Nanofiltration with fast feed flow reversal (FFFR) for highly concentrated industrial wastewater treatment

Tang, Di

2020

Tang, D. (2020). Nanofiltration with fast feed flow reversal (FFFR) for highly concentrated industrial wastewater treatment. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/142744>

<https://doi.org/10.32657/10356/142744>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 20:20:14 SGT

**Nanofiltration with Fast Feed Flow Reversal (FFFR)
for Highly Concentrated Industrial Wastewater
Treatment**

TANG DI

School of Civil and Environmental Engineering

2020

**Nanofiltration with Fast Feed Flow Reversal (FFFR)
for Highly Concentrated Industrial Wastewater
Treatment**

TANG DI

School of Civil and Environmental Engineering

**A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of Master of
Engineering**

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

01/13/2020

.....
Date

唐迪

.....
Tang Di

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

01/13/2020

.....
Date

.....
Assoc. Prof. Law Wing-Keung
Adrian

Authorship Attribution Statement

This thesis contains 1 paper published in the following peer-reviewed journal in which I am listed as an author.

One statement of Chapter 4 is published in T. Li, D. Tang, J. Song, and A. W-K. Law. Reverse osmosis desalination process with feed flow reversal operation: experimental studies. *Desalination and Water Treatment*. **144**, 339-344 (2019). DOI: 10.5004/dwt.2019.23587.

The contributions of the co-authors are as follows:

- Assoc/Prof. Law provided the initial projection direction and edited the manuscript drafts.
- Dr. Li Tian and Song Jie prepared the manuscript drafts. The manuscript was revised by Assoc/Prof. Law.
- Dr. Li Tian and Song Jie co-designed the laboratory setup. Dr. Li Tian and I performed the laboratory work at the Environmental Process Modeling Centre (EPMC), Nanyang Environment & Water Research Institute, and we analyzed the experimental data.

01/13/2020

.....
Date

唐迪

.....
Tang Di

Acknowledgments

I would like to express my sincere appreciation to my supervisor, Professor Law Wing-Keung, Adrian, for his patience, kind guidance and support regarding my research study as well as the other useful academic knowledge he has taught me. This study could not be accomplished without him. He has become my mentor in both the academic and personal aspects, but more importantly, he is always caring, loving, and with the best heart in treating anyone around him.

I would also like to say thank you to my seniors Dr. Li Tian and Dr. Song Jie, with whom I have been working on the iRO project for almost two years. During the time we were working together as a team, they had given me much guidance and support. After I started my master's degree study, they also helped me with the academic issues and provided me with the mental support.

I have also received much help from the research associates in the team, Mdm Li Min and Dawn Pang. Li Min was always responsive to my enquiry for the procurement related issues, this study would not have come this far if it wasn't for her timely arrangements. Dawn helped me in the refinement of my QE report, in which I had very little experience until she generously shared her knowledge with me. I sincerely express my appreciation for their hard work and kind assistance.

Table of Contents

Statement of Originality.....	i
Supervisor Declaration Statement.....	ii
Authorship Attribution Statement.....	iii
Acknowledgments.....	iv
Summary	viii
List of Tables	xi
List of Figures	xiii
Chapter 1 Introduction	1
1.1 Background.....	1
1.2 Objective	2
Chapter 2 Review of Theory and Previous Work	4
2.1 Unconventional Oil & Gas Production	4
2.1.1 Produced Water (PW).....	5
2.1.2 Constituents of Produced Water (PW)	7
2.1.3 Disposal and Re-injection of Produced Water (PW).....	8
2.1.4 Reuse of Produced Water (PW).....	8
2.1.5 Treatment of Produced Water (PW).....	9
2.1.6 Produced Water (PW) Treatment Using Conventional Technologies...	10
2.1.7 Produced Water (PW) Treatment Using Membrane Technologies	13
2.1.8 Summary of Shale Gas Produced Water (PW) treatments	15
2.2 Feed Flow Reversal (FFR).....	16
2.2.1 Background.....	16
2.2.2 Introduction to Feed Flow Reversal (FFR).....	17
2.2.3 Summary of Feed Flow Reversal (FFR).....	18

2.3	Introduction to Zero Liquid Discharge (ZLD)	19
2.3.1	Zero Liquid Discharge (ZLD) & Flue Gas Desulfurization (FGD).....	21
2.3.2	Zero Liquid Discharge (ZLD) & the Coal Industry in China.....	22
2.3.3	Zero Liquid Discharge (ZLD) & Reverse Osmosis (RO) Concentrate Treatment	22
2.3.4	Zero Liquid Discharge (ZLD) & Shale Gas Produced Water (PW).....	24
2.3.5	Summary for Zero Liquid Discharge (ZLD)	24
	Chapter 3 Experimental Setup & Methodology.....	25
3.1	Experimental Setup & Working Principle of the System	25
3.2	Materials and Methodologies.....	26
3.2.1	Nanofiltration (NF) Membrane.....	26
3.2.2	Chemicals & Synthetic Wastewater	26
3.2.3	Other Information of the System's Operation	28
3.2.4	Data Measurement	29
3.2.5	Cleaning of the Setup.....	32
3.3	Classification of Experiments Conducted with Different Operations	32
3.3.1	Cross-Flow Filtration (CFF)	32
3.3.2	Fast Feed Flow Reversal (FFFR)	32
3.4	Classification of Experiments Conducted with Different Membrane Models	33
3.5	Data Analysis	34
	Chapter 4 Results & Discussions	35
4.1	Part 1 of the Study: Performance of Applying FFFR in Desalination using NF90-2540 Membrane	35
4.1.1	Numerical Results and Discussion on FFFR Operation Performance in Treating Feedwater with Higher Concentrations	36
4.1.2	Summary of the FFFR Application using NF90-2540 Membrane	45

4.1.3	Recovery Drop Discussion	47
4.2	Part 2 of the Study: Effect of the Value of Ratio R being Larger than 1 on the Membrane Desalination Permeate Flux	60
4.2.1	Modification of the Experimental Setup in Part 2 of the Study	60
4.2.2	Experimental Results & Discussion	61
4.3	Comparison between Experimental and Modelling Results	68
4.3.1	Development of the Mathematical Model	68
4.3.2	Comparison between the Experimental and Modelling Results for Cross-Flow Filtration (CFF).....	72
4.3.3	Comparison between the Experimental and Modelling Results for Fast Feed Flow Reversal (FFFR) Operation.....	78
4.3.4	Summary for the Mathematical Model Developed in Predicting the Concentration and Permeate Flowrate for Membrane Desalination Processes	85
	Chapter 5 Conclusions	87
	References	90
	Appendix A. Experimental Results arranged according to Table x-z.....	97
	Appendix B. Omitted Results from Averaging the data for those Experiments with the same Operating Conditions	161
	Appendix C. Results of the NaCl Conductivity Standard Calibration.....	163

Summary

Feed flow reversal (FFR) is a novel approach that can potentially mitigate the primary challenges of fouling/scaling for membrane treatment processes. In particular, the concept may be particularly effective to mitigate membrane fouling/scaling for highly concentrated industrial wastewaters e.g., shale gas produced water (PW) and Reverse osmosis (RO)/Nanofiltration (NF) membrane desalination brine. However, the innovation has not been widely adopted for industrial applications thus far, partly owing to the additional costs for the system construction and uncertain cost-effectiveness for the operation. Overall, the adaption of FFR might be more justifiable in terms of cost, for challenging and hazardous conditions with highly concentrated wastewaters whereby scaling is the major concern.

Previous studies on the FFR technique utilized wastewater/synthetic solutions with a relatively low level of total dissolved solids (TDS) only, and the reversal period was consequently long due to the slow formation of scaling and solute crystallization. Therefore, this study focuses on the feasibility of fast feed flow reversal (FFFR) for treating highly concentrated wastewaters experimentally. The FFFR operation has shorter flow reversal intervals as the name indicates, to tackle the issue of shorter induction times due to the higher solute concentrations. A literature review of the PW is first performed. Previous studies on FFR, zero liquid discharge (ZLD), and RO/NF brine management are introduced and summarized.

The experimental setup for this study is then presented. Various desalination performances, such as water recovery rate and salt rejection in managing highly concentrated feedwater, incorporating the FFFR technique are investigated. Laboratory experiments using the NF90-2540 model with feedwater containing various mixtures of solutes, including NaCl, MgSO₄, and CaCl₂ with a wide range of concentrations were conducted. The tested TDS level is ~1-70 g/L, which is much higher than the concentrations used in the previous studies on FFR. Results in the energy recovery efficiency (ERE), specific energy consumption (SEC), permeate recovery rate, and salt rejection rate are investigated for these experiments. The overall range of the above-mentioned performance indicators were found to be, ERE in 90-95%, SEC in 0.86-2.03 kWh/m³, permeate recovery rate in 5.7-22.6%, and salt rejection rate in 47.5-73.4%. The upper operating limits for the NF desalination setup

used in this study are 70 g/L in the feedwater TDS level and ~35 bar in the applied pressure. The desalination performances reported in this study are in the hope to be used as a reference for the future FFFR applications, especially with NF desalination systems in dealing with highly concentrated wastewaters.

In addition, a mathematical model is developed in this study to predict how the solute concentration changes both spatially and temporal inside the membrane module, which consequently affects the desalination permeate flux. The development of the mathematical model is first introduced, and the modelling predictions are compared with the experimental results. For cross-flow filtration (CFF), modelling predictions on the permeate flowrate show good agreement with most of the experimental results. However, it was found that for the post-compaction tests, the modelling results of the permeate flowrate were generally larger than that of the experimental results. Therefore, it is concluded that the membrane compaction effect is not considered in the predicting process. This conclusion is further supported by the much better agreements between the modelling and experimental results for the MgSO_4 tests, of which the initial compaction processes were unable to be fully established due to the instability of the system resulted from the low-pressure operations. The model was found to be incapable of predicting the desalination performance for the FFFR operations under a specific operating condition of $R > 1$, where R is the ratio between the hydraulic retention time T_H and feed flow reversal period T_R .

Finally, another major finding in this study is that in order to successfully incorporate the flow reversal concept into conventional membrane desalination processes, one significant operating parameter that needs to be considered is the value of R . R needs to be smaller than or equal to 1, to avoid the formation of concentration accumulation within the membrane module, which may cause deterioration to the permeate flux due to the higher osmosis pressure build-up with time. So far, no experimental data on this situation has been reported to the best of our knowledge. The effects of $R > 1$ on the membrane desalination permeate flux are investigated and presented for the first time. R in a range of 1.16-1.43 was achieved with FFFR using the NF90-4040 model. Permeate flux decline was found in 11 out of the 14 tests, and the decline percentage was as high as 18.5%. The three tests with no permeate flux decline observed were mainly clustered within the lowest feedwater concentration range for

the NaCl tests. It was found that the average bulk concentration within the membrane module needs to reach a certain level for the negative effect of $R > 1$ to be observed experimentally. The concentration range used in the current study was relatively large, thus the critical value could not be narrowed down to an accurate value. Nevertheless, after calculating the average bulk concentration for each experiment, the threshold value of the average bulk concentration was found to be 34 g/L of NaCl.

List of Tables

Table 2.1: Most commonly found dissolved ions in oil & gas extraction produced water	7
Table 2.2: Representative water quality indicators of produced water	8
Table 2.3: Treated PW quality standards for various purposes	10
Table 4.1: Desalination performance of FFFR operation for treating feedwater containing NaCl + MgSO ₄	37
Table 4.2: Desalination performance of FFFR operation for treating feedwater containing NaCl + CaCl ₂	41
Table 4.3: Desalination performance indicators of the FFFR operation for treating feedwater containing NaCl + MgSO ₄ /CaCl ₂ under similar operating conditions	42
Table 4.4: Desalination performance of the FFFR operation for treating feedwater containing NaCl only	44
Table 4.5: Desalination performance of the FFFR operation for treating feedwater containing NaCl only, or NaCl + MgSO ₄ /CaCl ₂ under similar operating conditions	44
Table 4.6: Slope value of the recovery trend line in NaCl experiments	49
Table 4.7: Slope value of recovery trend line in NaCl + MgSO ₄ experiments	49
Table 4.8: Slope value of recovery trend line in NaCl + MgSO ₄ experiments	49
Table 4.9: Change in the slopes of the recovery trend line for the cross-flow filtration experiments run with the NF90-2540 model	51
Table 4.10: Change in the permeate conductivity and the slope of the recovery trend line of cross-flow filtration experiments run with the NF90-2540 model	52
Table 4.11: Values of T _H and T _R for experiments run with the FFFR operation using the NF90-2540 model	59
Table 4.12: Experimental results of FFFR tests conducted with the ratio R being larger than 1	63
Table 4.13: Comparison between experimental and modelling results in the permeate flowrate at steady state for NF90-2540 cross-flow filtration	73

Table 4.14: Comparison between experimental and modelling results in the permeate flowrate at steady state for NF90-4040 cross-flow filtration	74
Table 4.15: Modelling result of cycles 1-15 from FFFR test RN13	80
Table 4.16: Comparison between experimental and modelling results in the permeate flowrate at steady state for NF90-4040 FFFR operations with $R > 1$...	82
Table A.1: Experimental results of FFFR operation with NaCl added in feed water	98
Table A.2: Experimental results of FFFR operation with NaCl & MgSO ₄ added in feedwater	99
Table A.3: Experimental results of FFFR operation with NaCl & CaCl ₂ added in feedwater	99
Table A.4: Experimental results of Cross-flow filtration with NaCl added in feedwater	100
Table A.5: Experimental results of cross-flow filtration with NaCl & MgSO ₄ added in feedwater	100
Table A.6: Experimental results of cross-flow filtration with NaCl & CaCl ₂ added in feedwater	101
Table B.1: Recovery trend slope of the emitted experiments from Table 4.4	161
Table B.2: Recovery trend slope of the emitted experiments from Table 4.5	161
Table B.3: Recovery trend slope of the emitted experiments from Table 4.6	162
Table B.4: Modelling result of cycles 1-15 from FFFR test RNM15	162

List of Figures

Fig 2.1: Flow chart of the general steps of PW management	10
Fig 2.2: The commercial PW treatment system of OPUS by Veolia (Jiménez et al., 2018)	12
Fig 2.3: ZLD & near-ZLD process illustration	21
Fig 3.1: The simplified illustration of the laboratory experimental setup.....	25
Fig 3.2: Picture of the laboratory experimental setup in partial: (a) feed water tank, (b) compressed gas cylinder, (c) hydraulic pumps	28
Fig 3.3: Picture of the laboratory experimental setup in partial: (a) Pressure valve, (b) flow meters, (c) membrane module, (d) piston cylinders.	29
Fig 3.4: The controlling interface of the iRO system.....	30
Fig 3.5: The simplified experimental setup involving the pressure meters and flowrate meters.....	31
Fig 4.1: Performance indicators of test RNM4-6 versus the tests' feed flowrates ..	38
Fig 4.2: Performance indicators of test RNM7,8,10 versus the tests' applied pressures	39
Fig 4.3: Performance indicators of test RNM12-14 versus the tests' applied pressures	40
Fig 4.4: Recovery trend of 2 hours initial cross-flow (compaction) followed by 2 hours FFR operation	53
Fig 4.5: Permeate flux vs. pressure (kPa) before and after compaction (Md et al., 2017)	54
Fig 4.6: Continuously conducted experiment with increasing and decreasing pressure	55
Fig 4.7: Separately conducted experiments with increasing and decreasing pressure	56
Fig 4.8: Specifications of NF90-2540 & NF90-4040 models used in this study.....	60
Fig 4.9: Recovery and pressure trend for experiments conducted with insufficiently long flow reversal period	64
Fig 4.10: Recovery and pressure trend for experiments conducted with insufficiently long flow reversal period (cont'd).....	65
Fig 4.11: The illustration of the control volume of the membrane desalination solute concentration modelling	70

Fig 4.12: Modelling and experimental results for cycles 1-15 from test RN13	81
Fig 4.13: Modelling results of the permeate flowrate for cycles 1-6 with Δx in 0.1L, 0.05L, and 0.02L	83
Fig 4.14: Modelling results of the permeate flowrate for cycles 1-6 with Δt in 1s, 0.5s, and 0.2s.....	84
Fig A.RN.1: Pressure and recovery trends of test RN1	102
Fig A.RN.2: Pressure and recovery trends of test RN2	102
Fig A.RN.3: Permeate conductivity, salt rejection, pressure and recovery trends of test RN3	103
Fig A.RN.4: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RN4	104
Fig A.RN.5: Permeate conductivity, salt rejection, pressure and recovery trends of test RN5	105
Fig A.RN.6: Permeate conductivity, salt rejection, pressure and recovery trends of test RN6	106
Fig A.RN.7: Permeate conductivity, salt rejection, pressure and recovery trends of test RN7	107
Fig A.RN.8: Permeate conductivity, salt rejection, pressure and recovery trends of test RN8	108
Fig A.RN.9: Permeate conductivity, salt rejection, pressure and recovery trends of test RN9	109
Fig A.RN.10: Pressure and recovery trends of test RN10	110
Fig A.RN.11: Pressure and recovery trends of test RN11	110
Fig A.RN.12: Pressure and recovery trends of test RN12	111
Fig A.RN.13: Pressure and recovery trends of test RN13	111
Fig A.RN.14: Pressure and recovery trends of test RN14	112
Fig A.RN.15: Pressure and recovery trends of test RN15	112
Fig A.RN.16: Pressure and recovery trends of test RN16	113
Fig A.RN.17: Pressure and recovery trends of test RN17	113
Fig A.RN.18: Pressure and recovery trends of test RN18	114
Fig A.RN.19: Pressure and recovery trends of test RN19	114
Fig A.RNM.1: Pressure and recovery trends of test RNM1	115
Fig A.RNM.2: Pressure and recovery trends of test RNM2	115

