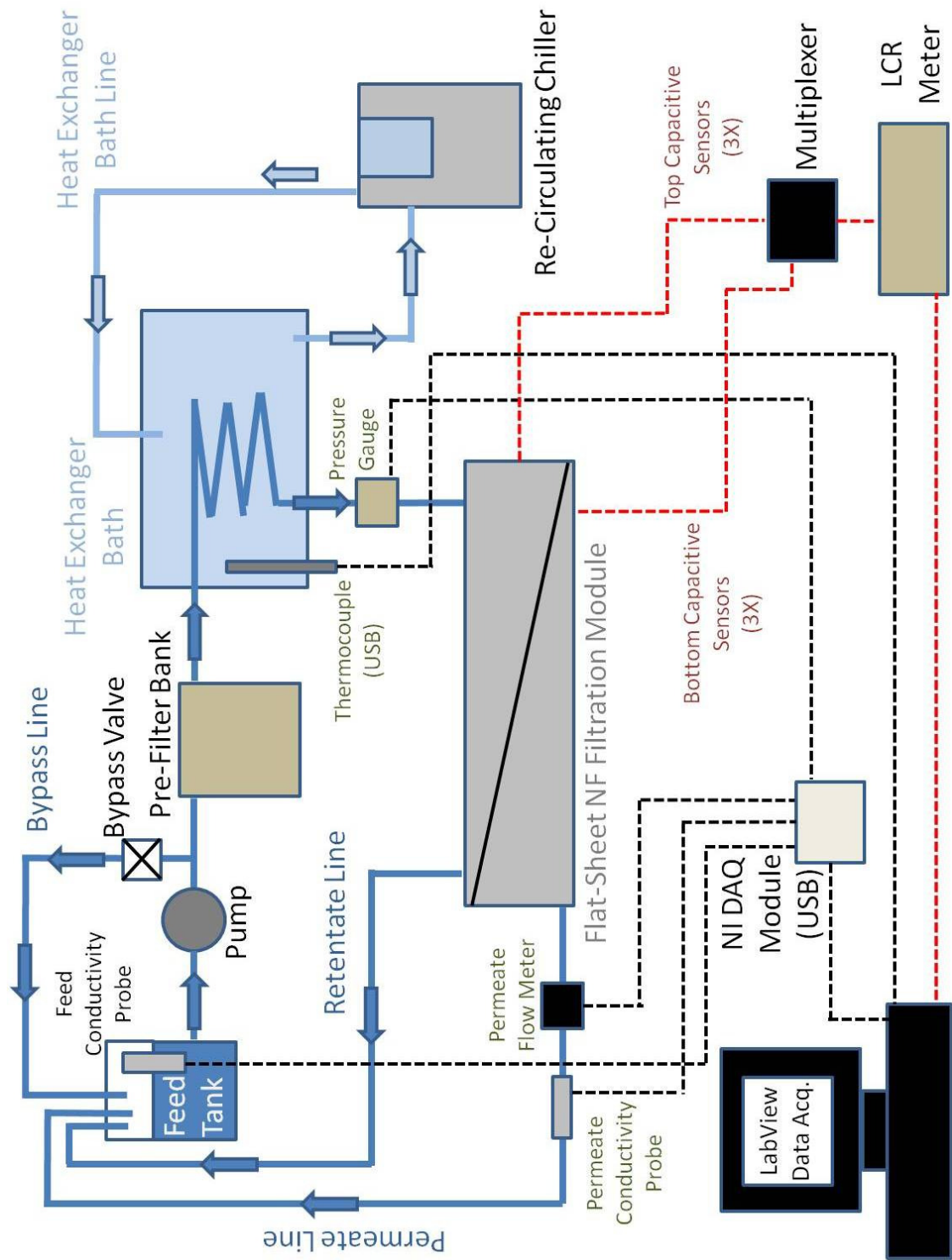
Appendix B: Engineering Drawings of Flat-Sheet Cross Flow Module



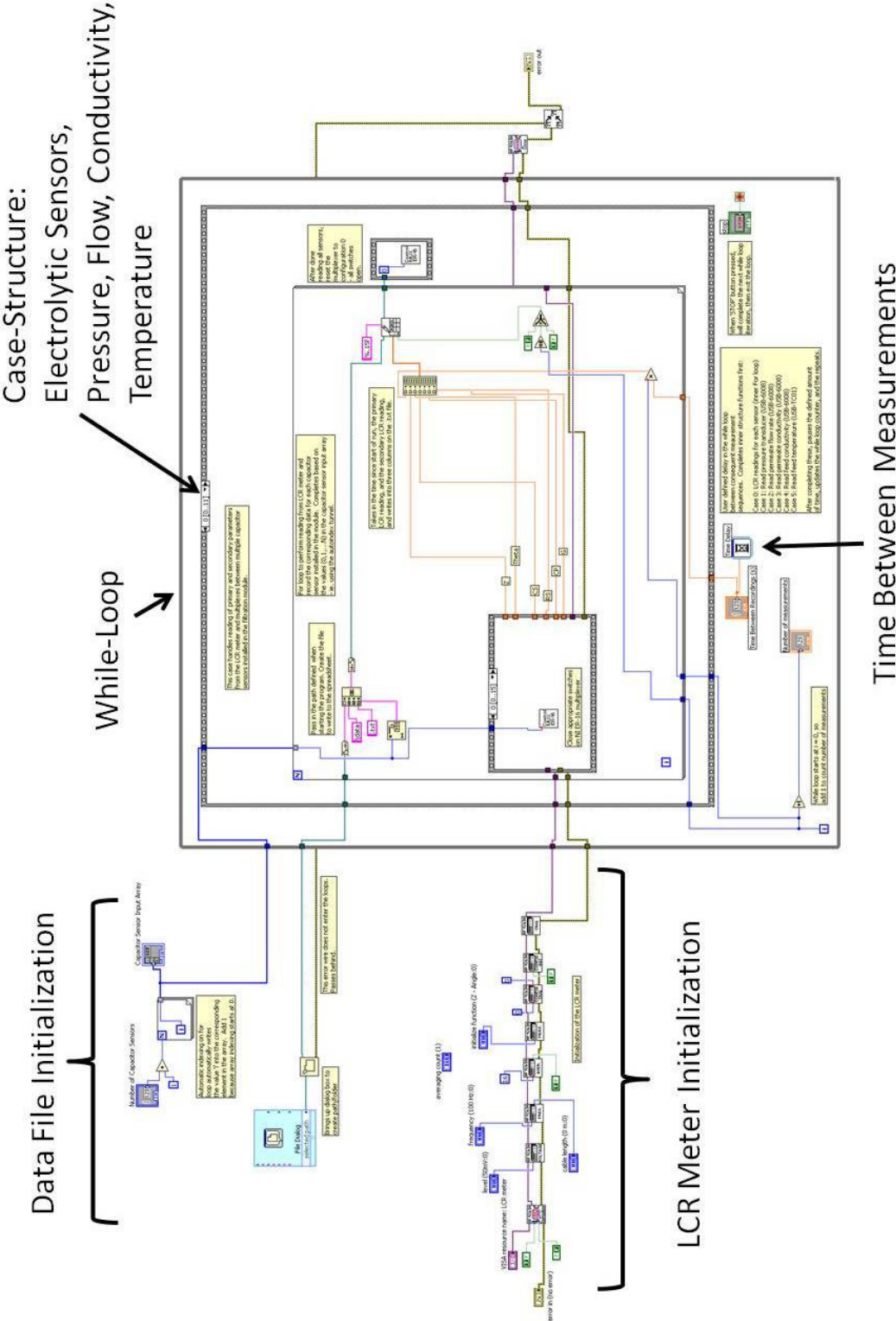
Drawing by K. Cobry
Modified from drawing by A. Mairal