Fig A.RNM.3: Pressure and recovery trends of test RNM3	116
Fig A.RNM.4: Pressure and recovery trends of test RNM4	116
Fig A.RNM.5: Pressure and recovery trends of test RNM5	117
Fig A.RNM.6: Pressure and recovery trends of test RNM6	117
Fig A.RNM.7: Pressure and recovery trends of test RNM7	118
Fig A.RNM.8: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM8.....	119
Fig A.RNM.9: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM9	120
Fig A.RNM.10: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM10.....	121
Fig A.RNM.11: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM11	122
Fig A.RNM.12: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM12.....	123
Fig A.RNM.13: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM13.....	124
Fig A.RNM.14: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM14.....	125
Fig A.RNM.15: pressure and recovery trends of test RNM15	126
Fig A.RNM.16: pressure and recovery trends of test RNM16	126
Fig A.RNM.17: pressure and recovery trends of test RNM17	127
Fig A.RNC.1: Pressure and recovery trends of test RNC1	128
Fig A.RNC.2: Pressure and recovery trends of test RNC2	128
Fig A.RNC.3: Pressure and recovery trends of test RNC3	129
Fig A.RNC.4: Pressure and recovery trends of test RNC4	130
Fig A.RNC.5: Pressure and recovery trends of test RNC5	130
Fig A.RNC.6: Pressure and recovery trends of test RNC6.....	131
Fig A.RNC.7: Pressure and recovery trends of test RNC7	132
Fig A.RNC.8: Pressure and recovery trends of test RNC8.....	133
Fig A.RNC.9: Pressure and recovery trends of test RNC9.....	133
Fig A.CN.1: Pressure and recovery trends of test CN1	134

Fig A.CN.2: Permeate conductivity, salt rejection, pressure and recovery trends of test CN2	135
Fig A.CN.3: Pressure and recovery trends of test CN3	136
Fig A.CN.4: Pressure and recovery trends of test CN4	136
Fig A.CN.5: Pressure and recovery trends of test CN5	137
Fig A.CN.6: Permeate conductivity, salt rejection, pressure and recovery trends of test CN6	138
Fig A.CN.7: Pressure and recovery trends of test CN7	139
Fig A.CN.8: Permeate conductivity, salt rejection, pressure and recovery trends of test CN8	140
Fig A.CN.9: Pressure and recovery trends of test CN9	141
Fig A.CN.10: Pressure and recovery trends of test CN10	141
Fig A.CN.11: Permeate conductivity, salt rejection, pressure and recovery trends of test CN11	142
Fig A.CN.12: Permeate conductivity, salt rejection, pressure and recovery trends of test CN12	143
Fig A.CN.13: Pressure trend, recovery trends throughout the experiment and after compaction of test CN13	144
Fig A.CN.14: Pressure trend, recovery trends throughout the experiment and after compaction of test CN14	145
Fig A.CN.15: Pressure trend, recovery trends throughout the experiment and after compaction of test CN15	146
Fig A.CN.16: Pressure trend, recovery trends throughout the experiment and after compaction of test CN16	147
Fig A.CN.17: Pressure trend, recovery trends throughout the experiment and after compaction of test CN17	148
Fig A.CN.18: Pressure trend, recovery trends throughout the experiment and after compaction of test CN18	149
Fig A.CN.19: Pressure trend, recovery trends throughout the experiment and after compaction of test CN19	150
Fig A.CN.20: Pressure trend, recovery trends throughout the experiment and after compaction of test CN20	151

Fig A.CN.21: Pressure trend, recovery trends throughout the experiment and after compaction of test CN21	152
Fig A.CN.22: Pressure trend, recovery trends throughout the experiment and after compaction of test CN22	153
Fig A.CNM.1: Pressure and recovery trends of test CNM1	154
Fig A.CNM.2: Pressure and recovery trends of test CNM2	154
Fig A.CNM.3: Pressure and recovery trends of test CNM3	155
Fig A.CNM.4: Pressure and recovery trends of test CNM4	155
Fig A.CNM.5: Pressure and recovery trends of test CNM5	156
Fig A.CNM.6: Pressure trend, recovery trends throughout the experiment and after compaction of test CNM6	157
Fig A.CNM.7: Pressure trend, recovery trends throughout the experiment and after compaction of test CNM7	158
Fig A.CNC.1: Pressure and recovery trends of test CNC1	159
Fig A.CNC.2: Pressure and recovery trends of test CNC2	159
Fig A.CNC.3: Pressure and recovery trends of test CNC3	160
Fig C.1: NaCl conductivity standard calibration for concentration between 0-7mol	163
Fig C.2: NaCl conductivity standard calibration for concentration between 0- 0.7Mmol.....	163

Chapter 1 Introduction

1.1 Background

Membrane technologies have been widely used for industrial applications in various fields. Some well-established applications are seawater desalination, brackish wastewater treatment, food processing, and pharmaceutical production. Compared to other traditional water purification methods such as chemical precipitation, thermal treatment, and biological treatment, membrane technologies have the advantageous capabilities of producing purer permeate, generating less solid waste, requiring lower energy consumption, and being able to provide flexible modularity. However, the high fouling/scaling propensity remains the primary challenge when applying membrane technologies, which can limit their ability to handle wastewaters particularly those with a high level of total dissolved solids (TDS). Fouling/scaling will have negative effects on both the quantity and quality of the permeate production, causing a deterioration of the overall purification performance. The associated frequent replacement of membrane modules and chemical cleaning or backwashing will lead to prolonged operating downtime as well as an incremental operating cost. The development of new innovations targeting the mitigation of fouling/scaling is therefore highly desirable.

Fouling/scaling issues can be exceptionally severe in managing wastewater with high salinity. For instance, the shale gas production as an unconventional and emerging technology for natural gas extraction, typically produces wastewater in large volumes with high pollutant concentration and significant toxicity levels. The proper management of such wastewater is therefore considered vital as the consequences of potential pollution to the surrounding environment can be severe. The RO/NF desalination brine is another example of the highly concentrated wastewaters that requires sophisticated treatment processes prior to its discharge or reuse for various purposes.

Another example occurs at the final steps of ZLD treatment. Due to the increasing environmental concerns arising from industrial wastewater discharges, regulations mandating ZLD have been not only promulgated but also brought to practice in recent

years. ZLD is a forward-looking concept when dealing with the volume control of the ever-growing industrial wastewaters being discharged into the environment. In a ZLD system, highly concentrated wastewaters will be present at the downstream end of the treatment processes. The final step is usually evaporation or thermal-based technologies to remove the residual water content in the effluent coming from the preceding treatment stages. A significant issue associated to reducing the capital and operating cost of the final step is the influent volume. The smaller the volume, the less the energy consumption it requires, and the lower the overall cost shall be. However, difficulties have been recognized when the wastewater concentration becomes exceptionally high with more water being extracted along the treatment processes. Therefore, the development of innovative technologies for improving the dewatering capability and efficiency is of primary importance for the ZLD systems.

The feed flow reversal (FFR) technique was developed to solve the scaling plight in the membrane desalination processes. The basic principle of FFR is to periodically change the feed flow direction so that the induction time of the solute crystallization phenomenon adjacent to the membrane surface due to the increasing ambient solute concentration, can be reset to zero. Therefore, the conventional desalination systems incorporating the FFR technique is a potential solution for handling feedwater with higher concentrations. Feedwater with low concentrations of less than ~2 g/L was used in the previous studies on the FFR technique. Therefore, the focus of this study is to investigate the possibility of implementing the fast feed flow reversal (FFFR) concept, which is a derivative of the FFR technique into dealing with feedwater with much higher concentrations.

1.2 Objectives

The objectives of this study are as follows:

- (a) To investigate the capability of the flow reversal technique incorporated with a conventional membrane system in handling highly concentrated wastewaters experimentally. In particular, the flow reversal period is shortened in the laboratory experiments to examine the feasibility of FFFR in treating wastewater with much higher TDS levels.

- (b) To examine the pros & cons of applying the flow reversal technique in membrane applications. In addition to the potential benefit in handling highly concentrated industrial wastewaters with FFFR, shortening the reversal period is expected to result in amplified effects of the flow reversal technique. Thus, the pros & cons of applying the technique in the membrane desalination processes could be understood more clearly.
- (c) To perform a mathematical modelling analysis on FFFR. The experimental results are compared with the modelling results, to understand the applicability and the limitations of the model in predicting how the ratio R between T_H and T_R affects the successful incorporation of FFFR into membrane desalination processes. In particular, the effects of the ratio R on the permeate flux are examined comprehensively.

Chapter 2 Review of Theory and Previous Work

2.1 Unconventional Oil & Gas Production

Unconventional oil & gas production methods have been increasingly applied on a global scale during the past several decades. Unconventional gas production practices mainly include extraction from shale gas, tar sand, and coal bed methane. The world natural gas production is predicted to increase from 342 billion cubic feet per day (Bcf/d) to 554 Bcf/d from 2015 to 2040. Shale gas production, although account for only 12% of the total global natural gas output in 2015, is projected to increase from 42 Bcf/d to 168 Bcf/d in 2040. Shale gas growth will contribute ~59% of the total production growth according to the current expectation. At present, the top four countries (in terms of output) that are commercially practicing shale gas extraction are United States, Canada, China, and Argentina. U.S. is the apparent leader with respect to the natural gas production using these unconventional methods. In 2015, shale gas took up half of the total national natural gas production in the U.S.. By 2040, ~66% of the U.S. natural gas production is expected to come from shale gas (U.S. Energy Information Administration, 2017).

Hydraulic fracturing, also known as fracking, refers to the process of injecting highly pressurized liquid against the rocks in the deep extraction wells to create fractures so that the oil & gas trapped underneath can be released (Struchtemeyer and Elshahed, 2012). The injecting liquid typically consists of 90% of water, 8-9.5% of sands (often called proppants), and 0.5-2% of chemical additives. Fracking happens in both the vertical and horizontal directions, which makes it a water-intensive operation. Proppants are normally added in the injecting liquid for holding the fractures open even when the injection stops. Detailed analysis of various proppants and their transportation behaviors can be found in Chang (2018).

Compositions of the chemical additives used in fracking are largely unknown to the public since companies usually claim the recipes of these chemicals as proprietary information. Up to ~40,000 gallons of undisclosed chemicals are being injected in each extraction well during its service life. The unregulated usage of chemical additives poses potential health and safety threats to the ecological environment and

the public (Maule et al., 2013). Several studies have investigated the various negative effects caused by the chemicals added into the hydraulic fracturing fluid (Mumford et al., 2018; Hu et al., 2018; Stringfellow et al., 2017).

In the U.S., the percentage of the daily natural gas produced by hydraulic fracturing had increased from 7% in 2000 to 67% in 2015 with a nominal annual growth rate of 4% (Jack and Troy, 2016). The number of hydraulic fracking wells grew from ~23,000 in 2000 to ~300,000 by 2015, surging thirteen times during this period (Troy and Jack, 2016). These numbers strongly indicate continuous and potential accelerating growth of the unconventional oil & gas production market.

The total amount of water needed for each hydraulic fracturing well has been reported to be increasing. The common usage of water was ~3-5 million gallons per fracking well a decade ago. Nowadays, the number is ~5-15 million gallons, mainly attributed to the repeated fracking operations of the aging wells, also commonly known in the industry as 'denser completion' (Mccurdy, 2018). The water to oil ratio (WOR) is defined as the volume of water used per volume of oil produced. The estimated WOR for unconventional oil production is ~0.2-1.4, which is in the lower range of the conventional oil production WOR of ~0.1-5. The study also revealed that the water to oil equivalent ratio of hydraulic fracturing in the gas zone (WOER~0.6) is considerably lower than that in the oil zone (WOR~1.4) (Scanlon et al., 2014). In 2015, oil and gas production from hydraulic fracturing was 4.3 million barrels per day (b/d) and 53 billion cubic feet per day (Bcf/d), respectively. Based on the WOR values being referenced above, the estimated total fracking water consumption in the U.S. in 2015 was ~2.3 billion m³. This amount of water can supply the gross water consumption of New Zealand, which was reported to generate the largest water consumption per capita in 2016, for 83 days (United Nations Population Division, 2017; STATISTA, 2018).

2.1.1 Produced Water (PW)

PW is broadly referred to the wastewater engendered during the oil & gas extraction operations (Jiménez et al., 2018). Other than the primary injection water, water trapped underground is also a critical component of PW. The characteristics of PW

progressively vary during the fracking process. During the initial stage of fracking, PW (called flow back waters at this stage) characteristics are akin to that of the injection liquid. Subsequently, the flow back waters being contacted with the geology-specific environment will gradually transform into the PW of which the characteristics have not been fully defined so far (Oetjen et al., 2018). The total amount of PW for both conventional and unconventional oil & gas production in the U.S. was estimated to be ~3.2 billion m³ in 2007 (Clark and Veil, 2009). This number and the above estimation (~2.3 billion m³) of the U.S. hydraulic fracturing water consumption in 2015, both reflect the thriving development of the fracking industry in the States. The reason for the PW amount being larger than the water usage referred in WOR is probably due to a significant portion of PW is re-injected for maintaining the formation pressure and enhancing the oil recovery. This portion is counted for PW but not in the water usage in WOR.

The exact volume produced at each well depends on the geological & formation conditions, extraction methods, and the age of the extraction well. With respect to the potential negative impacts on the surrounding freshwater resources related to PW, public concerns have been raised and the ensuing assessments have been comprehensively conducted. For example, threats to the freshwater system imposed by unconventional oil production in the Bakken shale located in North Dakota has been identified as (1) deficiency of natural water supply owing to excessive withdrawals used for fracking (2) transportation of PW by reason of leakage and failures in the well construction and (3) accumulation of toxic and radioactive elements due to accidental spills into the surrounding water systems (Shrestha et al., 2017).

The lack of sufficient information on the fracking operations greatly hindered the development and implementation of the regulations on PW discharge standards. Hence, proper in-situ monitoring has become an indispensable controlling method to facilitate the enactment of laws and regulations (Gagnon et al., 2016). Due to the complex physical-chemical properties of PW over disparate geological locations and operation methods, it is impossible to achieve exhaustive water quality examination at each fracking well. Yost et al. (2017) developed a framework termed multi-criteria

decision analysis (MCDA) to quantify the chemical toxicity level of PW by harmonizing multiple lines of measurement. Horizontal analysis can be brought about by adopting this framework.

2.1.2 Constituents of Produced Water (PW)

The constituents of PW from each extraction well may vary with the (1) chemicals added into the injection liquid, (2) geological conditions of the extraction wells and, (3) characteristics of the hydrocarbon being harvested. PW is usually acidic, consisting of various suspended and dissolved salts with salinity being ~100 times higher than seawater. Dissolved salts are present in PW primarily owing to the additive chemicals in the injection liquid and the soluble minerals from the formation. The nature of these salts greatly depends on the individual geological condition. The most commonly found dissolved ions in PW are listed in Table 2.1 (Jiménez et al., 2018).

Table 2.1: Most commonly found dissolved ions in oil and gas extraction PW

Cations	Concentration, mg/L	Anions	Concentration, mg/L
Na ⁺	0-150,000	Cl ⁻	0-250,000
Ca ²⁺	0-74,000	SO ₄ ²⁻	0-15,000
Sr ²⁺	0-6,250	HCO ₃ ⁻	0-15,000
Mg ²⁺	8-6,000	SO ₃ ²⁻	10
K ⁺	24-4,300		
Ba ²⁺	0-850		
Fe ²⁺	0.1-100		

Oil & grease (O&G) is a common pollutant found in PW for oil and gas production. The forms of O&G that have been detected in PW include free, dispersed, dissolved, and emulsified states, depending on their stability and solubility in water. Particulate matters in PW are found to contain minerals falling off the formation, fouling, and various substances originated from the construction equipment (Jiménez et al., 2018).

Several critical and representative measurement indicators being commonly reported are listed in Table 2.2. (Fakhru'l-Razi et al., 2009; Nasiri and Jafari, 2017).