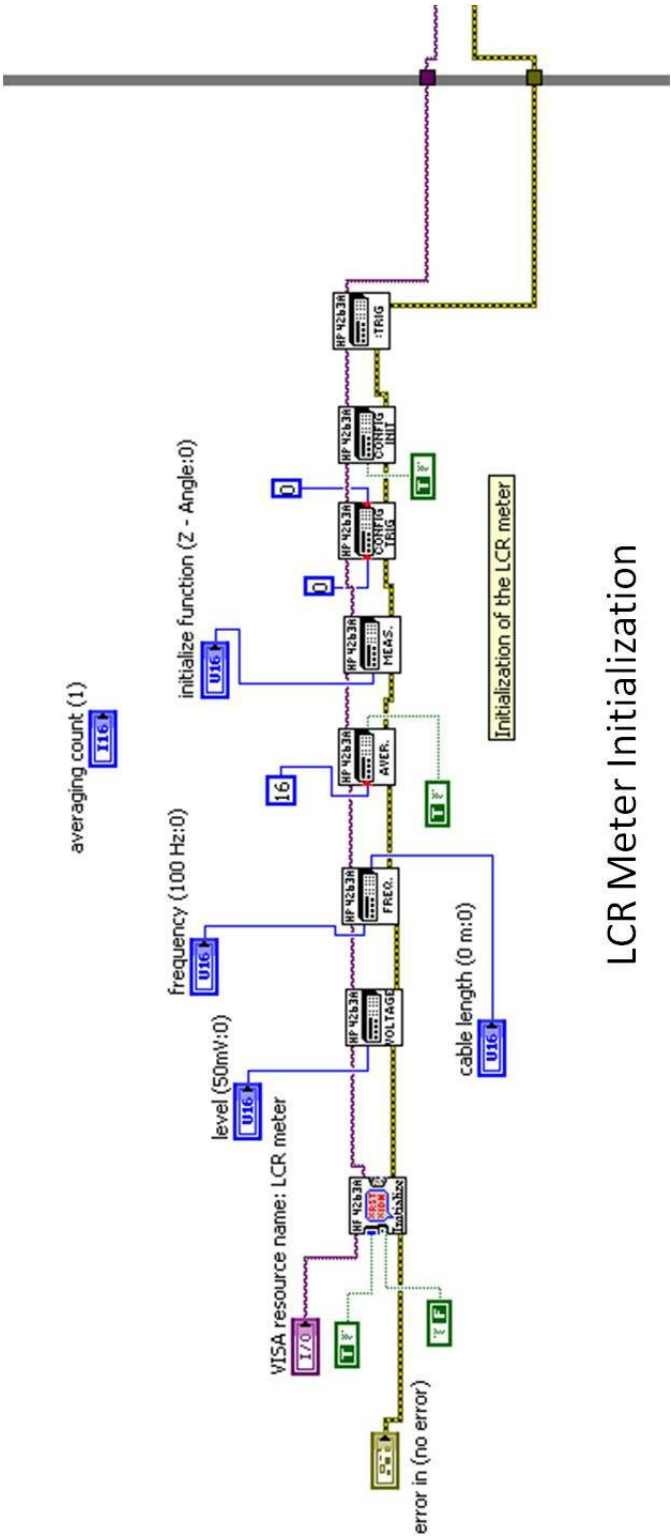


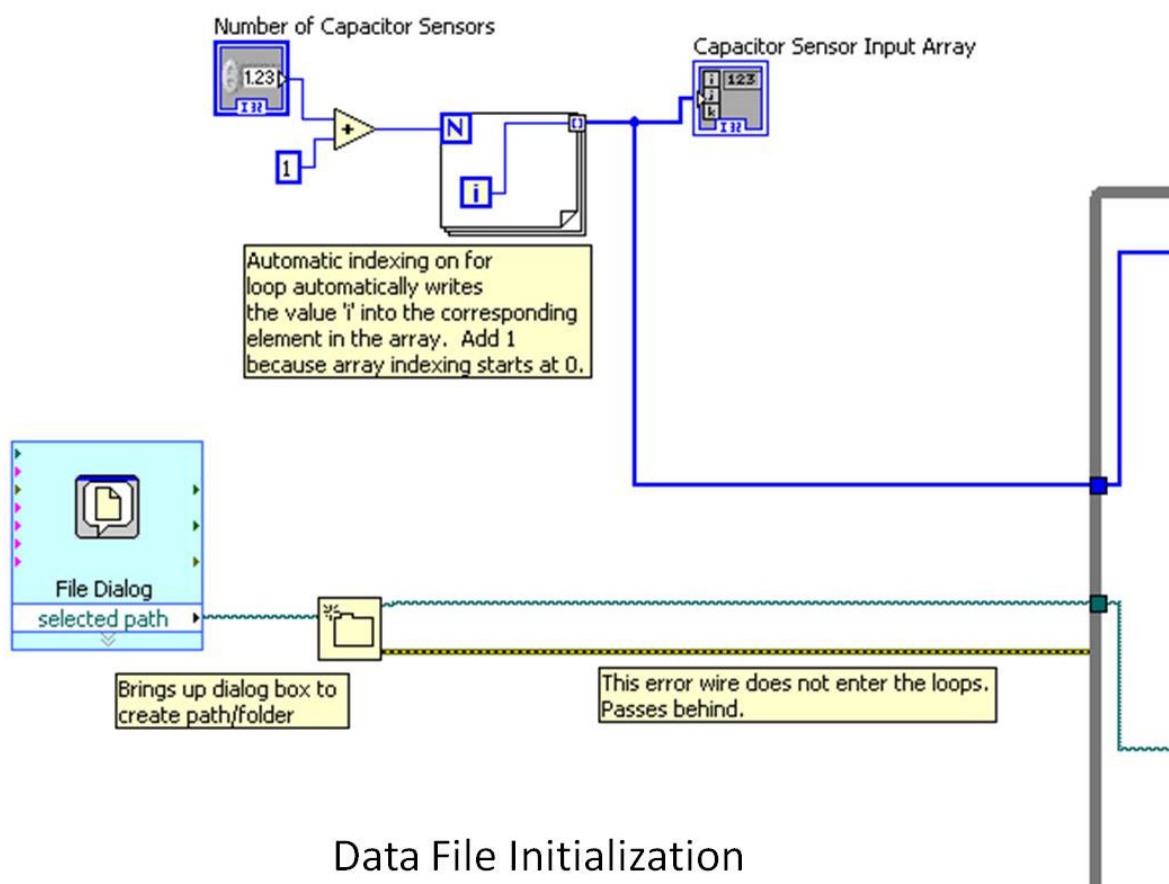
Appendix C: Schematic of Integrated Hydraulic and Electronic System: Electrolytic Experiments