Table 2.2: Representative water quality indicators of PW

	Concentration, mg/L
TDS	100-400,000
TSS	1.2-1,000
COD	1,220-2,600
TOC	0-1,500
O&G	2-560

2.1.3 Disposal and Re-injection of Produced Water (PW)

As cited in Oetjen et al. (2018), up to 98% of PW is being re-injected either to maintain the formation pressure and thus enhance oil recovery; or being re-injected for discharge into the underground environment. Despite being a relatively costly management method, re-injecting PW to the shale formation has the advantages of enhancing the oil production and reducing the discharge volume through recycling PW within the extraction process (Dolan et al., 2018; Siagian et al., 2018).

The PW management in the Marcellus formation in Pennsylvania was thoroughly investigated in Lutz and Doyle (2013). The resulting contamination of the surrounding waters with an exceptional high TDS level has hindered the treatment of the Marcellus PW at the less-intensive municipal and industrial facilities. Underground re-injection had surged to ~350 million liters in 2010 mainly by reason of regulatory provisions to prevent further shallow water body contamination. Moreover, advanced wastewater treatment methods were also invoked to conform to the growing unconventional oil & gas production with the ensuing large amount of PW generated (Lutz and Doyle, 2013).

2.1.4 Reuse of Produced Water (PW)

Due to the enormous volume of PW generated in the U.S. each year, various beneficial reuses have been proposed to alleviate the water stress in semi-arid and arid areas. The reuse of PW has been developed from the beginning of this century and surpassed re-injection after 2012 (Siagian et al., 2018). Feasibility of using treated PW for food crops irrigation has been assessed in Echchel and Sakrabani (2018). Out of the PW samples selected worldwide, less than 10 % were suitable for

food crops irrigation prior to water treatment approaches, and the primary concerns of irrigation water quality are salinity and sodicity. Another study targeted the state of Colorado which is relatively arid with a continuous growing population and water consumption (Dolan et al., 2018). An integrated decision selecting tool was adopted to interpret the economic justifiability of treating PW in pursuance of the irrigation standards. The study was devoted to converting the public perception of PW being wastewater to valuable resources. It was found that although treating PW for irrigation is costlier than re-injecting PW into private extraction wells, it is much cheaper than re-injecting PW into commercial wells.

Pica et al. (2017) examined irrigation trials employing treated PW on two salt-tolerant non-food biofuel crops with various treated effluence qualities. Low levels of organic substances (<50 mg/L) and total organic carbon (TOC <5 mg/L), and medium levels of TDS ($\sim 3,500$ mg/L) were found to be the optimal treated water characteristics for irrigation considering cost, scalability, and workability. The feasibility of using PW as growth mediums for cultivating microalgae was assessed in Sullivan Graham et al. (2017). Their conclusions indicated promising future applications if the intricacy of PW composition and the explicit metals consumed by algae can be fully understood.

2.1.5 Treatment of Produced Water (PW)

Facing the surging number of hydraulic fracturing wells and the ensuing enormous amount of wastewater, PW management regulations set by the related governmental institutions have become more and more stringent over time (Jiménez et al., 2018). O&G discharge limit set by Australia, USEPA, China, OSPAR are 30 mg/L (daily average) and 50 mg/L (instantaneous), 42 mg/L (daily maximum) and 29 mg/L (monthly average), 10 mg/L (monthly average) and, 40 mg/L (annually average) of the treated PW being discharged to the environment, respectively. Several other required treated PW effluent standards for various purposes were listed in Sullivan Graham et al. (2018) and are tabulated in Table 2.3.

Even though the specific treatment facilities will depend on the characteristics of the PW formed at various geological locations and by using different extraction methods, the course of PW treatment can be generally classified into the following steps:

- Removal of organic substances, comprising dispersed O&G such as insoluble

polyaromatic hydrocarbons, phenols, and other soluble organics

- Removal of suspended solids (i.e., minerals, clay, and sands) after disinfection
- Removal of dissolved inorganic mineral salts, hardness following dissolved gas handling processes
- Removal of naturally occurring radioactive material

Table 2.3: Treated PW quality standards for various purposes

	Suspended solids (mg/L)	Particle size (mm)	O&G (mg/L)	TDS (mg/L)
Offshore disposal	< 10	-	< 5	-
Reinjection	< 1	< 1	< 5	-
Irrigation	-	-	< 35	500-2,000
Cooling tower	-	-	-	< 2,700
Chemical Process	-	-	-	< 1,000

A flowchart of the general steps of PW management is shown as in Fig 2.1.

Fig 2.1: Flow chart of the general steps of PW management

2.1.6 Produced Water (PW) Treatment Using Conventional Technologies

Two distinguished review papers had assessed the shale gas PW treatment thoroughly (Fakhru'l-Razi et al., 2009; Jiménez et al. 2018). Both papers summarized the treatment methods into similar classifications. According to Fakhru'l-Razi et al. (2009), PW management methods can be broadly characterized into physical treatment, chemical treatment, biological treatment, and membrane treatment. Thermal technologies and advanced oxidation processes are added on in the later review paper (Jiménez et al. 2018). A brief introduction of each category with the most commonly applied methods will be provided in this section with the associating

pros and cons if available in the review papers.

2.1.6.1 Physical Treatment

Adsorption process based on various adsorbents, i.e. activated carbon, organoclay and copolymers are commonly used to remove organic and some inorganic compounds in PW. Drawbacks of these technologies are the chemical wastes produced from the adsorbent regeneration and high capital cost.

Cyclones are mainly used for phase separation in treating PW. Oil and sand removal efficiencies are moderate in applying cyclones. However, this technology is incapable of removing dissolved and other hazardous constituents in PW.

Flotation technology can moderately remove organic matters, especially oil and grease (O&G) in PW. The removal efficiency, however, can be negatively affected by the surfactants and high salinity that are commonly present in PW.

2.1.6.2 Biological Treatment

Biological treatment refers to the methods which utilize microorganisms to remove organic compounds through the mechanisms of biodegradation or bioflocculation. High removal efficiency up to 98-99% of total petroleum hydrocarbons and lower but satisfying removal efficiency for COD, BOD, TOC, and O&G can be achieved by various biological treatment methods. However, TDS level higher than 100 g/L was found to be detrimental on the biodegradation performance.

2.1.6.3 Thermal Treatment

In general, thermal treatment technologies have the advantage in possession of higher tolerance to water with high salinity, i.e. shale gas PW. Higher energy consumption, however, makes thermal treatment less competitive in places where the cost of energy is high. Examples of commonly used thermal treatment technologies are evaporation, multistage flash (MSF), multieffect distillation (MED), vapor compression distillation (VCD), among which MED and VCD are more suitable for treating PW with their tolerance to high salinity and their relatively low energy consumption.

2.1.6.4 Chemical Treatment

Chemical precipitation, i.e. coagulation and flocculation are effective in removing suspended and colloidal particles, but not with dissolved solids which is often found in shale gas PW. In addition, the by-production of chemical solid wastes which are potentially hazardous to the environment is another drawback of such treatment processes.

Electrochemical treatment, i.e. electrodialysis uses charged electrodes to prevent ions from passing through the membrane surface to obtain clean water. Effective treatment has been seen in treating PW with electrochemical methods containing both organic and inorganic compounds.

Demulsifiers are surface-active agents that can be used to disrupt the effects of surfactants in PW. The surfactants are commonly added in the extraction process and can reduce the interfacial tension between oil and water, which consequently lead to difficulties in the phase-phase separation.

2.1.6.5 Advanced Oxidation Process (AOPs)

Application of oxidation processes can help in removing colour, odour, COD, BOD, organics and partial removal of inorganics. AOPs have the advantage in completely mineralizing recalcitrant components over other conventional technologies. In addition, shorter operation duration is generally needed for AOPs. Nonetheless, feedwater with the COD concentration higher than 5 g/L, i.e. most of the shale gas PW, is unsuitable for treatment through AOPs. Therefore, proper pre-treatments are often required in applying AOPs for PW management.

Figure 2.2: The commercial PW treatment system of OPUS by Veolia (Jiménez et al., 2018)

Comprehensive information on the other existing commercial systems for PW treatment can also be found in Jiménez et al. (2018).

2.1.7 Produced Water (PW) Treatment Using Membrane Technologies

Membrane technology is broadly classified into microfiltration (MF), ultrafiltration (UF), NF, and RO based on the contaminant removal mechanisms and the size range of the removed substances. MF and UF operations are based on the convective pore-flow mechanism (Darcy's law); RO membrane operations are based on the solution-diffusion mechanism (Fick's law), while the mechanism of NF operation falls in between.

As mentioned in the background, membrane technologies have many advantages over traditional water management methods. Compared with thermal-based treatment methods which are considerably energy-intensive, membrane technologies require moderate energy consumption. Compared with chemical methods, membrane technologies require less chemical injection and produce less amount of sludge wastes to be discharged at the end of the treatment, which can potentially lead to environmental pollution. Membrane technologies are usually more compact, and can provide more flexible modularity. In addition, wastewaters that are being produced with large and ever-growing volumes, i.e. shale gas PW would require water recovery and reuse to alleviate the global water stress. Membrane technologies, especially RO/NF are essential if high effluent quality is desired since they can produce purer permeate. Among all the membrane technologies, NF has been identified as the optimal option considering the balance of energy consumption and permeate quality (Jiménez et al. 2018).

Due to the concerns regarding the environmental impacts and subsequent more stringent regulatory requirements towards the treated PW quality, membrane technologies have been identified as a promising solution attributed to its outstanding water purification performance. Studies have shown the importance of proper pretreatments to the overall treated PW quality using membrane technologies. The primary purpose of incorporating pretreatments is to remove both the organic and inorganic fouling precursors of the membranes.

The general process of PW treatment using membrane technologies consists of primary and/or secondary treatments in the pretreatment stage, and contingent biological treatments followed by membrane desalination as the tertiary treatment (Fakhru'l-Razi et al., 2009; Jiménez et al., 2018). Primary treatments may include screening, grit removal, gravity-assisted sedimentation, demulsification, coagulation,

adsorption, dissolved air precipitation, and induced air flotation (IAF). Secondary treatments primarily deal with removal of the dissolved components through chemical and biological methods. Mechanical vapor compression (MVC), membrane distillation (MD), and forward osmosis (FO) have been suggested as promising solutions for handling highly concentrated PW. Shaffer et al. (2013) have pointed out that the advancement of PW treatment using membrane technologies is expected to be achieved through the establishment of modular and scalable operations, together with more streamlining and efficient pretreatments.

2.1.7.1 Microfiltration (MF) & Ultrafiltration (UF)

MF is usually placed after sedimentation, coagulation, flocculation & secondary sedimentation and used as a pretreatment to enhance the effectiveness of the subsequent UF, NF or RO processes. It was substantiated that MF can effectively remove the dispersed oil droplets and other particulates larger than 100nm (Munirasu and Banat, 2016). MF was used as a pretreatment to diminish fouling propensity for the subsequent treatment by UF and RO (Motta et al., 2014). 93.0-100% in the oil removal was achieved. O&G concentration in the final effluent was between 0.1 and 14.8 mg/L, which is in compliance with the average global standard of 30 mg/L.

On the other hand, UF has been found to be effective in treating less toxic PW with lower salinity (Seyed and Reyhani, 2014). Moreover, fouling has been found to be well controlled by using membranes with more hydrophilicity and less roughness. The transmembrane pressure was demonstrated to have a significant impact on the permeate flux and fouling resistance of UF filtration, whereas TOC removal performance is more relevant to the cross-flow velocity. Through adjusting for the optimal operating conditions, up to 100% of O&G, 100% of TSS, 99% of turbidity, and ~50% of TOC removal was attained. The effectiveness of coagulation as a pretreatment for UF was addressed in Loganathan and Gamal (2015). Results showed complete solids removal, less fouling by dosing softening agent to reduce the hardness, > 99% of turbidity and < 20% of TOC removal. In general, fouling was realized to be a major impediment of large-scale UF applications.

2.1.7.2 Nanofiltration (NF) & Reverse Osmosis (RO)

Theoretically, RO membranes can reject all contaminants including small weighted

monovalent ions like Na^+ and Cl^- , allowing only H_2O molecules to pass through. On the other hand, NF membranes can only partially block monovalent ions (Munirasu and Banat, 2016). However, the actual performance of membrane desalination processes in real applications can hardly meet the theoretical capacity.

Çakmakce and Koyuncu (2008) showed that NF can effectively remove COD to the level that is within the regulated discharge limit. However, the effluent TDS concentration did not meet the required criterion. The process design was as follows. Primary settlement for oil separation was followed by DAF, 1 m cartridge filter, MF, activated carbon, and NF. Though Cl^- and F^- removal were found to be poor using NF, NF was suggested as an acceptable candidate as the pretreatment of RO for fouling prevention purpose (Alzahrani et al., 2013). Xu and Drewes (2006) have compared the performance of one RO membrane (TFC-HR), three ULPRO membranes (XLE, TFCULP, and TMG-10), and three NF membranes (NF-90, TFC-S, and ESNA) by purifying methane PW and examined the effluent qualities. TMG-10 exhibited higher water recovery by either basic or sodium dodecyl sulphate wash. NF90 required the lowest operating pressure to sustain high permeate flux, but at the same time provided lower rejection compared with RO and ULPRO. ULPRO required lower marginal operating and maintenance cost compared with RO. ULPRO will be considered as a more cost-effective candidate assuming energy becomes costlier in the future.

2.1.8 Summary of Shale Gas Produced Water (PW) treatments

Investigations on treating PW using membrane technologies have been thoroughly conducted. However, it is still unclear whether applying membrane technologies is an appropriate method for treating PW with sufficient cost-effectiveness. The main difficulties encountered are the complexity of the wastewater compositions, the variation of PW compositions over disparate extraction sites, high salinity that can lead to significant fouling/scaling problems, and the fluctuation of the wastewater quality during the extraction process together with the aging of the extraction wells. Membrane desalination with FFR might be able to alleviate the challenges of handling such highly polluted PW with insignificant or even without fouling/scaling issues.

2.2 Feed Flow Reversal (FFR)

2.2.1 Background

The primary issues with RO desalination are fouling and scaling. Fouling arises when particulate matters or biofilms develop onto the membrane surface. Deposition and growth rate of the fouling layers will vary with the hydrodynamic conditions, inflow characteristics, membrane materials, and membrane surface properties, together with the concentration polarization mechanism (She et al., 2016). Scaling refers to the precipitation of dissolved minerals by reason of the exceedance in the salt solubility. Calcium sulfate di-hydrate, also known as gypsum, is the most commonly found mineral scale in RO desalination systems (Boerlage, 2001). Ex-situ monitoring of gypsum formation was conducted with real-time observation on the development of the crystal surface number density (SND) (Uchymiak et al., 2008). With the characterization of individual crystal growth by a crystal fluid mass transfer coefficient, the study established the basic understandings of scaling formation with a variety of feedwater supersaturation levels.

Temperature, pressure, axial flow velocity, and pH have been investigated as the most critical factors affecting the RO membrane fouling formation (Mohammadi et al., 2003). Theoretically, the diffusion coefficient increases with temperature while the water viscosity decreases with temperature, thus causing the Schmidt number to reduce and consequently promote fouling. On the other hand, lower water viscosity can enhance permeate flux. The optimal operating temperature has been found to be ~35 °C within the testing range of 17-45°C. Higher pressure can improve permeate production but can also exacerbate fouling due to the phenomenon of cake compression. The optimal pressure was determined to be 13 bar within the testing range of 8-17 bar. The higher the cross-flow velocity, the more turbulence can be created which would lead to less fouling/scaling and greater permeate production without considering the operating cost. Performance was the worst when pH was ~6. It was recommended to have a pH value either < 5 or > 7 .

Scaling can be effectively controlled using either or both physical and chemical methods (Rouina et al., 2016). Physical approaches including lowering the recovery ratio to prevent the solute concentration on the feed side from exceeding the salt solubility limit. Proper control of the hydrodynamic conditions can initiate the desired turbulence, hence to prevent precipitation from attaching onto the membrane surface.

Adoption of membrane spacers will engender similar effects to create turbulence. In addition, utilization of electromagnetic field was found to be beneficial in improving salt rejection and permeate production, and also resulted in lower density gypsum precipitation.

Backwash is another commonly used method for fouling and scaling control. However, the accurate time interval for the backwash method and the interference to the system's operation remain the major challenges (Warsinger et al., 2015). Dosing pH-adjusting chemicals and scale inhibitors (anti-scalant) into the feedwater can effectively prevent or delay scale formation (Qin et al., 2009). Nevertheless, it was observed that, depending on the chemical properties of the anti-scalant, biofouling might be enhanced to some extent for membrane desalination processes (Sweity et al., 2015). Such finding imposes difficulties in selecting the most appropriate anti-scalant. In addition, the end product of the chemical reactions is discharged into the environment. Therefore, potential environmental pollution is also of significant concern.

2.2.2 Introduction to Feed Flow Reversal (FFR)

Motivated by the above-mentioned issues with the anti-fouling/scaling methods, FFR was first proposed by Gilron et al. (2006) for solving the scaling plight in the membrane desalination systems. In addition, the concept of resetting the induction time, which is defined as the filtration duration before the 1st crystal to be observed on the membrane surface, was incorporated in the FFR concept in a synchronous study (Pomerantz et al., 2006).

Bartman et al. (2009) pointed out the importance of the flow reversal timing to achieve successful incorporation of the FFR technique into membrane operations. Based on the authors' interpretation, setting the FFR operation too short may not provide enough dilution and dissolution, or it can be ineffective in resetting the induction time when no precipitation has formed yet. On the other hand, prolonged FFR operation will result in scaling at the alternate tail-end. Water hammer induced pressure wave was introduced as another prominent issue for FFR, as the excessive flow velocity fluctuation may cause damage to the desalination equipment. The simulation results of a model-predictive control (MPC) system developed in the study

showed successful elimination of the above-mentioned problems and consequently, solved the systematic optimization problem.

A later study focused on incorporating an ex-situ scale observation detector (EXSOD) to achieve automatic instruction of the FFR operation (Christofides et al., 2009). An additional plate-and-frame RO cell was integrated in the operating system at the end of the tail element of the membrane modules, to receive a side stream from the inflow side of the membrane to monitor the scale formation conditions. The fractional surface area coverage (FSAC) and the crystal number density (CND) were employed as the scaling indicators for triggering the FFR operation. It was concluded that monitoring CND would be more effective than FSAC taking scale formation rate into consideration. Successful mitigation of precipitation due to sparingly soluble salts scaling was demonstrated in the study. However, the selection of the most appropriate triggering indicator remains uncertain. In addition, the concentration of the feedwater used in the experiments was relatively low with a TDS level of ~2.5 g/L. Thus, the feasibility of applying this system in handling more polluted feedwater remains unclear.

An improved version of EXSOD was later introduced with a self-adaptive feature for more precise control of the FFR operation (Lu et al., 2012). Ultrasonic sensor was utilized for controlling FFR through monitoring the ultrasonic waveforms as a scaling indication. Membranes were analyzed after the experiments to compare with real-time ultrasonic monitoring for determining the accuracy of the simulation procedures. Proper control of the FFR triggering cycle in terms of timing and duration was also considered as a prominent aspect in the study. A pair of benchmark amplitude boundaries was used for establishing the FFR controlling system that can detect signal deviation from this ‘dynamic amplitude window’ when scaling formation reaches the pre-defined limit. Nevertheless, the feedwater TDS concentration was even lower compared to the previous study (being 1.8 g/L).

2.2.3 Summary of Feed Flow Reversal (FFR)

The investigation on the FFR concept to mitigate the scaling issues in RO membrane desalination processes is summarized in this section. Based on the excellent experimental and simulation results obtained through the development of

comprehensive algorithms together with meticulous monitoring and analysis procedures in the previous studies, FFR has been introduced as a potential alternative solution to mitigate fouling/scaling issues. Scaling was found to be successfully prevented through proper operations of FFR. The automation of FFR is another focus among the existing studies. Overall, efforts have been made to implement the concept of FFR into laboratory experiments. However, the number of studies on this topic is so far considerably limited, improvements are thus expected to be made in many aspects as follows.

Previous studies have been greatly focused on real-time detection of the crystallization onset to achieve a timely triggering of the FFR operation, which is expected to provide perfect flow reversal timing and thus effective scaling prevention. However, sophisticated devices are required for this kind of real-time detection and flow reversal triggering instruction. The additional costs might become a burden to implement FFR with such devices into practical applications. In addition, the water qualities used in the above studies were relatively clean, with TDS all being lower than 2 g/L. Fouling/scaling can become more severe as the concentration of wastewater to be treated gets higher, i.e. shale gas PW, RO/NF desalination brine, and the downstream of zero liquid discharge (ZLD) systems which will be introduced in later sections. The exceptionally complex feedwater compositions in real industrial situations may give rise to potential operational issues. The lack of investigations on FFR in treating feedwater with higher concentrations is therefore another issue to be solved.

Considering the above mentioned aspects that can be improved upon the existing literatures on FFR, further adoption of the concept is hampered by the lack of a simple control system for more straightforward operations, as well as a wider range of the feedwater concentration needs to be tested to ascertain the operational viability of incorporating FFR in membrane desalination operations for managing highly concentrated wastewaters.

2.3 Introduction to Zero Liquid Discharge (ZLD)

ZLD or near-ZLD has been proposed as an advanced wastewater management approach in recent years to minimize the environmental impacts of highly polluted

and toxic industrial wastewater discharges. The commonly adopted ZLD applications and some emerging ZLD-oriented technologies with their advantages and limitations were presented in Tong and Elimelech (2016). The downstream brine concentrating stages commonly adopt vapor compression technology to further reduce the wastewater volume. Approaching the final dewatering stage, the boiling point of the solution containing highly soluble substances such as calcium chloride will increase drastically as the solution concentration elevates. The crystallizer must be provided with a large amount of energy to sustain the desired operating temperature. Such high temperature will cause the solvents to undergo the hydrolysis process and produce hydrochloric acid which can be tremendously harmful to the equipment (Feng et al., 2015). Thus, costly corrosion-resistant construction material becomes essential thereby raising the capital expenses. Brine crystallizers or evaporation ponds are the final step to complete the ZLD systematic scheme. To genuinely achieve ZLD, the final dewatering step is indispensable thus far. Therefore, efforts are expected to be devoted in diminishing the highly concentrated wastewater volume coming from the previous treatment stages.

Membrane-based technologies used in ZLD or near-ZLD systems had been thoroughly reviewed in Tsai et al. (2017). Comparing to other traditional treatment methods, membrane-based technologies have the advantages of requiring relatively low energy consumption, possessing technical maturity, and being able to provide flexible modularity. However, fouling/scaling again remains the primary challenge of applying membrane-based technologies in the ZLD systems. For instance, the feasibility of using RO as the final step in the ZLD processes will depend on the TDS level of the effluent obtained from previous treatments, as shown in Fig 2.3 (Subramani and Jacangelo, 2014). After the removal of the limiting constituents from the RO concentrate, the treated water quality will determine whether RO can be utilized for further treatment. Otherwise, the energy-intensive thermal-based methods will be applied instead. The upper operating limit of the feedwater concentration for RO desalination in terms of TDS level is ~70,000 mg/L (Coday et al., 2014). Once the limit is exceeded, the concentration polarization effect and fouling/scaling formation associated with the redundant osmotic pressure will impede the application of RO desalination. Therefore, it is imperative to develop more advanced technologies to boost the tolerance of membrane desalination in respect

with higher feedwater concentrations (> 70,000 mg/L) for the ultimate ZLD pursuance.

Fig 2.3: ZLD & near-ZLD process illustration

2.3.1 Zero Liquid Discharge (ZLD) & Flue Gas Desulfurization (FGD)

Flue gas desulfurization (FGD) wastewater is another example of the highly concentrated wastewaters. In addition to the trace amount of heavy metals, FGD wastewater also encompasses a large quantity of highly soluble substances such as Cl^- , SO_4^{2-} , Mg^{2+} , and Ca^{2+} . Jia and Wang (2018) has designed a FGD wastewater treatment system which can achieve near-ZLD. The system consists of chemical softening and NF filtration as pre-treatments, followed by a tertiary vacuum membrane distillation step. Chemical softening was incorporated for calcium and magnesium removal. NF filtration was adopted to separate the chloride and sulfate ions for further recovery of the sodium sulfate and sodium chloride. The rejection rate of each ion greatly depends on the characteristics of the NF membranes being

utilized.

2.3.2 Zero Liquid Discharge (ZLD) & the Coal Industry in China

ZLD applications in the coal production industry of China have been review in Xiong and Wei (2017). All the major intensive coal production areas in China are experiencing various levels of stress on their fresh water supply. In 2015, the Ministry of Environmental Protection of China has introduced a mandatory requirement for all coal producing plants in China to implement ZLD. The major challenges faced during the ZLD implementation for the coal industry are the existence of recalcitrant organic matters, high capital expenses & operating costs associated with the comprehensive pre-treatments as well as the high energy consumption, together with the management of the crystallized solids. Hence, membrane technologies with its advantages of lower energy consumption requirement compared to the thermal evaporation processes, fewer solid wastes production compared to that of the chemical precipitation, and minimal brine production with relatively high recovery rate, have the potential to alleviate the above-mentioned concerns.

2.3.3 Zero Liquid Discharge (ZLD) & Reverse Osmosis (RO) Concentrate management

Facing the growing number of industrial applications with RO/NF membrane desalination technologies, the proper management and discharge of the large amount of highly concentrated RO/NF brine has been realized as an inevitable issue to be solved. Examples of potential environmental damage include pH disruption, eutrophication in various water bodies, and bioaccumulation in marine species. It has been reported that one desalination plant in Ashkelon, Israel, is discharging 330,000 m³/day of RO brine into the environment. It was predicted that the annual desalination brine production in the Kingdom of Saudi Arabia will be several hundred million in m³ (Sauvet-Goichon, 2007). Being threatened by this large amount of highly concentrated wastewater which may lead to various environmental issues, suitable and efficient methods are expected to be developed in managing the RO/NF brine.

Some conventional methods which have been used in industrial applications for managing RO/NF brine include underground injection, surface water discharge, and dewatering in evaporation ponds. Issues with discharging RO/NF brine into the

environment include the higher cost associated with burdensome transportation, resulted from dealing with inland desalination plants compared to that of coastal area, and contamination in freshwater bodies when leakage occurs. Problems with using evaporation ponds are mainly associated with spacing requirement. Larger evaporation ponds are needed for increasing amount of the influent, which would lead to larger space requirement and thus higher capital expenditure. In addition, under the situation of operating at over capacity, overflow can cause contamination to the surrounding environment (Khedr, 2012).

To improve the justifiable as well as to alleviate the concerns for possible environmental contamination, one logical solution is to minimize the RO/NF brine volume entering the final step to the largest extent by applying effective pre-dewatering treatments. Cost of the transportation and evaporation ponds construction can therefore be reduced through dealing with a smaller amount of influent. The ultimate goal is to achieve ZLD of which the concept has becoming more prevalent among the regulatory authorities in different countries, and the relevant compulsory regulations are expected to be enacted.

Likewise, the adoption of ZLD was investigated for the management of RO brine. Pre-treatments have been realized as the most critical elements of the RO brine ZLD systems (Semblante et al., 2018). Effective removal of the scaling precursors is the primary objective of the pre-treatment steps. Chemical precipitation as a traditional pre-treatment method has been widely adopted. However, the significant operating cost, vulnerability towards temporal water quality fluctuation, and burdensome solid waste management are the downsides of chemical precipitation, which consequently entails further improvements or alternative treatment methods for RO brine management.

NF was found to be more effective in removing polyvalent cations as well as reducing the TDS level for the desalination brine, compared with hot lime softening (HLS) without causing any additional sludge formation. Another study has proved that NF and low-pressure RO can be more effective in removing isotopes and HMCs compared to the conventional methods such as ion exchange, HLS, and chemical precipitation (Pérez -González, 2015). Using NF membrane to remove two types of the most commonly used antiscalants found in the desalination brine, which are

sodium hexametaphosphate (SHMP) and disodium ethylenediaminetetraacetate (Na_2EDTA), was shown to be highly effective with >96% removal efficiency. NF was also advocated as one of the emerging pre-treatment methods for RO brine ZLD systems (Istirokhatun, 2018). NF has outstanding proficiency in removing polyvalent ions (scaling precursors) with moderate energy consumption and capital expenses (Semblante et al., 2018). However, limited information is available by far on the NF performance as a pre-treatment step for the RO brine management.

2.3.4 Zero Liquid Discharge (ZLD) & Shale Gas Produced Water (PW)

Although no literature review has been found so far regarding the implementation of the ZLD concept in the shale gas PW water treatment, ZLD provides a promising solution for PW management to comply with the increasingly stringent regulatory requirements. Membrane desalination can be viewed as an encouraging competitor of thermal-based technologies in terms of alterable modularity, scalability, lower capital cost, and lower energy consumption. The complexity of the shale gas wastewater compositions, high pollutant concentration, elevated energy consumption, and fouling/scaling issues are the main challenges for membrane based ZLD applications in the shale gas PW management, which are expected to be overcome by the future technological advancements.

2.3.5 Summary for Zero Liquid Discharge (ZLD)

ZLD is an emerging and ever-growing concept for achieving minimal wastewater volume discharge into the environment. ZLD has been applied in various industrial applications such as FGD, coal industry in China, and RO/NF concentrates management. As mentioned, to genuinely achieve ZLD, the final step of the crystallization is indispensable. Hence, efforts are expected to be devoted into diminishing the highly concentrated wastewater volume coming from the preceding treatment stages. Therefore, membrane technologies with the flow reversal concept might be a promising solution to further dewater the highly concentrated wastewater at the downstream of the ZLD systems, thus reducing the influent volume entering the final crystallization step and eventually reducing the operating cost.

Chapter 3 Experimental Setup, Materials & Methodology

3.1 Experimental Setup & Working Principle of the System

The integrated RO (iRO) system had been built to implement the concept of fast feed flow reversal (FFFR) into the conventional membrane desalination processes, aiming to mitigate the issues on the fouling/scaling formation in treating highly concentrated wastewaters. A previous study on investigating the iRO system in managing synthetic wastewaters containing NaCl concentration similar to that of seawater has been conducted, results of the study can be found in Li et al. (2019). The working principle of the iRO system can be interpreted by the illustration shown in Fig 3.1. The system is automatically controlled by a specifically designed operation program. No manual intervention is required during the operations once the system is started with the pre-set desired operating conditions. A complete cycle consists of two sub-sections. The 2-way pneumatic valves V1-V8 shown in the diagram are used to control the switching of the FFFR system.

Fig 3.1: The simplified illustration of the laboratory experimental setup

During the first half of each complete cycle, valves 1, 4, 5, and 7 are open while the other valves are closed. Feedwater is pumped by the high-pressure pump and flows

into the membrane module passing valve 1. Two streams, the brine and permeate are produced during the desalination process. The brine stream bypasses valve 4 so that piston 2 is subsequently pushed from the left- to the right-side inside the piston cylinder. Simultaneously, feedwater coming from the low-pressure pump bypasses valve 7 and pushes piston 2 to the left. Brine stored on the left side coming from the previous cycle bypasses valve 5 and is recycled back into the system. This portion of the brine is indicated with the dashed line on the diagram. The permeate stream is directly recycled back to the system.

During the second half cycle, valves 2, 3, 6, and 8 are open while the others are closed. Feedwater flows into the membrane from the tail-end of the previous half cycle to attain the flow reversal operation. Piston 1 and 2 separately moves towards the opposite direction during each half cycle and the moving direction is switched between every two consecutive half cycles. When both piston 1 and 2 reach their designated positions during each half cycle, the following half is automatically triggered. In addition, water stored inside the right-hand side of the piston is the feedwater coming from the previous half cycle through the low-pressure pump. This portion of the feedwater flowrate is boosted as the flowrate of the brine pushing the piston to the right. A booster pump is needed to supplement the brine flowrate drop along the system's pipelines. The involvement of the pistons was designed to recover the energy stored in the highly pressurized brine, so that the energy efficiency of the overall system can be improved. However, in this study, the focus is on the feasibility of treating highly concentrated wastewater through implementing the FFFR concept.

3.2 Materials and Methodologies

3.2.1 Nanofiltration (NF) Membrane

NF membrane was deliberately selected in this study over RO, which is the more commonly used membrane in treating various wastewaters in the industrial applications, as the operating pressure for the RO desalination systems in treating highly concentrated wastewaters might exceed the allowable pressure limit of the membrane material. NF90-2540 from DOW FILMTEC™ Membranes was selected in the first part of the study due to its relatively high rejection for divalent ions and moderate rejection for monovalent ions, together with its moderate energy

consumption and a wider range of the treatable wastewater concentrations. During the second part of the study, NF90-4040 was found to be requisite, of which the reason will be discussed into details in the later sections.

3.2.2 Chemicals & Synthetic Wastewater

Based on the reported data from the relevant studies introducing the commonly found shale gas PW compositions, NaCl, MgSO₄ and CaCl₂, have been chosen as the solutes added in the synthetic wastewaters in this study, as shown in Table 2.1. NaCl was adopted as the base element of the synthetic wastewaters since it is the most commonly found substance in various industrial wastewaters and is often present in high concentrations. Each set of the experiments were conducted using synthetic wastewaters with a fixed concentration of NaCl mixed with different concentrations of MgSO₄ or CaCl₂. NaCl concentration in 30-35 g/L which is close to that of seawater, was used as a starting point and later was gradually raised to a certain operating limit of the NF membrane. ~2-6g/L is the commonly found concentration range for MgSO₄ and CaCl₂ in the industrial wastewaters and was therefore applied in this study. However, experiments with feedwater containing 45 g/L of CaCl₂ were conducted in the second part of the study, due to the higher solubility of CaCl₂ in water compared with MgSO₄. In addition, the rejection rate for NF membranes in removing divalent ions like Ca²⁺ is particularly high so that the bulk concentration inside the membrane is expected to be higher compared to operations with feedwater containing monovalent ions only, and thus could potentially provide amplified effect of the concentration accumulation owing to $R > 1$ compared with the NaCl experiments.