Appendix D: LabView Code for Real-Time Acquisition of Electrolytic Data

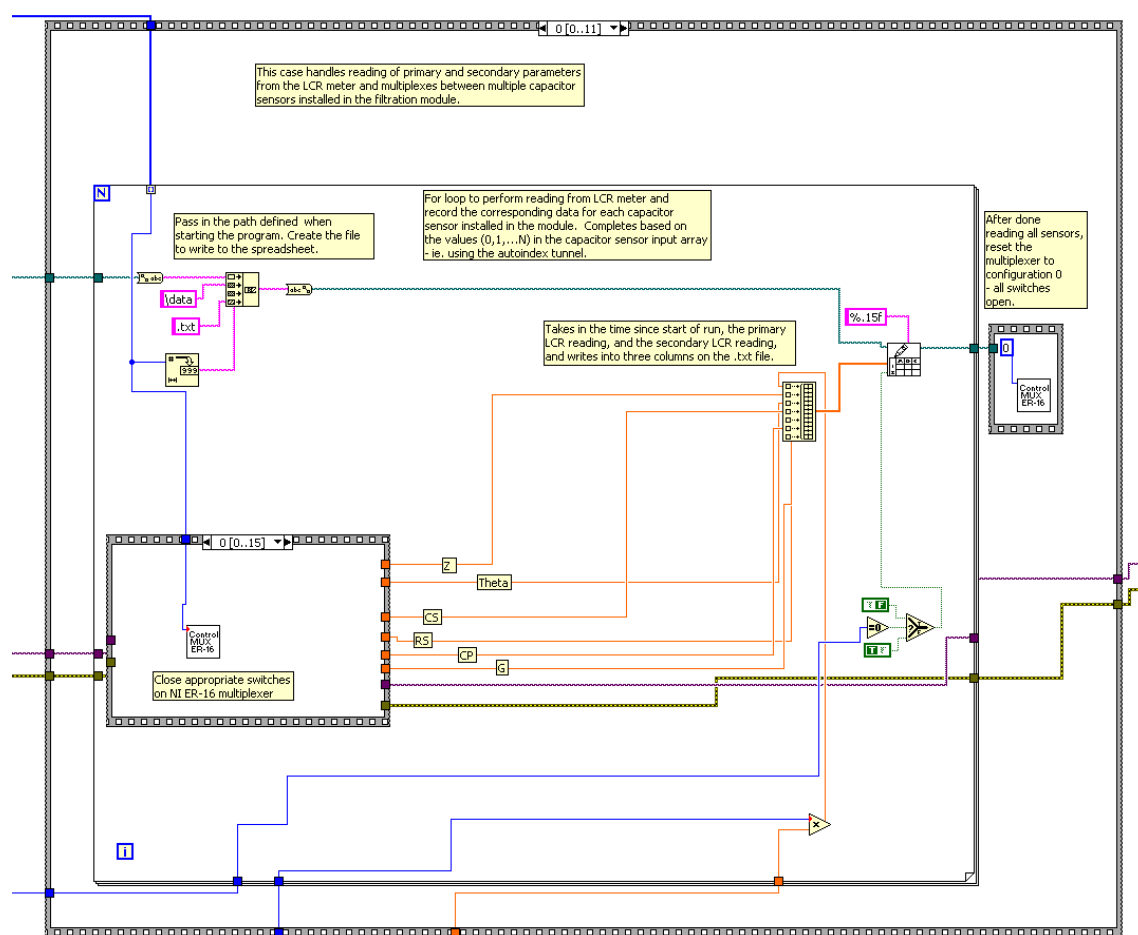




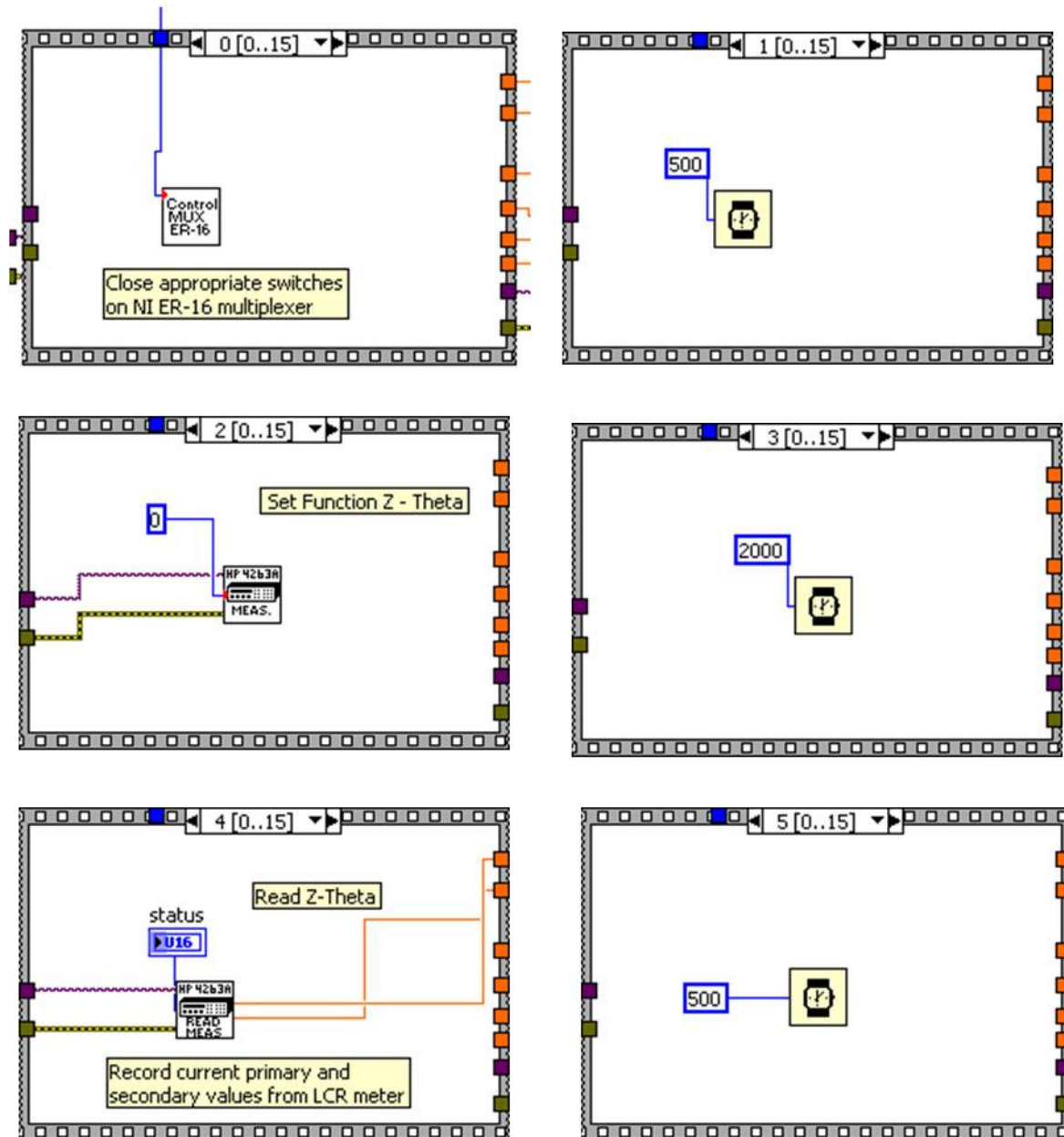


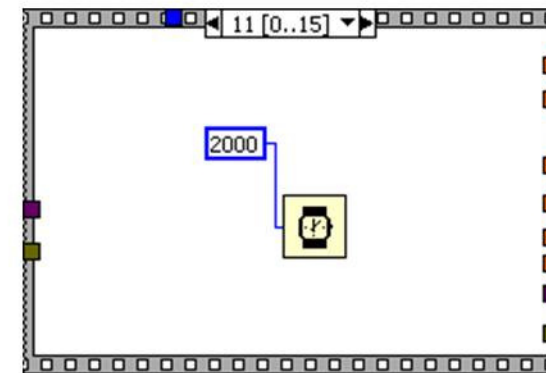
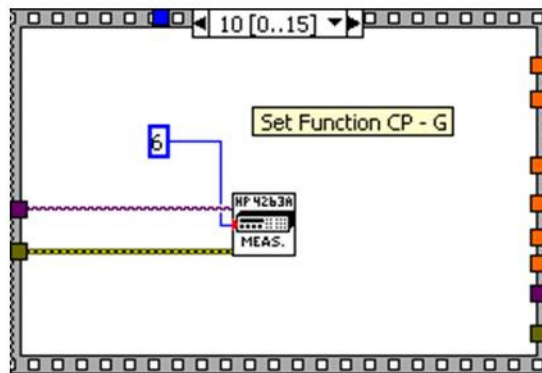
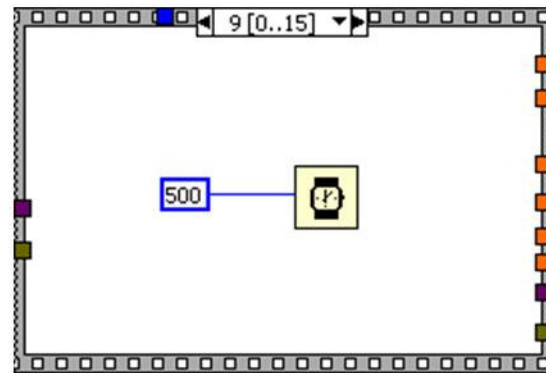
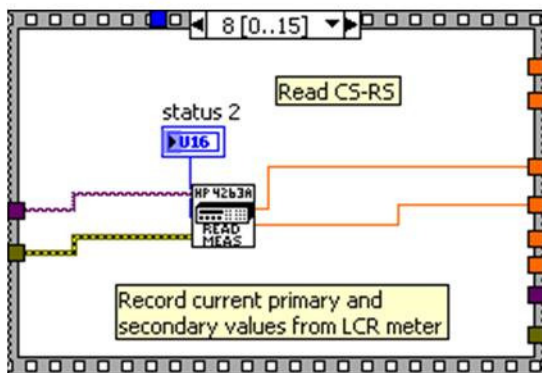
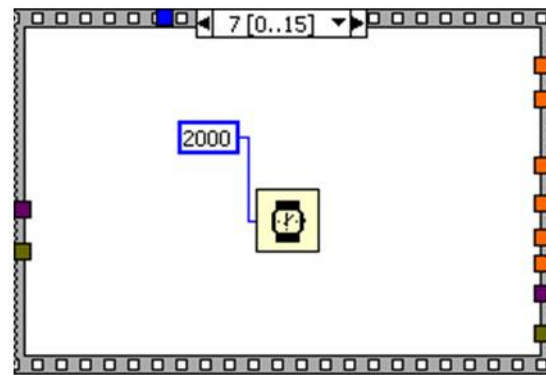
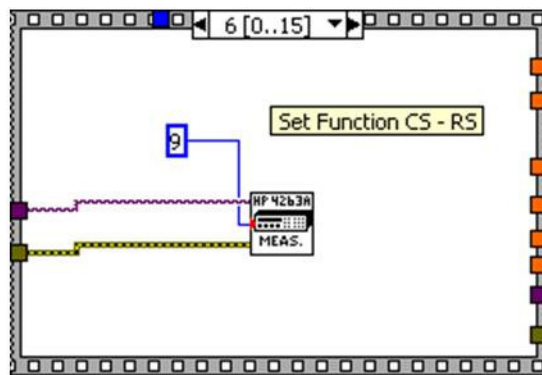
Measure and Record Case Structure

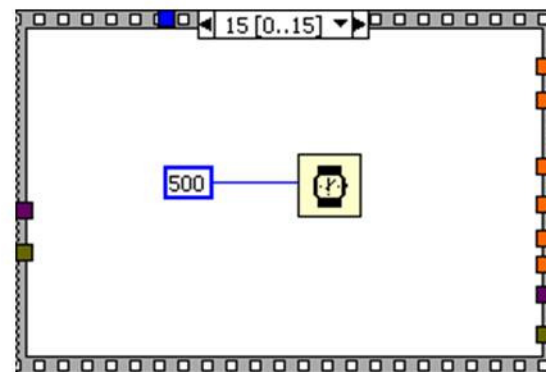
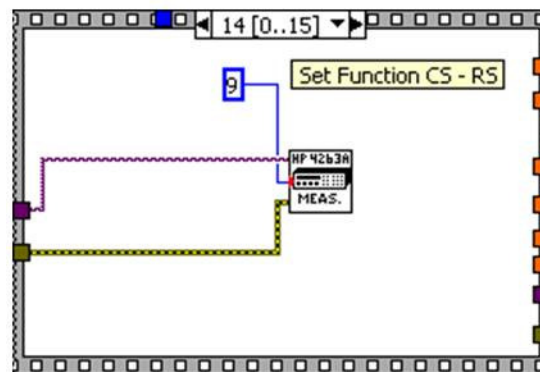
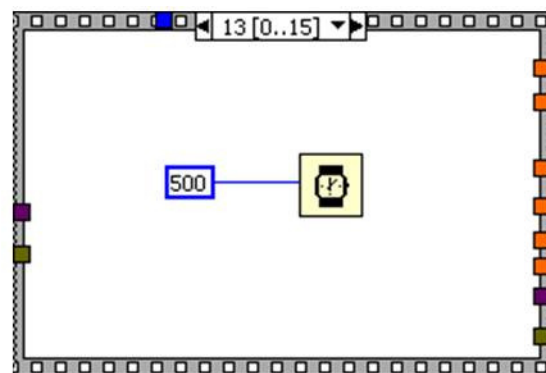
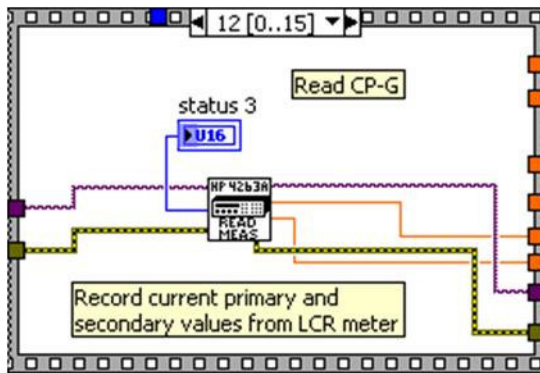
A case structure consisting of multiple frames is used for measuring and recording output from system monitoring devices: integrated electrolytic sensors (case 0), pressure (case 2), permeate flow rate (case 4), permeate conductivity (case 6), feed conductivity (case 8), and feed temperature (case 10). A 0.5 second pause is included before switching from one device to the next. The pressure transducer, permeate flow rate meter and permeate and feed conductivity probes are 0-5 V output devices that interface with LabView via a NI USB 6008 data acquisition module. The integrated electrolytic sensors interface through an LCR meter via GPIB, and the thermocouple interfaces via a NI USB-TC01 data acquisition module. The case structure frames for the electrolytic sensor measurements and pressure measurement are shown in this appendix. The frames for the remaining measurements follow a form similar to that of the pressure sensor frame.



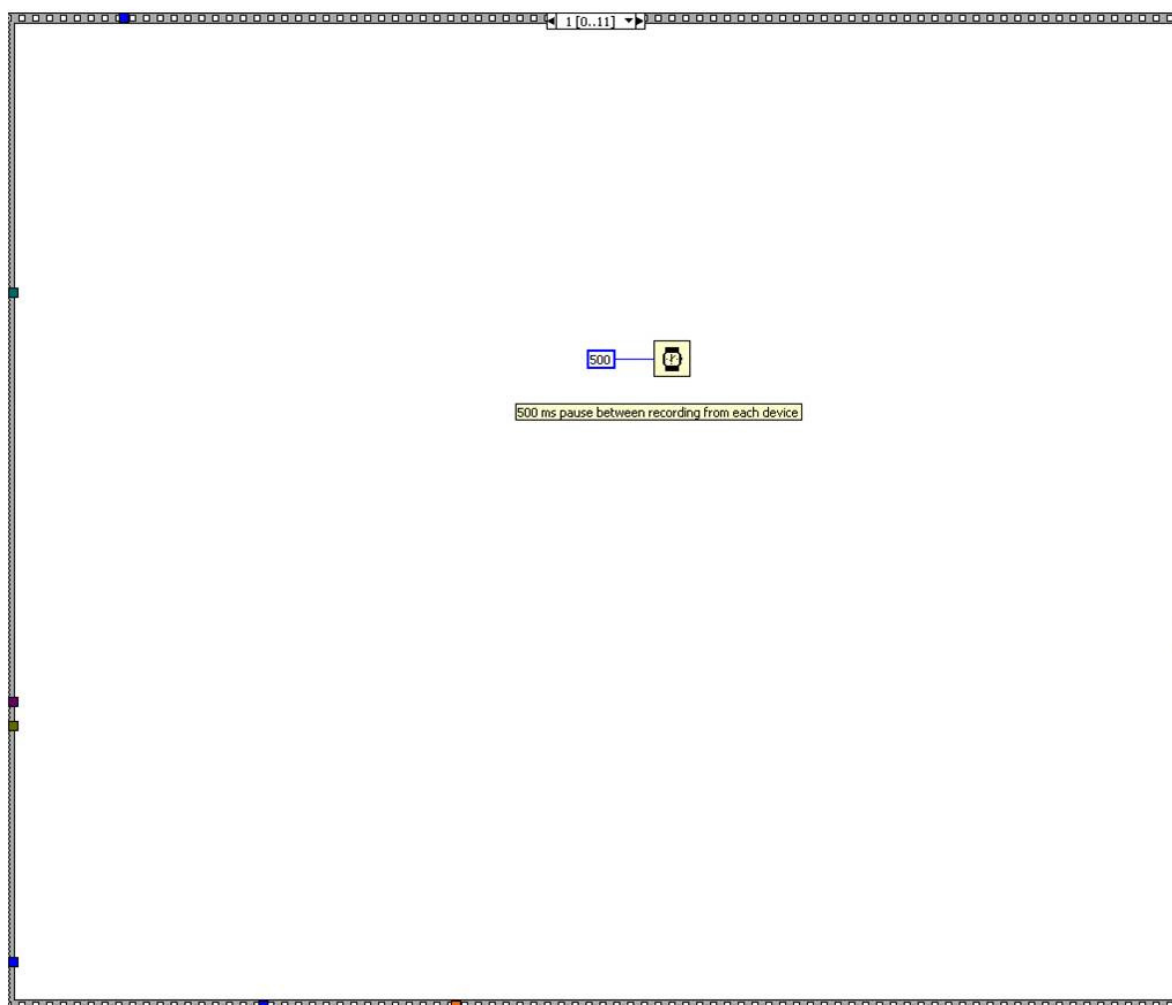
Switch Multiplexer to Correct Sensor Record Multiple Electronic Parameters