An acrylic feedwater tank with the dimensions of 60cm*60cm*100cm was customized from IDSG Engineering & Trading Pte Ltd., as shown in Fig 3.2 (a). To make the synthetic wastewater for each experiment, the acrylic tank was initially filled with 100L of the tap water, and the desired amount of chemicals were then dissolved and mixed well into the water before it entered the system by the work of the hydraulic pumps. All the hydraulic pumps used in this study were purchased from KROHNE PTE LED. They are located at the bottom of the main part of the setup, shown as (c) in Fig 3.2.

Fig 3.2: Picture of the laboratory experimental setup in partial: (a) feed water tank, (b) compressed gas cylinder), (c) hydraulic pumps

Due to the large amount of NaCl needed to imitate the highly concentrated wastewaters, conductivity standard calibrations of NaCl have been established prior to conducting the experiments to ensure accurate base concentrations can be obtained. The detailed plots of the standard calibrations are appended in Appendix C.

3.2.3 Other Information of the System's Operation

A compressed hydrogen gas cylinder labeled as Fig 3.2 (b) was supplied by Leeden National Oxygen Ltd., and was used to control the switching of the valves introduced in the section of the experimental setup. Fig 3.3 is a picture of the core part of the setup. The detailed description of each part can be found in the caption.

Fig 3.3: Picture of the laboratory experimental setup in partial: (a) Pressure valve, (b) flow meters, (c) membrane module, (d) piston cylinders.

The hydraulic flow rates and operating pressure were preset on the controlling interface shown in Fig 3.4, prior to the commencement of the experiments. A smaller portion of the total pressure within the system was generated by the feedwater hydraulic pumps, and the desired ultimate operating pressure for each experiment was then adjusted by a pressure valve installed in the setup, which is indicated as (a) in Fig 3.3. There are two tanks used in the setup. One is the feedwater tank in which the synthetic feedwater is made. Another tank is for receiving the permeate and brine streams after treatment, and their mixture flows back into the feedwater tank. Both tanks are open aired, thus the temperature of the feedwater is similar to the room temperature.

3.2.4 Data Measurement

Seven pressure meters and four flowrate meters are installed in the system for data measurements as indicated in Fig 3.5. P1-7 and FT1-4 indicate the location of the pressure meters and flowrate meters inside the system, respectively. The output of

P1-7 separately represents the applied pressure, pressure on the left- and right- hand side of piston 1, pressure on the left- and right-hand side of piston 2, and pressure before and after the booster pump. FT1-4 measures the feedwater flowrates, flowrate to push the pistons moving from left to right, flowrate of the booster pump, and permeate flowrate, respectively. All data were instantly recorded during the experiments and logged into the designated files created with the system. Therefore, all the above-mentioned data can be checked anytime during the operation, and timely reaction can be made if any abnormality is observed.

Fig 3.4: The controlling interface of the iRO system

The concentration of the added chemicals, feedwater flowrate, and applied pressure were used as the main operating variables in running the experiments, to understand their effects on the system's performance. The primary performance indicators obtained from the experimental data were the permeate recovery rate, energy recovery efficiency (ERE), specific energy consumption (SEC), permeate flux, and salt rejection. The permeate recovery rate was measured using the permeate flowrate divided by the feed flowrate entering the membrane module. ERE was determined by calculating the flow rate recovery ratio of the pistons. The permeate flux was obtained

using the average feed flowrate times the average recovery rate and divided by the membrane surface area provided by the manufacturer. The permeate water was manually collected intermittently to record the treated water quality during some of the experiments for the solute rejection measurement.

Fig 3.5: The simplified experimental setup involving the pressure meters and flowrate meters

After the initial assessment of the system's feasibility and stability, the concentration of the pollutants added in the synthetic wastewater was increased gradually. Two other important operating variables, the applied pressure and feedwater flowrate were also controlled to understand how they would affect the performance of the FFR setup. In particular, higher applied pressure is expected to increase the permeate production, but it can potentially harm the water quality due to the effect of the concentration polarization mechanism and weakened effect of the shear stress adjacent to the membrane surface. The impact of the feedwater flowrate was found to be insignificant on the overall performance of the iRO system in a previous study by Li et al. (2019). Nevertheless, the effect of the feed flowrate, although not as the primary focus of this study, was also used as an operating variable in several experiments.

3.2.5 Cleaning of the Setup

The setup was cleaned after each experiment to avoid any unwanted salt residual and subsequent lethal erosion to the metallic pipelines of the system. To clean the setup, tap water was used as the feedwater, and the system was kept running until the brine conductivity reached a stable value, which indicating that no more chemicals was left to be flushed out of the system. The stabilized value of the brine conductivity reached after each cleaning process was ~ 0.6 mS/cm, which is the brine conductivity obtained using water as the feed, and operated with a new post-compaction membrane.

3.3 Classification of Experiments Conducted with Different Operations

3.3.1 Cross-Flow Filtration (CFF)

CFF, also known as tangential flow filtration, is a common method applied for desalination using the spiral wound membrane modules. In CFF, the feedwater flows tangentially along the membrane surface with a single flow direction throughout the desalination process. The experiments conducted with the CFF mode in this study were mainly for the measurements required in studying the effect of the initial membrane compaction, calculating the membrane resistance. Although the setup used in this study was originally constructed to implement the FFFR concept, CFF can still be achieved by controlling the valves.

3.3.2 Fast Feed Flow Reversal (FFFR)

As mentioned earlier, FFR is an innovative technique developed to eliminate the fouling and scaling issues in membrane desalination processes, and FFFR can be seen as a derivative with much shorter reversal intervals. Therefore, experiments with the FFFR operation were conducted in this study to understand its feasibility as well as any unexpected issues in applying this emerging concept into the NF membrane desalination processes. In addition, the experiments conducted in the current study are named according to the nature of their operating methods. Tests run under CFF and FFFR are named with an initial letter C, stands for cross-flow, and R, stands for reversal, respectively.

3.4 Classification of Experiments Conducted with Different Membrane Models

3.4.1 NF90-2540

NF90-2540 was first selected due to the design specifications of the iRO system. iRO was previously designed and constructed specifically for the RO membrane in the model of SW30-2540. Therefore, the membrane housing installed in the setup was designed to fit the dimensions of SW30-2540. After NF membranes were decided to be incorporated in this study, NF90-2540 with the same dimensions as SW30-2540 was logically selected to start the experiments with.

NF90-2540 was used for all experiments in part 1 of the study, namely with the efforts to implement the FFFR operation in a lab-scale NF desalination setup for the first time.

3.4.2 NF90-4040

The second part of the study mainly focused on understanding how the ratio R of the hydraulic retention time T_H and flow reversal period T_R affects the permeate flux of the membrane desalination process in the FFFR operation, especially under the situations where $R > 1$ so that concentration accumulation within the membrane module would occur. However, due to the original design of the iRO setup, such desired condition described above was found to be unachievable using the NF90- 2540 model. R was found to be either smaller than or close to 1 in all experiments conducted in part 1 of the study. Therefore, NF90-2540 was later replaced by NF90- 4040 to resolve this problem.

NF90-4040 has the same length as NF90-2540 but with a larger cross-sectional area as well as a larger active membrane area. The idea of using NF90-4040 to achieve $R > 1$ is that, with the same length but a larger cross-sectional area, the spiral wound membrane cylindrical volume would become larger. On one hand, with a same feedwater flowrate, T_H would become longer due to the larger membrane volume of NF90-4040. On the other hand, T_R in this study largely depends on the brine flowrate which pushes the pistons until they reach their designated positions, and a signal is thereafter given to the system to initiate the flow reversal for the following cycle to begin. Therefore, NF90-4040 was used in all experiments conducted in part 2 of the study.

3.5 Data Analysis

Experimental data was continuously recorded and logged into the designated files every second or two, depending on the operating period. Because the data analysis performed in this study mainly focused on data variation trend versus time, experiments with longer operating period therefore required less frequent data logging. In addition, data was selected at each alternative cycle in the further processing and analyzation processes. Microsoft Excel was the primary analytical tool used in this study. Functions were written to process the raw data obtained from the readings of the pressure and flowrate meters. For each cycle to be analyzed, the average value of the applied pressure, feed flowrate, energy recovery efficiency (ERE), permeate flowrate, permeate recovery ratio, and specific energy consumption (SEC) were calculated and summarized in a single Excel worksheet. After data analysis was completed for all cycles, the average value of the above-mentioned operating and performance indicators were plotted against time to show how they have changed during the experiments. In addition, the permeate and/or brine conductivity values were manually measured to calculate the salt rejection, mostly for every 30 minutes during the experiments in part 1 of the study and were measured as approaching the end of the experiments for part 2 of the study.

Chapter 4 Results & Discussions

The following main topics will be presented in this chapter:

- (a) The performance of applying the fast feed flow reversal (FFFR) technique under various nanofiltration (NF) membrane desalination conditions in treating highly concentrated feedwaters.
- (b) The effects of the ratio R of the hydraulic retention time (T_H) and reversal period (T_R) of the FFFR operation, especially with $R > 1$, on the NF membrane desalination processes.
- (c) The performance of the mathematical model developed in predicting the solute concentration profile and permeate flowrate, for both the cross-flow filtration (CFF) and FFFR operations.

All experimental results obtained in this study are listed in Appendix A. The names and operating conditions are listed in the corresponding tables, categorized based on the operation mode and the solutes involved in the specific experiment. As mentioned, the capital letter R and C refers to the FFFR operation and cross-flow filtration (CFF), respectively. The letters followed by that indicates the chemicals added in the feedwater. For example, CNM indicates that the experiment was conducted in the CFF mode, with NaCl and MgSO₄ added in the feedwater. In addition, the experiments conducted with NF90-2540 and NF90-4040 are separately annotated as 2540 and 4040 in the tables. The numerical results are plotted against time and are presented below the tables in Appendix A. The applied pressure & permeate recovery rate for all tests, and the permeate & brine conductivity with the salt rejection for some of the tests are shown in the plots.

4.1 Part 1 of the Study: Performance of Applying FFFR in Desalination using NF90-2540 Membrane

As mentioned in the introduction section, the FFFR technique in dealing with the highly concentrated wastewater has not been previously studied. Experiments were therefore conducted with the FFFR-incorporated desalination system using NF90-

2540, to investigate the performance of the system. The primary purpose of this part of the study is to provide a feasibility assessment of the technique based on the indicators as follows:

- (a) The desalination performance, e.g. the permeate recovery and salt rejection rates in dealing with various pollutants in different concentration levels
- (b) The operating limits in terms of the highest concentration that can be managed by the system with lower but acceptable dewatering effect
- (c) The operational stability of the system with different levels of the applied pressure corresponding to the feedwater concentrations.

These results are presented here in hoping to provide a reference for future applications of the FFR technique in managing highly concentrated wastewaters, particularly with NF desalination systems.

4.1.1 Numerical Results and Discussion on FFR Operation Performance in Treating Feedwater with Higher Concentrations

4.1.1.1 Results of the experiments with Feed Water containing NaCl and MgSO₄

For the experiments conducted with feedwater containing NaCl and MgSO₄, the operating conditions in terms of the feedwater constituent, applied pressure, feedwater flowrate and, the operating performances in the energy recovery efficiency (ERE), specific energy consumption (SEC), permeate recovery rate and salt rejection are listed in Table 4.1. The maximum applied pressure is often limited by factors such as the tolerance level of the membrane material used towards the applied pressure. For the NF90-2540 membrane used in this study, the maximum applied pressure was set at ~35 bar to ensure that no irreversible deterioration to the membrane structure and function would occur.

The results of these experiments are divided into three groups based on the concentration of NaCl as the base solute. For each group, the experiments are listed in ascending order of the corresponding applied pressure and the concentration of MgSO₄ as the affiliated solute. The feed flowrate was found to be an insignificant

factor in affecting the performance of the experiments in the previous study using the iRO system in treating feedwater containing NaCl only. Therefore, the feedwater constituent and the applied pressure are viewed as the primary operating variables in this study. Nevertheless, various feed flowrates can still be found in some of the experiment groups, e.g., tests RNM4-6 as shown in Table 4.1. The feedwater concentrations and applied pressures for these three tests are almost the same, whereas the feed flowrates were set at different levels. The permeate recovery and solute rejection are found to be close for the three experiments as shown in Fig 4.1, which agrees with the conclusion drawn from the previous study that, the feed flowrate is insignificant in affecting the system's performance.

Table 4.1: Desalination performance of FFR operation for treating feedwater containing NaCl + MgSO₄

Test	NaCl + MgSO ₄ (g/L)	Pressure (bar)	Feed flowrate (L/min)	ERE (%)	SEC (kWh/m ³)	Recovery (%)	Rejection (%)
RNM4	30 + 1	19.6	1.9	90	0.97	12.7	65.8
RNM5	30 + 1	19.7	2.4	92	1.01	10.5	66.6
RNM6	30 + 1	20.6	2.8	91	1.12	10.5	68.4
RNM7	35 + 3	23.2	2.0	91	0.73	16.5	66.6
RNM8	35 + 3	25.3	2.3	91	1.11	15.9	66.4
RNM9	35 + 3	28.5	2.2	93	1.15	24.6	72.7
RNM10	35 + 3	33.0	2.2	93	1.15	23.6	71.6
RNM11	35 + 6	28.9	2.1	95	1.13	22.1	71.3
RNM12	50 + 3	28.2	2.2	92	1.35	10.6	56.8
RNM13	50 + 3	30.3	1.8	94	1.20	13.6	57.1
RNM14	50 + 3	35.7	1.9	94	1.34	16.3	62.9

For the experiments with feedwater containing 30g/L of NaCl and 1g/L of MgSO₄, or with the TDS level of 31g/L under the applied pressure ranging between 19.6-20.6 bar, results of ERE, SEC, permeate recovery and salt rejection were found to range within 90-92%, 0.97-1.12 kWh/m³, 10.5-12.7% and 65.8-68.4%, respectively. For the experiments with feedwater containing 35g/L of NaCl and 3-6 g/L of MgSO₄, or with the TDS level of 38-41g/L under the applied pressure ranging between 23.2-28.9 bar, results of ERE, SEC, permeate recovery and salt rejection were found to

range within 91-95%, 0.73-1.15 kWh/m³, 15.9-24.6% and 66.4-72.7%, respectively. For the experiments with feedwater containing 50g/L of NaCl and 3 g/L of MgSO₄, or with the TDS level of 53g/L under the applied pressure ranging between 28.2-35.7 bar, results of ERE, SEC, water recovery and salt rejection were found to range within 92-94%, 1.20-1.35 kWh/m³, 10.6-16.3% and 56.8-62.9%, respectively. Therefore, the general performance indicators for the experiments run with feedwater containing NaCl + MgSO₄ in the TDS level of 31-53 g/L, and with the applied pressure in 19.6-35.7 bar, results of ERE, SEC, water recovery and salt rejection were found to range within 90-95%, 0.73-1.35 kWh/m³, 10.5-24.6%, and 56.8-72.7%, respectively.

Fig 4.1: Performance indicators of test RNM4-6 versus the tests' feed flowrates

It can be observed that for the experiments with the same feedwater quality, both the permeate recovery and overall salt rejection improved with the increasing applied pressure as shown in Fig 4.2 and Fig 4.3. The permeate velocity v can be calculated with Equation (1).

$$v = \frac{\Delta p - \Delta \pi}{R_m} \quad (1)$$

Where Δp , $\Delta \pi$ and R_m refers to the applied pressure, pressure difference across the membrane surface, and membrane resistance, respectively. $\Delta \pi$ is proportional to the

bulk concentration c , ion numbers in a single solute molecule n , gas constant R , absolute temperature T_a , and solute rejection r . Therefore, the permeate velocity v depends on both the applied pressure and bulk concentration. On the other hand, the permeate flowrate Q_p is proportional to v , the increasing recovery rate observed therefore indicates that under these specific operating conditions, the change in the applied pressure Δp surpassed the change in the osmosis pressure difference $\Delta\pi$, which is proportional to the bulk concentration c , and thus resulted in a positive change in the permeate flowrate Q_p .

Fig 4.2: Performance indicators of test RNM7-9 versus the tests' applied pressures

The overall salt rejection can be calculated based on Equation (2),

$$R_{salt} = \frac{c_f - c_p}{c_f} = 1 - \frac{c_p}{c_f} \quad (2)$$

where C_f and C_p refers to the feedwater concentration and permeate water concentration, respectively. When C_f remains the same, an increase in the rejection rate indicates that the concentration on the permeate side of the membrane surface C_p has become lower. This lower permeate concentration was caused by the dilution effect due to the higher permeate recovery interpreted above.

Fig 4.3: Performance indicators of test RNM12-14 versus the tests' applied pressures

The permeate recovery values in the third group were found to be generally lower than that of the second group. This can be explained by that, the higher transmembrane osmosis pressure $\Delta\pi$ induced by the higher solute concentration, would require more counteract applied pressure Δp to produce the same amount of the permeate water Q_p , compared with an operation with a lower level of the feedwater concentration.

The salt rejection value was observed to decrease with feedwater concentration C_f in Table 4.1. Although C_f became larger with more chemicals added in the feedwater, the observed rejection decline indicates that the increase in the concentration on the permeate side of the membrane surface C_p was larger than the increase in C_f . This observation can be explained based on the lower permeate flux observed at the same time, which consequently resulted in a more concentrated permeate flux.

The ERE values for the above experiments were found to increase with applied pressure due to the smoother movement of the pistons, which consequently resulted in more efficient energy conversion processes. The SEC value is closely associated with the frequencies of all water pumps as well as the permeate production for each

experiment. The higher the frequency of the hydraulic pumps and the desired permeate production, the higher the SEC value would be due to the elevated electricity consumption.

4.1.1.2 Results of the experiments with Feed Water containing NaCl and CaCl₂

Listed in Table 4.2 are the operating conditions in the feedwater constituent, applied pressure and feed flowrate and, the operating performances in the permeate recovery and salt rejection of the experiments conducted with feedwater containing NaCl and CaCl₂. These experiments are listed in ascending order in both the concentrations of NaCl and CaCl₂.

Table 4.2: Desalination performance of FFFR operation for treating feedwater containing NaCl + CaCl₂

Test	NaCl + CaCl ₂ (g/L)	Pressure (bar)	Feed flowrate (L/min)	ERE (%)	SEC (kWh/ m ³)	Recovery (%)	Rejection (%)	Comment
RNC3	30 + 1	25.0	2.3	91	1.00	18.6	-	Rejection is not available for some tests. However, at least one result can be found for each feed constituent condition.
RNC4	30 + 1.11	24.3	2.3	92	1.04	16.4	67.8	
RNC5	30 + 3	24.8	2.3	91	1.05	16.2	-	
RNC6	30 + 3	26.3	2.3	95	0.91	16.6	67.6	
RNC7	35 + 1	24.1	2.3	95	0.86	14.5	67.6	
RNC8	35 + 1	24.6	2.3	93	1.03	13.5	-	
RNC9	35 + 3	24.6	2.3	93	1.08	11.5	63.2	

The applied pressures are similar ranging within 24.1-26.3 bar, and the feed flowrates are also identical for all experiments. Therefore, the feedwater constituent can be viewed as the only variable. The experiments are divided into two groups based on the base NaCl concentration. For the 30g/L NaCl group, with the TDS level ranging between 31-33g/L and an average applied pressure of 25.1 bar, results of ERE, SEC, water recovery and salt rejection are found to range within 91-95%, 0.91-1.05 kWh/m³, 16.2-18.6% and 67.7%, respectively. For the 35g/L NaCl group, with the TDS level ranging between 36-38g/L and an average applied pressure of 24.4 bar, results of ERE, SEC, water recovery and salt rejection are found to range within 93-95%, 0.86-1.08 kWh/m³, 11.5-14.5% and 65.4%, respectively. Therefore, the general performance indicators for the experiments run with the feedwater containing NaCl + CaCl₂ in 31-38 g/L of TDS and with the applied pressure in 24.1-26.3 bar, the ERE,

SEC, water recovery and salt rejection were found to range within 91-95%, 0.86-1.08 kWh/m³, 11.5-18.6%, and 63.2-67.8%, respectively. The effect of the feedwater concentration and applied pressure on the permeate recovery and salt rejection obtained from the NaCl + CaCl₂ experiments, are found to be similar compared with the findings from the NaCl + MgSO₄ experiments.

As mentioned in the earlier sections, MgSO₄ and CaCl₂ as two of the most commonly found compositions in the highly concentrated industrial wastewaters, were selected in this study for the feasibility assessment of the FFR technique. The comparison between the performance indicators with MgSO₄ and CaCl₂ as the affiliated solute to the base NaCl under similar operating conditions is shown in Table 4.3. The average value of the operating conditions and the performance indicators are shown for each concentration combination of the solutes. For example, the results of test RNM4,5,6 shows the average results for these three tests, of which the feedwater constituent and their corresponding concentrations are the same. The experiments are categorized into two groups, with the feedwater consists of NaCl + MgSO₄ and NaCl + CaCl₂.

Table 4.3: Desalination performance indicators of the FFR operation for treating feedwater containing NaCl + MgSO₄/CaCl₂ under similar operating conditions

Test	NaCl + MgSO ₄ /CaCl ₂ (g/L)	Pressure (bar)	Feed flowrate (L/min)	ERE (%)	SEC (kWh/ m ³)	Recovery (%)	Rejection (%)
RNM4,5,6	30 + 1	20.0 ± 0.5	2.4 ± 0.4	91.0 ± 1.0	1.03 ± 0.08	11.2 ± 1.1	66.9 ± 1.3
RNM7,8	35 + 3	24.3 ± 1.0	2.15 ± 0.15	91.0 ± 0	0.92 ± 0.19	16.0 ± 0.5	66.5 ± 0.1
RNC3,4	30 + 1	24.7 ± 0.3	2.3 ± 0	91.5 ± 0.5	1.02 ± 0.02	17.5 ± 1.1	67.8 ± 0
RNC5,6	30 + 3	25.6 ± 0.7	2.3 ± 0	93.0 ± 2.0	0.98 ± 0.07	16.4 ± 0.2	67.6 ± 0
RNC7,8	35 + 1	24.4 ± 0.2	2.3 ± 0	94.0 ± 1.0	0.95 ± 0.08	14.0 ± 0.5	67.6 ± 0
RNC9	35 + 3	24.6	2.3	93	1.08	11.5	63.2

The operating conditions in the applied pressure and feed flowrate are similar for all tests except for the applied pressure of test RNM4,5,6, which is lower than the rest. As shown in Table 4.3, no unexpected large difference can be observed in comparing the performance indicators between the two groups of experiments with the two different affiliated solutes added in the feedwater. The difference of the rejection rate among these tests are all close to 1% which are negligible except for

tests RNM7,8 and RNC9, of which the operating conditions are almost identical, but the rejection rate was found to be 3.3% larger in test RNM7,8. Nanofiltration membranes are well known for their high rejection rates in removing divalent ions. The rejection rate is found to be as high as 99% in the experiments conducted with feedwater containing MgSO_4 only in this study, i.e., RNM15-17, of which the results can be found in Appendix A. Therefore, the rejection rate for feedwater containing MgSO_4 shall be larger compared with CaCl_2 , due to the lower rejection rate in removing Cl^- with the NF membranes.

4.1.1.3 Results of the experiments with Feed Water containing NaCl only

The operating conditions in the feedwater constituent, applied pressure and feed flowrate, together with the performances in the permeate recovery and salt rejection for experiments with feedwater containing NaCl only are listed in Table 4.4. The experiments are listed in ascending order of the NaCl concentration as well as the applied pressure. With the TDS level ranging within 30-70 g/L, and the applied pressure ranging between 19.4-35.3 bar, results of ERE, SEC, permeate recovery and salt rejection for NaCl experiments are found to range within 90-95%, 0.94-2.03 kWh/m^3 , 5.7-20.8% and 44.3-66.3%, respectively.

ERE, permeate recovery and salt rejection all increased the applied pressure for operations with the same feedwater quality as expected. In addition, both the permeate recovery and salt rejection decreased with the feedwater concentration when a similar pressure was applied. As mentioned earlier, the TDS level of 70 g/L and applied pressure of ~35 bar are the upper operating limits for most of the commercial NF membranes. Based on the average values of tests RN10 and RN7, the FFFR-incorporated desalination system using the NF90-2540 model resulted in 5.4% in the permeate recovery rate and 47% in the salt rejection, when treating feedwater containing 70g/L of NaCl with an applied pressure of 34.2 bar. In addition, the average results of ERE and SEC for tests RN10 and RN7 was 94% and 1.95 kWh/m^3 , respectively.

Table 4.4: Desalination performance of the FFR operation for treating feedwater containing NaCl only

Test	NaCl (g/L)	Pressure (bar)	Feed flowrate (L/min)	ERE (%)	SEC (kWh/m ³)	Recovery (%)	Rejection (%)	Comment
RN1	30	19.4	2.4	90	1.02	10.4	66.3	Rejection is not available for test RN2. However, the experimental observation is not affected by the lack of this information.
RN2	30	25.4	2.3	93	0.96	18.2	-	
RN3	35	27.9	2.1	95	0.94	20.8	65.2	
RN4	50	24.4	1.7	91	1.30	9.7	48.4	
RN5	50	29.1	1.8	93	1.23	13.0	56.3	
RN6	60	28.9	2.1	91	1.67	8.4	47.5	
RN8	60	35.2	2.2	93	1.55	11.1	50.1	
RN9	60	35.3	2.2	93	1.62	10.5	53.5	
RN10	70	33.8	2.8	94	2.03	5.7	44.3	
RN7	70	34.6	2.6	93	1.87	7.7	50.5	

Table 4.5: Desalination performance of the FFR operation for treating feedwater containing NaCl only, or NaCl + MgSO₄/CaCl₂ under similar operating conditions

Test	NaCl + MgSO ₄ /CaCl ₂ (g/L)	Pressure (bar)	Feed flowrate (L/min)	ERE (%)	SEC (kWh/m ³)	Recovery (%)	Rejection (%)
RN1	30	19.4	2.4	90	1.02	10.4	66.3
RN2	30	25.4	2.3	93	0.96	18.2	-
RN3	35	27.9	2.1	95	0.94	20.8	65.2
RN5	50	29.1	1.8	93	1.23	13.0	56.3
RNM4,5,6	30 + 1	20.0 ± 0.5	2.4 ± 0.4	91.0 ± 1.0	1.03 ± 0.08	11.2 ± 1.1	66.9 ± 1.3
RNM7,8,10	35 + 3	27.2 ± 4.9	2.2 ± 0.1	91.7 ± 1.0	1.00 ± 0.21	18.7 ± 3.9	68.2 ± 2.6
RNM12,13,14	50 + 3	31.4 ± 3.8	2.0 ± 0.2	93.0 ± 1.0	1.30 ± 0.08	13.5 ± 2.9	58.9 ± 3.1
RNC5,6	30 + 3	25.6 ± 0.7	2.3 ± 0	93.0 ± 2.0	0.98 ± 0.07	16.4 ± 0.2	67.6 ± 0
RNC9	35 + 3	24.6	2.3	93	1.08	11.5	63.2

The comparisons of the performance indicators for experiments with feedwater containing NaCl only, NaCl + MgSO₄, and NaCl +CaCl₂ are show in Table 4.5. The experiments run under the similar operating conditions are grouped together, and the average values of these tests ± the average value of the data deviations are presented. Based on the comparisons between tests RN1 and RNM4,5,6, RN2 and RNC5,6, RN3 and RNM7,8,10, RN5 and RNM12,13,14, it can be observed that with the

similar operating conditions, adding MgSO_4 or CaCl_2 as an affiliated solute to the base NaCl generally led to lower permeate recovery rates and higher rejection rates. The lower permeate recovery rate observed are attributed to the higher osmosis pressure induced at the feed side of the membrane surface, which would result in less permeate being pushed through while the applied pressure remains the same. The higher rejection rate observed in the experiments with feedwater containing the affiliated solutes was mainly caused by the different rejection rates for the monovalent and divalent ions of the NF membranes as discussed.

4.1.2 Summary of the FFFR Application using NF90-2540 Membrane

For the first time, the desalination performance obtained from incorporating the derivative of the feed flow reversal (FFR) technique, which is named as fast feed flow reversal (FFFR) into a NF membrane desalination system, in treating feedwater containing a higher and wider range of TDS levels compared with the previous relevant studies, were investigated. Various levels of permeate recovery and salt rejection rates in dealing with the feedwater containing the TDS level from $\sim 30\text{g/L}$ up to 70g/L , with different mixtures of the three commonly found constituents in the industrial wastewaters added into the synthetic feedwater, are presented in the current study. Both the permeate recovery and salt rejection rates increased the applied pressure and decreased with the feedwater concentration in the experiments presented in this section. The most significant observations from this section are summarized as follows.

- (a) The feed flowrate is insignificant in affecting the system's performance.
- (b) The general performance indicators for the FFFR operations run with the feedwater containing $\text{NaCl} + \text{MgSO}_4$ in 31-53 g/L of TDS and with the applied pressure between 19.6-35.7 bar, the ERE, SEC, water recovery and salt rejection were found to range within 90-95%, 0.73-1.35 kWh/m^3 , 10.5-24.6%, and 56.8-72.7%.

The general performance indicators for the FFFR operations run with the feedwater containing $\text{NaCl} + \text{CaCl}_2$ in 31-38 g/L of TDS and with the applied pressure between 24.1-26.3 bar, the ERE, SEC, water recovery and salt rejection were found to range within 91-95%, 0.86-1.08 kWh/m^3 , 11.5-18.6%,

and 63.2-67.8%.

The general performance indicators for the FFFR operations run with the feedwater containing NaCl in 30-70 g/L of TDS and with the applied pressure between 19.4-35.3 bar, the ERE, SEC, water recovery and salt rejection were found to range within 90-95%, 0.94-2.03 kWh/m³, 5.7-20.8% and 44.3-65.2%, respectively.

- (c) The ERE values were found to increase with applied pressure due to the smoother movement of the pistons, and thus resulted in a more efficient energy conversion process. SEC was closely associated with the frequencies of all water pumps as well as the permeate production for each experiment. The higher the frequencies of the hydraulic pumps and the desired permeate production, the higher the SEC value would be due to the elevated electricity consumption.
- (d) No significant difference was found between the experiments with MgSO₄ and CaCl₂ as the affiliated solute to NaCl in the feedwater. Nevertheless, the rejection rate was found to be higher for the tests containing MgSO₄ compared with CaCl₂ due to the better rejection in removing the divalent ions for the NF membranes.
- (e) 5.4% in the permeate recovery rate, 47% in the salt rejection, 94% and 1.95 kWh/m³ of ERE and SEC were obtained with the FFFR operation when treating feedwater containing 70g/L of NaCl with an applied pressure of 34.2 bar, which are the operating limits for the setup used in this study.
- (f) Adding another solute to the NaCl feedwater was found to result in lower permeate flux rates and higher salt rejection rates, while the other operating conditions remained the same.

The ERE and SEC levels, although not the emphasis in the FFFR feasibility assessment, are found to be satisfying. The ERE values are found to be relatively low compared with the previous study on the iRO system, of which the result reached 98-99% due to the higher pressure applied. Nevertheless, 90-95% of energy recovery would be considered significant in larger scale operations. The SEC level of 0.73

2.03 kWh/m³ is lower compared with RO membrane desalination systems and the thermal-based technologies, which are widely used for the final step of the ZLD systems as mentioned in the earlier sections. The permeate recovery rate and salt rejection rate although are not exceptionally high, would still be meaningful in managing the highly concentrated wastewaters, as the operation is meant for inducing the dewatering effect as an intermediate or pre-treatment step.

Results from this study can be used as a reference for future FFFR applications in the NF membrane desalination systems. Since NF membranes can provide moderate desalination performances and requires relatively low energy consumption in comparison with other high-pressure membrane desalination processes and the energy-intensive thermal techniques that are being used in managing highly concentrated wastewaters, the FFFR application with NF desalination can be considered as an intermediate or pre-treatment step to improve the efficiency of the dewatering process when dealing with highly concentrated wastewaters such as the shale gas PW, RO brine, and the downstream of ZLD systems. For practical applications, the optimal operating conditions, i.e., the applied pressure, feed flowrate, and flow reversal period would depend on various aspects such as the operating cost, desired permeate flux, and permeate quality, etc.

4.1.3 Recovery Drop Discussion

A drop in permeate flux and consequently permeate recovery decline can be observed in nearly all above presented experiments. The recovery values for all experiments are plotted against time and are appended in Appendix A, to show how they changed throughout the experiments. Decline in the recovery can be caused by fouling/scaling, which is the main issue that FFFR is aiming to solve. Therefore, it is important to understand the reason for the presence of the recovery drop, as it might be a significant issue in the future FFFR applications. Finding the cause of the permeate flux decline would not only help in optimizing the lab-scale operations but also in implementing FFFR in pilot or industrial applications in the future.

There are three possible reasons that might have contributed to the decline in the permeate recovery rate:

1. The effect of increasing the feedwater concentration and, the effect of adding

other chemicals other than NaCl into the feedwater

2. The effect of the initial compaction of the membrane module
3. Fouling/scaling that have occurred during the operations, or because of the concentration accumulation occurred due to the ratio R of the hydraulic retention time (T_H) and flow reversal interval (T_R) being larger than 1.