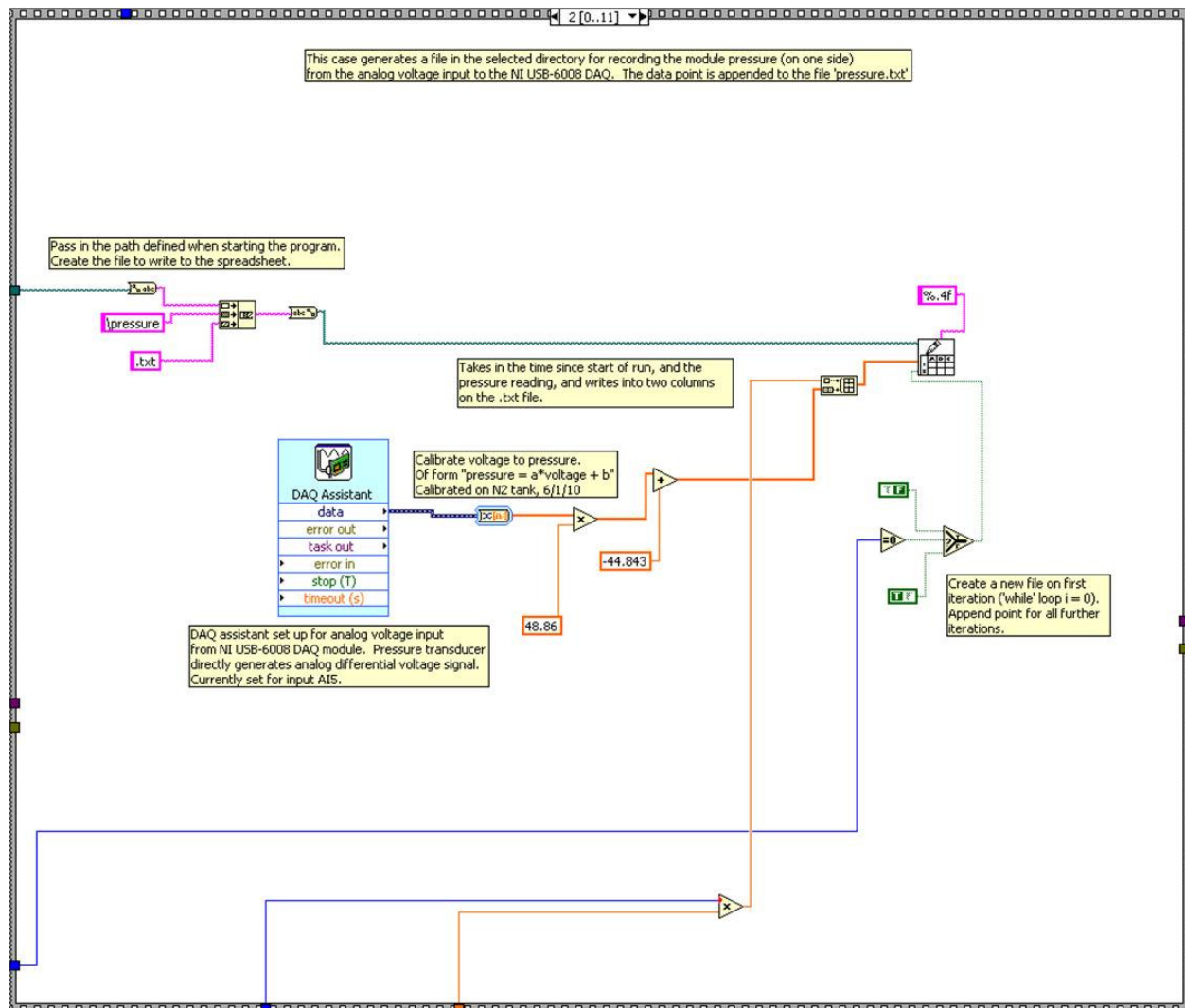




Pause Between Switching Devices



Record Pressure from Pressure Transducer Calibrated 0-5 V Output



Appendix E: Matlab Code for Real-Time Plotting of Electrolytic Data

```
% PlotElectrData_6Channel_realtime.m
% Load electronic data from each sensor channel, multiple parameters.
% Plot the data for each channel vs. time - real time.

% Keith Cobry
% University of Colorado, Department of Mechanical Engineering

close all
clear all

% Multiplexer-switch/sensor-electrode info:
% Device 0, Not connected - All open
% Device 1, Membrane Up. - NO1 and NO3 closed
% Device 2, Membrane Mid. - NO6 and NO8 closed
% Device 3, Membrane Down. - NO9 and NO11 closed
% Device 4, Bulk Up. - NO14 and NO16 closed
% Device 5, Bulk Mid. - NO12 and NO15 closed
% Device 6, Bulk Down. - NO4 and NO2 closed

% Initialize the size of the data file and total time
data_size0 = 0;
data_size1 = 0;
data_size2 = 0;
data_size3 = 0;
data_size4 = 0;
data_size5 = 0;
data_size6 = 0;

% Loop until program terminated with "ctrl+c"
while(1)
    % get file info on the files in the directory that LabView had
    % written to
    f0 = dir('data0.txt');
    f1 = dir('data1.txt');
    f2 = dir('data2.txt');
    f3 = dir('data3.txt');
    f4 = dir('data4.txt');
    f5 = dir('data5.txt');
    f6 = dir('data6.txt');
```

```

% specifically, get each file's current size
new_data_size0 = f0.bytes;
new_data_size1 = f1.bytes;
new_data_size2 = f2.bytes;
new_data_size3 = f3.bytes;
new_data_size4 = f4.bytes;
new_data_size5 = f5.bytes;
new_data_size6 = f6.bytes;

% if the size of any of the files is the same as the last time it
% was checked (every 0.5 sec), pause and check again.
if (data_size0 == new_data_size0 || data_size1 == new_data_size1
    || data_size2 == new_data_size2 || data_size3 ==
    new_data_size3 || data_size4 == new_data_size4 || data_size5
    == new_data_size5 || data_size6 == new_data_size6)

    pause(0.5);

else
% if the size of every file is different than the last time it was
% checked (data has been added),
% update the size of each, and proceed
    data_size0 = new_data_size0;
    data_size1 = new_data_size1;
    data_size2 = new_data_size2;
    data_size3 = new_data_size3;
    data_size4 = new_data_size4;
    data_size5 = new_data_size5;
    data_size6 = new_data_size6;

% Now that the files have been updated with new data, load them.
% These consist of three columns
% (1) Time, (2) Primary Reading, (3) Secondary Reading
    data0 = load('data0.txt');
    data1 = load('data1.txt');
    data2 = load('data2.txt');
    data3 = load('data3.txt');
    data4 = load('data4.txt');
    data5 = load('data5.txt');
    data6 = load('data6.txt');

% Also load the data from the thermocouple, flow meter,
% conductivity meters and pressure gauge to plot.
    feedcond = load('feedcond.txt');
    feedtemp = load('feedtemp.txt');
    permeatecond = load('permeatecond.txt');
    permeaterate = load('permeaterate.txt');
    pressure = load('pressure.txt');

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Multiplier Factors to get desired units when plotting.
    TimeMultFact = 1/60; % sec -> min
    ImpMultFact = 1/1e3; % Ohm -> kOhm
    CapMultFact = 1/1e-9; % F -> nF
    ResMultFact = 1/1e3; % Ohm -> kOhm
    InductMultFact = 1/1e-3; % H -> mH
    CondMultFact = 1e6; % S -> uS

% Plot Z, Theta for each of the sensors
% Z, Theta, membrane sensors
figure(1)
subplot(2,1,1),
plot(data1(:,1)*TimeMultFact, data1(:,2)*ImpMultFact,'r')
hold on
plot(data2(:,1)*TimeMultFact, data2(:,2)*ImpMultFact,'b')
hold on
plot(data3(:,1)*TimeMultFact, data3(:,2)*ImpMultFact,'k')
title('Impedance - Membrane Sensors')
xlabel('time [min]')
ylabel('Impedance [kOhm]')
legend('up','mid','down')

subplot(2,1,2),
plot(data1(:,1)*TimeMultFact, data1(:,3),'r')
hold on
plot(data2(:,1)*TimeMultFact, data2(:,3),'b')
hold on
plot(data3(:,1)*TimeMultFact, data3(:,3),'k')
title('Phase Angle - Membrane Sensors')
xlabel('time [min]')
ylabel('Phase Angle [deg]')
legend('up','mid','down')

% Z, Theta, top sensors
figure(2)
subplot(2,1,1),
plot(data4(:,1)*TimeMultFact, data4(:,2)*ImpMultFact,'r')
hold on
plot(data5(:,1)*TimeMultFact, data5(:,2)*ImpMultFact,'b')
hold on
plot(data6(:,1)*TimeMultFact, data6(:,2)*ImpMultFact,'k')
title('Impedance - Bulk Sensors')
xlabel('time [min]')
ylabel('Impedance [kOhm]')
legend('up','mid','down')

subplot(2,1,2),
plot(data4(:,1)*TimeMultFact, data4(:,3),'r')

```

```

hold on
plot(data5(:,1)*TimeMultFact, data5(:,3), 'b')
hold on
plot(data6(:,1)*TimeMultFact, data6(:,3), 'k')
title('Phase Angle - Bulk Sensors')
xlabel('time [min]')
ylabel('Phase Angle [deg]')
legend('up', 'mid', 'down')

% Plot CS, RS for each of the sensors
% CS, RS, membrane sensors
figure(3)
subplot(2,1,1),
plot(data1(:,1)*TimeMultFact, data1(:,4)*CapMultFact, 'r')
hold on
plot(data2(:,1)*TimeMultFact, data2(:,4)*CapMultFact, 'b')
hold on
plot(data3(:,1)*TimeMultFact, data3(:,4)*CapMultFact, 'k')
title('Capacitance - Membrane Sensors')
xlabel('time [min]')
ylabel('Capacitance [nF]')
legend('up', 'mid', 'down')

subplot(2,1,2),
plot(data1(:,1)*TimeMultFact, data1(:,5)*ResMultFact, 'r')
hold on
plot(data2(:,1)*TimeMultFact, data2(:,5)*ResMultFact, 'b')
hold on
plot(data3(:,1)*TimeMultFact, data3(:,5)*ResMultFact, 'k')
title('Resistance - Membrane Sensors')
xlabel('time [min]')
ylabel('Resistance [kOhm]')
legend('up', 'mid', 'down')

% CS, RS, top sensors
figure(4)
subplot(2,1,1),
plot(data4(:,1)*TimeMultFact, data4(:,4)*CapMultFact, 'r')
hold on
plot(data5(:,1)*TimeMultFact, data5(:,4)*CapMultFact, 'b')
hold on
plot(data6(:,1)*TimeMultFact, data6(:,4)*CapMultFact, 'k')
title('Capacitance - Bulk Sensors')
xlabel('time [min]')
ylabel('Capacitance [nF]')
legend('up', 'mid', 'down')

```

```

subplot(2,1,2),
plot(data4(:,1)*TimeMultFact, data4(:,5)*ResMultFact,'r')
hold on
plot(data5(:,1)*TimeMultFact, data5(:,5)*ResMultFact,'b')
hold on
plot(data6(:,1)*TimeMultFact, data6(:,5)*ResMultFact,'k')
title('Resistance - Bulk Sensors')
xlabel('time [min]')
ylabel('Resistance [kOhm]')
legend('up','mid','down')

% Plot CP, G for each of the sensors
% CP, G, membrane sensors
figure(5)
subplot(2,1,1),
plot(data1(:,1)*TimeMultFact, data1(:,6)*CapMultFact,'r')
hold on
plot(data2(:,1)*TimeMultFact, data2(:,6)*CapMultFact,'b')
hold on
plot(data3(:,1)*TimeMultFact, data3(:,6)*CapMultFact,'k')
title('Capacitance (CP) - Membrane Sensors')
xlabel('time [min]')
ylabel('Capacitance [nF]')
legend('up','mid','down')

subplot(2,1,2),
plot(data1(:,1)*TimeMultFact, data1(:,7)*CondMultFact,'r')
hold on
plot(data2(:,1)*TimeMultFact, data2(:,7)*CondMultFact,'b')
hold on
plot(data3(:,1)*TimeMultFact, data3(:,7)*CondMultFact,'k')
title('Conductance - Membrane Sensors')
xlabel('time [min]')
ylabel('Conductance [uS]')
legend('up','mid','down')

% CP, G, top sensors
figure(6)
subplot(2,1,1),
plot(data4(:,1)*TimeMultFact, data4(:,6)*CapMultFact,'r')
hold on
plot(data5(:,1)*TimeMultFact, data5(:,6)*CapMultFact,'b')
hold on
plot(data6(:,1)*TimeMultFact, data6(:,6)*CapMultFact,'k')
title('Capacitance (CP) - Bulk Sensors')
xlabel('time [min]')
ylabel('Capacitance [nF]')
legend('up','mid','down')

```

```

subplot(2,1,2),
plot(data4(:,1)*TimeMultFact, data4(:,7)*CondMultFact,'r')
hold on
plot(data5(:,1)*TimeMultFact, data5(:,7)*CondMultFact,'b')
hold on
plot(data6(:,1)*TimeMultFact, data6(:,7)*CondMultFact,'k')
title('Conductance - Bulk Sensors')
xlabel('time [min]')
ylabel('Conductance [uS]')
legend('up','mid','down')

% Plot temperature, pressure, permeate flow rate
figure(7)
subplot(3,1,1),
plot(feedtemp(:,1)*TimeMultFact, feedtemp(:,2))
title('Feed Temperature')
xlabel('time [min]')
ylabel('temperature [deg C]')

subplot(3,1,2),
plot(pressure(:,1)*TimeMultFact, pressure(:,2))
title('Pressure')
xlabel('time [min]')
ylabel('pressure [psi]')

subplot(3,1,3),
plot(permeaterate(:,1)*TimeMultFact, permeaterate(:,2))
title('Permeate Flow Rate')
xlabel('time [min]')
ylabel('flow rate [mL/min]')

% Plot permeate and feed conductivities
% let's also calculate the observed rejection, based on
% conductivity
R_obs = 1 - permeatecond(:,2)./feedcond(:,2);
figure(8)
subplot(3,1,1),
plot(feedcond(:,1)*TimeMultFact, feedcond(:,2))
title('Feed Conductivity')
xlabel('time [min]')
ylabel('conductivity [uS/cm]')