Each of these proposed reasons was testified and will be discussed into details in the following sections.

4.1.3.1 Effect of the Base Solute Concentration & Adding other Chemicals into the Feed Water

To understand how the base solute concentration as well as adding other chemicals other than NaCl into the feedwater affected the rate of the recovery decline, groups of experiments with the same solutes added into the feedwater are listed separately into Table 4.6-Table 4.8 in ascending order of the solute concentration. The average values of the applied pressure, experimental duration, and recovery trend slope are shown for those experiments with the same feedwater constituent as well as their corresponding concentrations. The test names of those presented with the average experimental results are separated with comma, and the detailed results for the individual experiments can be found in Appendix B. For example, test RN1,2 in Table 4.6 shows the average value of the applied pressure, experimental duration, and recovery trend line slope of test RN1 and RN2. They are grouped together as the feedwater concentration was 30 g/L of NaCl for both tests. Based on the observation on how the recovery trend line slopes changed with the various concentrations of NaCl as well as the presence of $MgSO_4$ and $CaCl_2$, their correlations are expected to be understood, if any.

As shown in Table 4.6, no clear sign of the presence for higher recovery drop rate was observed from the experiments with higher NaCl concentrations. The change of the rate was found to be rather irregular, which indicates that increasing the NaCl concentration in the feedwater did not cause any acceleration in the recovery drop. In other words, the recovery drop is unlikely to be induced by the NaCl concentration in the first place.

Table 4.6: Slope value of the recovery trend line in NaCl experiments

	NaCl concentration (g/L)	Pressure (bar)	Duration (hours)	Slope of the Recovery Trend Line (*10000)
RN1,2	30	22.4 ± 3.0	1.6 ± 0.5	-4.5 ± 0.5
RN3	35	27.9	2.0	-1.0
RN4,5	50	26.8 ± 2.3	3.0 ± 1.0	0.4 ± 0.6
RN6,8,9	60	33.1 ± 3.2	1.9 ± 0.1	-5.7 ± 3.0
RN10,7	70	34.1 ± 0.5	1.55 ± 0.05	-2.0 ± 0

Table 4.7: Slope value of recovery trend line in NaCl + MgSO₄ experiments

	NaCl + MgSO ₄ concentration (g/L)	Pressure (bar)	Duration (hours)	Slope of the Recovery Trend Line (*10000)
RNM1,2	0+1	5.0	0.55 ± 0.05	-9.0 ± 5.0
RNM3	0+4.5	6.0	2.1	-1.0
RNM4,5,6	30+1	20.0 ± 0.5	1.4 ± 0.5	-0.1 ± 0.3
RNM7,8,9,10	35+3	27.5 ± 4.9	1.9 ± 0.1	-5.8 ± 3.0
RNM11	35+6	28.9	1.8	-6.0
RNM12,13,14	50+3	31.4 ± 3.8	2.5 ± 0.7	-6.0 ± 4.0

Table 4.8: Slope value of recovery trend line in NaCl + MgSO₄ experiments

	NaCl + CaCl ₂ concentration (g/L)	Pressure (bar)	Duration (min)	Slope of the Recovery Trend Line (*10000)
RNC3,4	30+1	24.7 ± 0.3	2.6 ± 0.5	-5.5 ± 1.5
RNC5,6	30+3	25.6 ± 0.7	2.4 ± 0.3	-5.0 ± 1.0
RNC7,8	35+1	24.4 ± 0.2	2.6 ± 0.5	-6.0 ± 3.0
RNC9	35+3	24.6	2.6	-4.0

Table 4.7 shows the recovery trend slopes for the experiments with MgSO_4 added into the feedwater in addition to the base solute NaCl . Same as the results shown for the NaCl experiments, change of the slope tends to be again irregular, which shows no positive correlation between the recovery drop formation and the addition of MgSO_4 as an affiliated solute. Table 4.8 gives the results of the experiments with NaCl and CaCl_2 as solutes. The slopes of the recovery trend for these tests were found to be similar with a variety of solute concentrations, which again is an indication of the irrelevance between adding CaCl_2 in addition to NaCl in the feedwater and the recovery drop observed.

Based on the results and observations shown on the slopes of the tests with the various operating conditions, no clear evidence of any certain correlation between the feedwater solute concentration/addition of an affiliated substance, and the rate of the recovery decline of the experiments conducted with the FFFR operation in part 1 of the study can be found.

4.1.3.2 Effect of the Initial Compaction

After the observation of the permeate flux decline in the FFFR operations, experiments in the cross-flow filtration (CFF) mode were conducted as well, to detect whether the membrane module has undergone an initial compaction stage without the need to take the effects of the FFFR operation into consideration. Both the recovery trend line slope and the change in the applied pressure for each experiment need to be considered. Drastic decline in the applied pressure might contribute in the recovery drop as an interference in drawing the conclusion, and thus is desired to be precluded in the analysis process. NaCl concentration in the feedwater, recovery trend line slope, and change in the applied pressure for all CFF experiments run with NF90- 2540 are shown in Table 4.9.

The values of the slope are all negative except in test CN6, of which the applied pressure increased by 0.27 bar throughout the experiment. The increase in the recovery could be the result of the increased applied pressure. Decline in the applied pressure was present in test CN2, CN3, CN9, and CN12. Among these four tests, the pressure decline was particularly large for test CN9, which pairs with the largest

Table 4.9: Change in the slopes of the recovery trend line for the cross-flow filtration experiments run with the NF90-2540 model

Test	NaCl concentration (g/L)	Slope of the recovery trend line (*10000)	Change in the applied pressure (bar)
CN1	30	-5	0.07
CN2	30	-5	-0.06
CN3	30	-6	-0.02
CN4	30	-6	0.16
CN5	30	-3	0.49
CN6	30	0.5	0.27
CN7	30	-4	0.13
CN8	30	-4	0.47
CN9	35	-10	-0.74
CN10	35	-5	0.00
CN11	35	-5	0.18
CN12	35	-6	-0.02

magnitude of the recovery slopes among all tests. Negative recovery trend line slopes were found for the rest of the tests even with their corresponding increased applied pressures. Therefore, it can be preliminarily concluded based on the above observations that, despite the interference of the applied pressure decline on the permeate recovery, permeate flux decline was clearly observed in the CFF experiments even with the presence of applied pressure increase.

In addition, improvement of the solute rejection in the membrane desalination processes is often seen during the initial compaction stage, which is caused by a denser structure of the membrane module formed due to the membrane compaction effect. The permeate conductivity was measured for test CN2, CN6, CN8, CN11, and CN12, at every 30 minutes throughout the operating durations. The results of these measurements are shown in Table 4.10. The permeate conductivity decreased throughout the operating durations for all experiments tested, which is an indication of the improved rejection. Therefore, based on the observed permeate flux decline together with the presence of the improved solute rejection throughout the experiments, it is reasonable to conclude that the membrane module was experiencing an initial stage of compaction for the experiments conducted, which partially led to the recovery drop, if not all.

Table 4.10: Change in the permeate conductivity and the slope of the recovery trend line of cross-flow filtration experiments run with the NF90-2540 model

Test	NaCl conc. (g/L)	Permeate conductivity (mS/cm)	Slope of the recovery trend line (*10000)	Change in the applied pressure (bar)	Comment
CN2	30	14.5→14.5→14.4→14.3→14.2	-5	-0.06	An unexpected positive slope was found in test CN6. It was possibly caused by the relative large increase in the applied pressure.
CN6	30	11.9→11.8→11.7→11.7→11.6	0.5	0.27	
CN8	30	13.1→13.0→12.6→12.3→12.0	-4	0.47	
CN11	35	21.0→20.8→19.9→19.7	-5	0.18	
CN12	35	18.0→17.9→17.6→17.5	-6	-0.02	

To further confirm with the inferred theory of the initial compaction, one additional NaCl experiment was conducted initially with 2 hours of the CFF mode followed right away by another 2 hours of the FFFR operation under identical experimental conditions. Results of the two steps in the experiment are plotted in Fig 4.4 separately with blue and red colours. Similar as in the previous experiments, recovery drop was observed during the first 2 hours of CFF operation. The following 2 hours of the FFFR operation was conducted right after, aiming to reserve as much of the effect onto the membrane structure that has formed due to the potential compaction process. The recovery of the FFFR operation was found to be very much stable throughout the second 2 hours with a slight increase. Therefore, it can be interpreted that after the initial 2 hours of CFF, compaction has been established to a steady state, and after which no further permeate decline would persist.

In addition, the membrane swelling effect is often seen as an association with the membrane compaction phenomenon. The permeability of the polymer membranes, i.e., nanofiltration membranes, mainly depends on two factors, namely the effects of the membrane swelling and membrane compaction (Md et al., 2017). The swelling effect is associated with the expansion of the polymeric matrix of the membranes and the consequent permeate flux increase caused by the water molecules intrusion. The swelling effect would be intensified with the applied pressure up to a certain level,

Fig 4.4: Recovery trend of 2 hours initial cross-flow (compaction) followed by 2 hours FFR operation

beyond which no further membrane swelling would occur even with more pressure applied. The membrane swelling effect has also been explained by the presence of the repulsive interactions between the counterions within the membrane pores, and the effect would exacerbate with higher solute concentration. On the other hand, the compaction effect refers to the denser membrane structure formed with the reduced fractional free volume within the polymer matrix caused by the applied pressure, which would consequently result in a permeate flux decline. Similar to the swelling effect, the compaction process terminates at a certain threshold value of the applied pressure. Therefore, the permeability of the polymeric membranes at each applied pressure level depends on the combined effect of both the swelling and compaction.

Fig 4.5 shows the results of an experiment conducted by Md (2017) with the purpose to investigate on the combined effect of the compaction and swelling for a NF membrane, by comparing how the permeate flux changes versus the pressure for a new membrane as well as a post-compaction membrane. According to Md (2017), the swelling effect dominated over the compaction effect, and resulted in a non-linear accelerating increase rate in the permeate flux versus the applied pressure for a new membrane. When the pressure reached at a certain threshold value, being 1240 kPa in the study, the counter effects of the swelling and compaction were balanced. In addition, the equalized condition was also manifested by the observation of a constant hydraulic resistance. This threshold pressure value is the minimum value to be

applied for conducting a pre-conditioning compaction process.

Fig 4.5: Permeate flux vs. pressure (kPa) before and after compaction (Md et al., 2017)

To see if the swelling effect had any place in the FFFR experiments, similar experiments as in (Md et al., 2017) were conducted. However, the pressure range was set in between 15-30 bar, which is higher than the above study's pressure range of 3-12 bar. This higher applied pressure range corresponded to the relatively high concentration of 30 g/L NaCl in the synthetic feedwater, which is the lowest testing point of the feedwater concentrations used in the current study.

Fig 4.6 shows how the permeate flux value changed with both increasing and decreasing pressures from a single continuous experiment. During the experiment, the applied pressure was first gradually increased from 15 to 30 bar, and then decreased back to 15 bar with the same track of the pressure changing points without stopping the operation. At each applied pressure level, the system was operated for 20min.

The primary observations from the results shown in Fig 4.6 are as follows.

- (a) After the experiment was completed, the permeate flux value at 15 bar has dropped by a quarter from the initial value. The presence of the permeate flux drop complies with the prior experiments to which a constant pressure was applied throughout the experiments. As discussed, the compaction effect has

Fig 4.6: Continuously conducted experiment with increasing and decreasing pressure

caused the permeate flux decline due to the developed hindrance for both the water and salt molecules to pass through the membrane, which was induced by the denser membrane pore structure as a result of the membrane compaction.

- (b) The difference between the permeate flux value of the two trends at each pressure level kept increasing at first, and gradually became constant approaching the end of the experiment. In other words, the permeate flux value difference between the two trends tends to stabilize over time. This shows that the compaction process gradually terminated after a certain period, which also conforms to the results of the prior experiments in which the permeate flux decreased at first and tended to stabilize after ~2 hours, signifying the end of the compaction process.

Fig 4.7 shows how the permeate flux value changed with both increasing and decreasing pressures, however, conducted separately instead of being conducted on a continuous basis as in the experiment shown in Fig 4.6. The operating conditions in the applied pressure and influent flowrate were strictly controlled to be identical for the two experiments for the comparison purpose.

The primary observations from the results shown in Fig 4.7 are as follows.

Fig 4.7: Separately conducted experiments with increasing and decreasing pressure

- (a) the permeate flux decline was present for both the experiments, which is manifested by the value difference observed at each applied pressure value, the permeate flux at the intermediate pressures of 24 and 25 bar are identical. This shows that the permeate flux decrease pattern in terms of magnitude and rate was not so much affected by the opposite pressure changing directions.
- (b) There is no sign of the presence for the swelling effect, which should have caused more vigorous permeate flux increase when the experiment is conducted with increasing pressures as in (Md et al., 2017). This can be explained by that the pressure range in the experiment shown in Fig 4.7 was higher than 12.5 bar, which was the threshold value for the swelling effect surpassing the compaction effect according to Md (2017). Beyond the threshold value, the effect of swelling and compaction would equally contribute to the level of the permeate flux. Therefore, the permeate flux drop at each applied pressure shown in Fig 4.6 and Fig 4.7 is solely caused by the effect of compaction

Based on the observations on the decline in both the permeate flux and permeate conductivity, it can be concluded that the membrane module has experienced an initial stage of compaction in the experiments conducted in part 1 of the study. The effect of the membrane swelling was found to be irrelevant for these experiments

since higher pressures were applied, which are beyond the point where the effects of the compaction and swelling are just counterbalanced. Therefore, the initial membrane compaction is determined to be a significant cause for the recovery drop found in all FFFR experiments in part 1 of the study. In addition, it has been testified that the initial compaction should have been accomplished within the first 2 hours of the CFF operation, and no further permeate flux drop would persist in the following desalination process. It's worth mentioning that all performance indicators of the FFFR operation presented in this study, are either taken based on the end value of at least 2 hours' operation or taken after sufficient initial membrane compaction has been performed.

4.1.3.3 Hydraulic Retention Time (T_H) and Flow Reversal Time (T_R): Effect of the Value of Ratio R on Permeate Flux

T_H refers to the average time of a soluble substance remains within a container or a reactor. In a desalination system using a spiral wound membrane module like the lab scale setup used in the current study, T_H is the time for one water or solute molecule to travel from one end to the other end of the membrane module. On the other hand, T_R refers to the average time between the moment after the flow direction has been reversed from the previous cycle, and the moment before the flow direction is reversed again. Therefore, if T_H is longer than T_R , the flow direction will be changed before the concentrate within the membrane module is flushed out completely. The solute concentration would build up with time if the above situation occurs, which would also lead to an overall permeate flux decline due to the higher osmosis pressure induced around where the concentration accumulation is located.

To understand whether the recovery decline found in the above experiments was partially caused by the situation interpreted above, T_R and T_H for each experiment were measured. The setup used in this study is designed in a way that the flow reversal is triggered by a signal sent every time both the pistons reach the designated positions. Therefore, the T_R calculation is primarily determined by the brine flowrate. To calculate T_H , the void volume V_v inside the membrane module needed to be measured first. After V_v is determined, the average T_H can then be calculated using V_v divide by the average brine flowrate Q_b for each experiment.

To measure V_v , CFF experiments with feedwater dyed with food coloring were conducted. T_H for these V_v -measuring tests was recorded using a stopwatch and was defined as the time length between the moment when the colored feedwater enters the membrane module, and the moment when the colored brine is first observed in the semi-transparent brine outlet. Once T_H for each test was obtained, V_v was calculated by dividing T_H by the average Q_b of that specific test. An average value of V_v of all tests was obtained at the end. For instance, T_H for test RN1 measured with this method was ~52s. The average duration of each cycle for test RN1 was 116s, meaning that the flow reversal was triggered at every 58s which is half of a complete cycle duration ($T_R = 58s$). Therefore, T_R was found to be 6 seconds longer than the average value of T_H in test RN1.

The values of T_H and T_R for all experiments conducted in part 1 of the study are listed in Table 4.11. It was found that T_H for all experiments was considerably similar to T_R , resulting in the ratio R for these experiments being very close to 1. However, the unavoidable fluctuation in the system's operation during each cycle might cause changes in both T_H and T_R . In other words, with the value of T_H being very close to T_R , it is not reliable to affirm whether the concentration accumulation has formed owing to the small difference between the two values and the possible fluctuation that might have occurred during each experiment. Therefore, the flux decline found in these experiments run with the NF90-2540 model is unlikely to be caused by the theory of concentration accumulation due to the incomplete flushing of the concentrated brine.

4.1.3.4 Summary of the Recovery Drop Discussion

Based on the results shown in Fig 4.4, no further permeate decline can be observed beyond the 2 hours of CFF operation when the membrane compaction occurs. Thus, based on the observations, fouling/scaling has been mitigated with the FFFR operations under various experimental conditions conducted in this study.