```

```

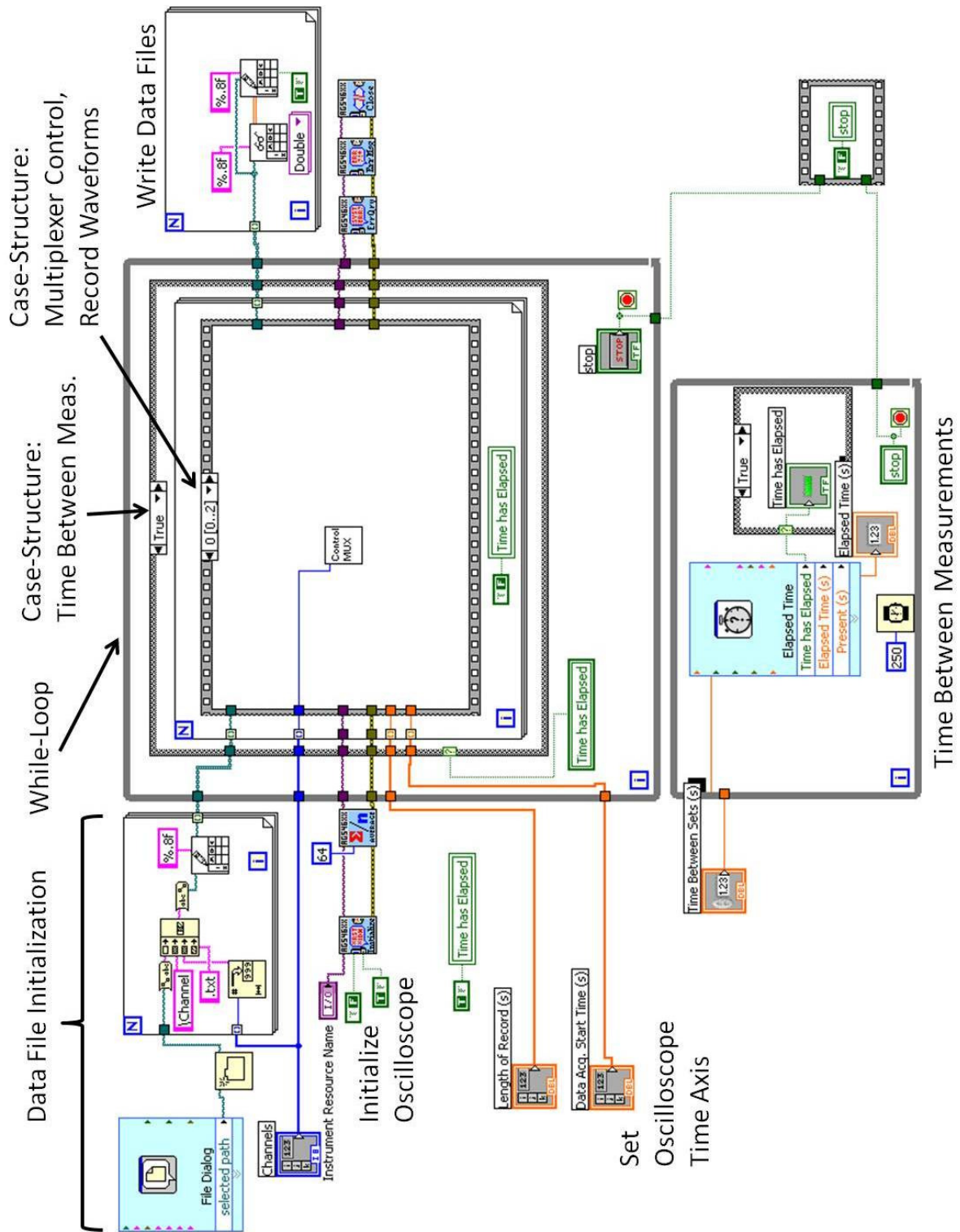
subplot(3,1,2),
plot(permeatecond(:,1)*TimeMultFact, permeatecond(:,2))
title('Permeate Conductivity')
xlabel('time [min]')
ylabel('conductivity [uS/cm]')

subplot(3,1,3),
plot(permeatecond(:,1)*TimeMultFact, R_obs)
title('Observed Rejection.  $R = 1 - R_p/R_b$ ')
xlabel('time [min]')
ylabel('R obs.')

end % for the if else structure (all the data files updated)
end % for the while loop

```

Appendix F: LabView Code for Real-Time Acquisition of Ultrasonic Waveforms



Appendix G: Matlab Code for Real-Time Analysis of Ultrasonic Waveforms

```
% ProcessWaveforms.m

% Load echo waveform vectors from each transducer stored in active
% directory.

% Calculate the cross-correlation rms similarity factor between the
% reference waveform from each transducer (at time = t_ref) and all
% other waveforms from the same respective transducer.

% Normalize and plot the processed ultrasonic data.

% Keith Cobry
% University of Colorado, Department of Mechanical Engineering

close all
clear all

testdate = 'xxxxxx';

% Correspondence between multiplexer channel and integrated
% transducers
ch1 = 'Upstream Internal Sensor';
ch2 = 'Midstream Internal Sensor';
ch3 = 'Downstream Internal Sensor';
ch4 = 'Upstream External Sensor';
ch5 = 'Midstream External Sensor';
ch6 = 'Downstream External Sensor';

% initialize the size of the data files
data_size1 =0;
data_size2 =0;
data_size3 =0;
data_size4 =0;
data_size5 =0;
data_size6 =0;

recordindex = 1; % initialize while-loop index

% continue looping until program is terminated with "ctrl+c"
while(1)

    % Record information on saved waveform files
    f1=dir('Channel1.txt');
    f2=dir('Channel2.txt');
    f3=dir('Channel3.txt');
    f4=dir('Channel4.txt');
```

```

f5=dir('Channel5.txt');
f6=dir('Channel6.txt');

% Reset the current file sizes (bytes)
new_data_size1=f1.bytes;
new_data_size2=f2.bytes;
new_data_size3=f3.bytes;
new_data_size4=f4.bytes;
new_data_size5=f5.bytes;
new_data_size6=f6.bytes;

% check whether new data have been appended to the waveform files
% if new data have been appended, proceed with analysis
if (data_size1==new_data_size1 || data_size2==new_data_size2
    || data_size3==new_data_size3 || data_size4==new_data_size4
    || data_size5==new_data_size5 || data_size6==new_data_size6)

    pause(0.5);

else

    % update the file sizes
    data_size1=new_data_size1;
    data_size2=new_data_size2;
    data_size3=new_data_size3;
    data_size4=new_data_size4;
    data_size5=new_data_size5;
    data_size6=new_data_size6;

    %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
    % Load the raw waveform data recorded by Labview
    Channel1 = load(Channel1.txt);
    Channel2 = load(Channel2.txt);
    Channel3 = load(Channel3.txt);
    Channel4 = load(Channel4.txt);
    Channel5 = load(Channel5.txt);
    Channel6 = load(Channel6.txt);

    %recordindex = recordindex + 1;

```

```

% These data are recorded midway thru the run, so transpose
% rows: waveform vector data points
% columns: number of waveforms from each transducer
Channel1 = Channel1';
Channel2 = Channel2';
Channel3 = Channel3';
Channel4 = Channel4';
Channel5 = Channel5';
Channel6 = Channel6';

% get the dimensions of the waveform vectors
% the dimensions of all arrays are the same
sizedata = size(Channel1);
numcolumns = sizedata(2); % columns: number of waveforms

% interval between subsequent measurements [min]
intervaltime = 10;
% set up time axis for filtration run [min]
time = 0:recordinterval:(numcolumns-1)*recordinterval;

% then smooth the waveforms using the function fastsmooth.m
% (from Matlab Centra File Exchange) - sliding averaging.
% a larger pointwise "smoothfactor" rounds it more
% third arg: 3 is equivalent to 3 sliding averaging passes
% (pseudo gaussian)
% fourth arg: 1 smooths the edges
% Further processing will use the smoothed data
% smooth the data, since the raw data can be choppy
smoothfactor = 30;
for i = 1:numcolumns
    data1(:,i) = Channel1(:,i);
    smoothdata1(:,i)= fastsmooth(data1(:,i),smoothfactor,3,1);
    data2(:,i) = Channel2(:,i);
    smoothdata2(:,i)= fastsmooth(data2(:,i),smoothfactor,3,1);
    data3(:,i) = Channel3(:,i);
    smoothdata3(:,i)= fastsmooth(data3(:,i),smoothfactor,3,1);
    data4(:,i) = Channel4(:,i);
    smoothdata4(:,i)= fastsmooth(data4(:,i),smoothfactor,3,1);
    data5(:,i) = Channel5(:,i);
    smoothdata5(:,i)= fastsmooth(data5(:,i),smoothfactor,3,1);
    data6(:,i) = Channel6(:,i);
    smoothdata6(:,i)= fastsmooth(data6(:,i),smoothfactor,3,1);
end

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Cross-correlation of echo signals

reftime = 1200; % time during filtration run of reference
                % waveform. Slightly before switch in feed.
                % [min]
% index of reference waveform
refechonum = floor(reftime/intervaltime);

% use function echo_xcorr to calculate rms cross-correlation
% similarity values for each transducer.
% input smoothed waveforms, reference waveform index,...
% returns vector of normalized rms cross-correlation values
[rmsxcorrel1] = echo_xcorr(smoothdata1, refechonum,
                           numcolumns, intervaltime);
[rmsxcorrel2] = echo_xcorr(smoothdata2, refechonum,
                           numcolumns, intervaltime);
[rmsxcorrel3] = echo_xcorr(smoothdata3, refechonum,
                           numcolumns, intervaltime);
[rmsxcorrel4] = echo_xcorr(smoothdata4, refechonum,
                           numcolumns, intervaltime);
[rmsxcorrel5] = echo_xcorr(smoothdata5, refechonum,
                           numcolumns, intervaltime);
[rmsxcorrel6] = echo_xcorr(smoothdata6, refechonum,
                           numcolumns, intervaltime);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Plot data

% Internal acoustic responses
figure
plot(time,rmsxcorrel1,'r.')
hold on
plot(time,rmsxcorrel2,'b*')
hold on
plot(time,rmsxcorrel3,'kv')
xlabel('time [min]')
ylabel('normalized ultrasonic response')
title('Acoustic Response - Internal Sensors')
legend('Upstream','Midstream','Downstream')

```

```

    % External acoustic responses
    figure
    plot(time,rmsxcorrel4,'r.')
    hold on
    plot(time,rmsxcorrel5,'b*')
    hold on
    plot(time,rmsxcorrel6,'kv')
    xlabel('time [min]')
    ylabel('normalized ultrasonic response')
    title('Acoustic Response - External Sensors')
    legend('Upstream','Midstream','Downstream')

end   %% for the if else structure (all the data file updated)
end   %% for the while loop

```

```

function SmoothY=fastsmooth(Y,w,type,ends)

% from Matlab Central File Exchange

% fastbsmooth(Y,w,type,ends) smooths vector Y with smooth
% of width w. Version 2.0, May 2008.
% The argument "type" determines the smooth type:
%   If type=1, rectangular (sliding-average or boxcar)
%   If type=2, triangular (2 passes of sliding-average)
%   If type=3, pseudo-Gaussian (3 passes of sliding-average)
% The argument "ends" controls how the "ends" of the signal
% (the first w/2 points and the last w/2 points) are handled.
%   If ends=0, the ends are zero. (In this mode the elapsed
%   time is independent of the smooth width). The fastest.
%   If ends=1, the ends are smoothed with progressively
%   smaller smooths the closer to the end. (In this mode the
%   elapsed time increases with increasing smooth widths).
% fastsmooth(Y,w,type) smooths with ends=0.
% fastsmooth(Y,w) smooths with type=1 and ends=0.
% Example:
% fastsmooth([1 1 1 10 10 10 1 1 1 1],3)= [0 1 4 7 10 7 4 1 1 0]
% fastsmooth([1 1 1 10 10 10 1 1 1 1],3,1,1)= [1 1 4 7 10 7 4 1 1 1]
% T. C. O'Haver, May, 2008.

if nargin==2, ends=0; type=1; end
if nargin==3, ends=0; end
switch type
    case 1
        SmoothY=sa(Y,w,ends);
    case 2
        SmoothY=sa(sa(Y,w,ends),w,ends);
    case 3
        SmoothY=sa(sa(sa(Y,w,ends),w,ends),w,ends);
end

function SmoothY=sa(Y,smoothwidth,ends)
w=round(smoothwidth);
SumPoints=sum(Y(1:w));
s=zeros(size(Y));
halfw=round(w/2);
L=length(Y);
for k=1:L-w,
    s(k+halfw-1)=SumPoints;
    SumPoints=SumPoints-Y(k);
    SumPoints=SumPoints+Y(k+w);
end
s(k+halfw)=sum(Y(L-w+1:L));
SmoothY=s./w;

```

```

% Taper the ends of the signal if ends=1.
if ends==1,
    startpoint=(smoothwidth + 1)/2;
    SmoothY(1)=(Y(1)+Y(2))./2;
    for k=2:startpoint,
        SmoothY(k)=mean(Y(1:(2*k-1)));
        SmoothY(L-k+1)=mean(Y(L-2*k+2:L));
    end
    SmoothY(L)=(Y(L)+Y(L-1))./2;
end

```



```

function normrmsxcorrel = echo_xcorr(data, refechonum, numcolumns,
intervaltime)

% Call waveform array from given transducer (input)

% Calculate cross-correlation between reference waveform and all
% others. Select rms value of cross-correlation vector and normalize
% to the rms value of the autocorrelation. Forms a vector of rms
% 'similarity' values for all waveforms recorded over the duration of
% the filtration run.

% normalize and return rms cross-correlation vector to main function
% for plotting.

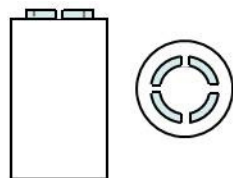
tracenumber = 1:1:numcolumns;

for i = 1:numcolumns
    % calculate cross-correlation vector
    % 'coef' normalizes to the autocorrelation = 1
    xcorrel(:,i) = abs(xcorr(data(:,refechonum),data(:,i),'coef'));
    % calculate rms value of cross-correlation vector
    rmsxcorrel(i) = sqrt((1/numcolumns)*sum(xcorrel(:,i).^2));
end

% normalize the rms-value vector and express as a percent deviation
% from reference value (autocorrelation)
normrmsxcorrel = (abs(rmsxcorrel./rmsxcorrel(refechonum)) - 1)*100;

```

Appendix H: Fabrication Process: In-House Ultrasonic Sensors



(1) Deposit SU-8 and pattern standoff ring on Pyrex. (2) If on wafer, dice chips.



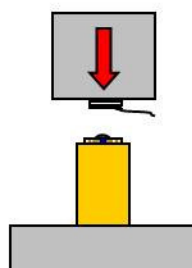
(3) Sputter-coat gold on Pyrex to form conductive ground.



(4) Solder wire to downward facing side of piezoelectric disc



(5) Deposit tungsten filled epoxy in standoff ring



(6) Mount piezoelectric disc to Pyrex rod.



(7) Ground bottom face of piezoelectric element to Pyrex rod. Connect signal wire to opposite side.



(8) Mount housing tube, fill with backing epoxy