Table 4.11: Values of T_H and T_R for experiments run with the FFFR operation using the NF90-2540 model

Test	NaCl concentration (g/L)	Pressure (bar)	Feed flowrate (L/min)	T_H (s)	T_R (s)	Ratio R
RN1	30	19	2.4	52	58	0.90
RN2	30	25	2.3	59	61	0.97
RN3	35	28	2.1	65	67	0.97
RN4	50	24	1.7	69	70	0.99
RN5	50	29	1.8	71	72	0.99
RN6	60	29	2.1	57	56	1.02
RN7	70	35	2.6	46	47	0.98
RN8	60	35	2.2	57	57	1.00
RN9	60	35	2.2	58	59	0.98
RN10	70	34	2.8	42	44	0.95
RNM4	30+1	20	1.9	67	72	0.93
RNM5	30+1	20	2.4	52	55	0.95
RNM6	30+1	21	2.8	44	47	0.94
RNM7	35+3	23	2.1	64	64	1.00
RNM8	35+3	25	2.3	57	57	1.00
RNM9	35+3	28	2.2	66	67	0.99
RNM10	35+3	33	2.2	67	68	0.99
RNM11	35+6	29	2.1	66	66	1.00
RNM12	50+3	28	2.2	55	54	1.02
RNC3	30+1.11	24	2.3	47	59	0.80
RNC4	30+1	25	2.3	55	54	1.02
RNC5	30+3	25	2.3	59	60	0.98
RNC6	30+3	26	2.3	58	59	0.98
RNC7	35+1	24	2.3	55	54	1.02
RNC8	35+1	25	2.3	56	58	0.97
RNC9	35+3	25	2.3	55	54	1.02

4.1.3.5 Summary of the Recovery Drop Discussion

Three possible reasons were proposed for the recovery drop observed in the FFFR experiments conducted in the part 1 of this study using the NF90-2540 membrane model:

1. The effect of increasing the feed water concentration and, the effect of adding other chemicals other than NaCl into the feed water
2. The effect of the initial compaction of the membrane module
3. Concentration accumulation due to the ratio R of the Hydraulic Retention Time (T_H) and Flow Reversal Time (T_R) being larger than 1

Among the three proposed reasons, only the theory of the initial compaction was proved to be a valid reason for the presence of the permeate recovery drop. In addition, the recovery drop was found to cease after 2 hours of the CFF operation, signifying the establishment of the initial membrane compaction process. The result of the recovery drop analysis is of paramount importance in assessing the feasibility of the FFFR operation incorporated in the NF membrane desalination systems in treating highly concentrated wastewaters. Having understood the significance of the initial compaction in the FFFR operations, it is recommended to start the operation after the initial membrane compaction has been fully performed so that stable permeate flux and salt rejection can be obtained in future FFFR applications, if necessary.

In addition, the performance indicators of the experiments conducted in this study are either presented with the end value of the operation, or with the results after the initial compaction process is fully performed. Therefore, the results presented in part one of the study can be seen as fully or at least partial post-compaction.

4.2 Part 2 of the Study: Effect of the Value of Ratio R being Larger than 1 on the Membrane Desalination Permeate Flux

4.2.1 Modification of the Experimental Setup in Part 2 of the Study

As mentioned in section 4.1.3.3, the ratio R of T_H and T_R was very close to 1 in the experiments operated with the NF90-2540 membrane in part 1 of the study. The ratio R mainly depends on the design limitations of the laboratory setup. Therefore, to

understand how the permeate flux would be affected by the concentration accumulation when $R > 1$, NF90-4040 was later used in part 2 of the study as a replacement of NF90-2540 to achieve the purpose. As shown in Fig 4.11, the most significant specification differences between the two membrane models are their active areas and cross-sectional diameters.

Fig 4.8: Specifications of NF90-2540 & NF90-4040 models used in this study

Therefore, with the same feed flowrate, the hydraulic retention time T_H for NF90-4040 should be longer compared with NF90-2540 since the cross-sectional area is larger. However, it was noticed that the permeate flowrate of NF90-4040 in the test done by the manufacturer was ~3 times larger compared with NF90-2540, which is most likely caused by the larger active area of NF90-4040. In other words, desalination using the NF90-4040 model could result in smaller brine flowrate compared with NF90-2540 under all or at least certain conditions like the one provided by the manufacturer. As mentioned earlier, T_R of the FFR operation in this study solely depends on the brine flowrate. Therefore, special attention was paid when designing the experiments in using NF90-4040 to avoid larger increase in T_R compared with the increase in T_H , so that the desired condition of $R > 1$ can be achieved.

4.2.2 Experimental Results & Discussion

4.2.2.1 Numerical Results of Change in Permeate Flux with Ratio $R > 1$

The FFFR experiments using the NF90-4040 model were conducted to understand the impact of the ratio R on the permeate production in membrane desalination processes, especially with $R > 1$ so that the concentration accumulation effect within the membrane module might occur, which would consequently deteriorate the permeate flux. All experiments presented in this section are post-compaction. Steady permeate flowrate was used as the indication on the compaction completion. The operating conditions and critical performance indicators of these experiments are listed in Table 4.12.

One of the three solutes, e.g., NaCl, MgSO₄, and CaCl₂ was added in the feedwater for each experiment. Results from the NaCl experiments are listed in ascending order of the NaCl concentration and followed by the MgSO₄ and CaCl₂ experiments. The operating conditions in the applied pressure, inflow rate, and test duration for each experiment are shown in the table. The values of T_H , T_R , and the ratio R for each test are listed after the operating conditions and followed by the salt rejection rate. All experiments were run under the desired condition of $R > 1$. The initial and end values of the permeate flux, as well as the difference between the two for each experiment are also presented, to show how the permeate flux changed during the operations. The applied pressure is another factor which would affect the permeate flux, of which the change throughout the experiments are therefore taken into consideration. The permeate recovery and applied pressure trends for these experiments are plotted against time in Fig 4.9 to show how the applied pressure took part in the change of the permeate flux, if any.

As shown in the table, permeate flux decline was observed in most of the experiments except for tests RN11,12, and 14. Among these post-compaction experiments observed with permeate flux decline, increased applied pressure was found in tests RN13,15,17-19, RNM17, and RNC1. Based on equation (1), an increase in the applied pressure should result in a higher permeate flux with other operating conditions remain the same. However, the permeate flux of the above experiments decreased with increased applied pressure, indicating the presence of the negative effect of the concentration accumulation on the permeate flux due to the ratio $R > 1$. For the NaCl experiments, the decline in the permeate flux in percentage ranged within 11.1-18.5%, with the feedwater concentration, value of the ratio R , and

Table 4.12: Experimental results of FFFR tests conducted with the ratio R being larger than 1

Test No.	Conc. (in g/L)	Applied pressure (bar)	Inflow rate (L/min)	Test duration (hours)	T _H (s)	T _K (s)	Ratio R	Rejection (%)	Initial permeate flux (L/h ² m ²)	End permeate flux (L/h ² m ²)	Δ Permeate flux (%)	Brine concentration (g/L)	Change in pressure (bar)
RN11	10	11.6	2.4	3.2	87	68	1.28	72	5.28	5.91	11.9	13	0.50
RN12	30	17.4	2.4	2.0	78	63	1.24	60	3.53	3.55	0.6	34	(-) 0.03
RN13	40	27.8	2.2	2.7	88	63	1.40	55	4.22	3.75	(-) 11.1	46	0.09
RN14	45	27.0	2.3	2.0	83	68	1.22	52	3.53	3.62	2.5	51	1.50
RN15	50	28.8	2.2	2.6	84	59	1.42	43	3.56	2.96	(-) 16.9	54	0.14
RN16	60	21.6	2.3	2.6	74	58	1.28	25	2.54	2.07	(-) 18.5	62	(-) 0.31
RN17	60	28.3	2.2	3.5	80	56	1.43	25	2.92	2.51	(-) 14.0	62	1.22
RN18	80	33.4	2.2	2.7	82	59	1.39	21	2.53	2.12	(-) 16.2	83	0.44
RN19	80	34.0	2.2	2.7	77	55	1.40	19	1.73	1.58	(-) 8.7	82	0.22
RNM15	3	3.9	2.5	0.8	85	73	1.16	99	6.01	5.88	(-) 2.2	43	(-) 0.03
RNM16	2.4	3.4	2.5	0.6	85	63	1.35	99	5.97	5.58	(-) 6.5	3.4	(-) 0.18
RNM17	4.5	4.9	2.5	1.7	82	66	1.24	99	5.27	5.24	(-) 0.6	5.9	0.11
RNC1	45	33.2	2.2	2.8	79	62	1.27	83	2.16	1.89	(-) 12.5	67	0.14
RNC2	45	33.1	2.2	2.4	78	61	1.28	82	1.99	1.75	(-) 12.1	66	(-) 0.50

experimental duration in 40-80 g/L, 1.28-1.43, and 2.6-3.5 hours, respectively. For the MgSO_4 experiments, the decline in the permeate flux in percentage ranged within 0.6-6.5%, with the feedwater concentration, value of the ratio R , and experimental duration in 2.4-4.5 g/L, 1.16-1.35 and 0.6-1.7 hours, respectively. For the CaCl_2 experiments, the decline in the permeate flux in percentage ranged within 12.1-12.5%, with the feedwater concentration, value of the ratio R , and experimental duration in 60 g/L, 1.27-1.28, and 2.4-2.8 hours, respectively.

The permeate flux decline percentage generally tends to be larger with the solute concentration for the NaCl experiments. Nevertheless, the decline percentages for tests RN17-19 are smaller than expected, probably due to the applied pressure increase observed for these three tests. For the MgSO_4 tests, the permeate flux decline percentages are smaller in the magnitude due to the much lower solute concentrations. The change in the applied pressure was negative for tests RNM15 & 16, and positive for RNM17. Nevertheless, permeate flux decline was found in all three experiments, again indicating the presence of the negative effect of the concentration accumulation on the permeate flux. Deterioration in the permeate flux was also found in the CaCl_2 experiments with a similar value of the decline percentage, despite the applied pressure declined by 0.50 bar in test RNC2.

4.2.2.2 Experiments with No Permeate Flux Decline

The possible reasons that might lead to no permeate flux decline in the FFFR operation are as follows:

- (a) The ratio R is close to or less than 1 so that the concentration accumulation would not occur.
- (b) The concentration accumulation is present due to $R > 1$, however, of which the effect is suppressed by the increase in the applied pressure.
- (c) The concentration accumulation is present due to $R > 1$, however, of which the effect is suppressed by other unknown factors.

Fig 4.9: Recovery and pressure trend for experiments conducted with insufficiently long flow reversal period

Fig 4.10: Recovery and pressure trend for experiments conducted with insufficiently long flow reversal period (cont'd)

For test RN11, although the ratio R is 1.28 which is larger than 1, the permeate flux increased by 11.9% throughout the experiment. This can be explained by the pressure increase shown in Fig 4.9 (a) due to the occasional fluctuation of the system. The applied pressure for test RN11 increased by 0.50 bar throughout the experiment, which partially contributed to the relatively large increase in the permeate flux.

For test RN12, the permeate flux was almost constant with only a slight increase of 0.6%, despite the value of R being 1.22. On the other hand, the trend line of the

applied pressure for test RN12 was also nearly constant with a negligible decline of 0.03 bar throughout the experiment, which is considered too small to affect the change in the permeate flux. Therefore, even with $R > 1$, no permeate flux decline due to the concentration accumulation was observed when the feedwater concentration was 30g/L of NaCl.

2.5% of permeate flux increase was found in test RN14, together with a relatively large increase of 1.50 bar in the applied pressure. On the other hand, 11.1% of permeate flux decline was observed in test RN13, however, the applied pressure increased slightly by 0.09 bar, which implies the presence of the effect of the concentration accumulation with the feedwater containing 40 g/L of NaCl.

All experiments with no permeate flux decline clustered in the lower range of the feedwater concentration, which implies that a positive correlation between the concentration and permeate flux decline might exist. If this assumption stands, concentration accumulation was also present in test RN14 with 45 g/L of NaCl in the feedwater, which is higher than that of test RN13, however, in which the effect of the concentration accumulation was surpassed by the increased applied pressure. Permeate flux decline was observed even with an increase in the applied pressure throughout the experiments for test RN15, RN17-19, to which the NaCl concentrations higher than 30g/L were applied.

Based on the above observations, it is reasonable to assume that the concentration accumulation with a certain value of R would only affect the permeate flux experimentally, when the average bulk concentration within the membrane module reaches a certain level. This assumption can be categorized into the third reason mentioned earlier for no permeate flux to be observed in the FFR operation.

4.2.2.3 Threshold Value of Average Bulk Concentration for Permeate Flux Decline to Be Seen Experimentally when $R > 1$

Based on equation (1), the permeate velocity v is negatively related to the bulk concentration c . The smaller the c , the less the negative effect on v is induced.

$$v = \frac{\Delta p - \Delta \pi}{R_m} \quad (3)$$

The average value of the bulk concentration for each experiment was calculated based on the law of mass conservation and are listed in Table 4.12. The change in the permeate flux begins to be negative beyond test RN13, except for test RN14, which was caused by the larger pressure increase of 1.5 bar throughout the experiment coming from the occasional instability of the system. Based on the bulk concentration calculation, the lowest effective average bulk concentration which has resulted in an experimental permeate flux decline with R values tested in this study, is the NaCl concentration of 34g/L. However, this value is not suggested to be seen as the accurate threshold bulk concentration value, since the concentrations used in the NaCl experiments had relatively large gaps between any two consecutive tests.

Permeate flux decline was observed in all MgSO_4 tests even though the average bulk concentration was much lower compared with NaCl experiments. Due to the constant instability of the system under low-pressure operations as mentioned earlier, the duration of the MgSO_4 experiments were much shorter compared with the other tests run under the higher applied pressures. Nevertheless, the permeate flux decline was found to be as high as 6.5% with ratio $R = 1.35$ in test RNM 16, of which the operating duration was 34 minutes only. However, a decline of 0.18 bar in the applied pressure might be another contributor to the permeate flux decline. These observations suggest that the mechanism for $R > 1$ in affecting the permeate flux might be different for monovalent and divalent ions.

Owing to the design limitation of the setup in this study, the range of the ratio R tested is limited within 1.16-1.43. Therefore, the threshold bulk concentration in the NaCl experiments found is applied to the specific R values achieved in this study only.

4.2.2.4 Summary of the Analysis on the Effect of Ratio $R > 1$ on the Permeate Flux

Based on the results and discussion shown in this section, the most significant conclusions drawn are as follows.

- (a) The negative effect of the concentration accumulation induced by the ratio R of T_H and T_R being larger than 1, on the permeate flux of the desalination process incorporating the FFR technique is for the first time confirmed experimentally.

- (b) With the tested range of the ratio R between 1.16-1.43, the percentage in the permeate flux decline was found to be as high as 18.5% under the operating conditions applied in this study. This permeate flux decline would be considered significant in the large-scale pilot or industrial applications. Therefore, the importance of maintaining the value R less than 1 to avoid concentration accumulation was verified experimentally, and this issue is suggested to be carefully assessed in the future applications of the flow reversal technique.
- (c) In addition, the average bulk concentration was found to be another factor affecting the permeate flux deterioration under the condition of $R > 1$. It was found that the bulk concentration needs to reach a certain level before any permeate flux decline can be experimentally observed. The threshold value for the average bulk concentration with R values tested in this study, was found to be ~ 34 g/L of NaCl. However, this concentration is not suggested to be seen as the accurate threshold value due to the large gaps between the tested concentrations in this study.

4.3 Comparison between Experimental and Modelling Results

4.3.1 Development of the Mathematical Model

A mathematical model was developed in this study to understand how the solute concentration changes with location x and time t inside the membrane module, and consequently affects the desalination permeate flux, which is closely associated with the solute concentration. In this model, it is assumed that the concentration only varies along the x -axis and is evenly distributed vertically inside the membrane at any point in time.

The total length of the membrane module L is divided into N segments. Each segment can be seen as a control volume with the length of Δx , width of w , and height of H . w is calculated using the active area of the membrane module A_m given by the manufacturer, divided by the membrane length L . H can be obtained using the void cross-sectional area A_v measured earlier, divided by w . Equations of the above-mentioned parameters are listed below as in Equation (4)-(6).

$$\Delta x = \frac{L}{N} \quad (4)$$

$$w = \frac{A_m}{L} \quad (5)$$

$$H = \frac{A_v}{w} \quad (6)$$

c and u represent the bulk concentration and cross-flow velocity, respectively. During the desalination process, the permeate extraction occurs continuously along the membrane module. Thus, the cross-flow velocity decreases along the cross-flow direction due to continuity. At the same time, the build-up of concentration is also expected along the membrane module due to the cumulative permeate leaving the desalination system. Therefore, both c and u are expected to change with location and time until a steady state is reached. The solute concentration can be seen as a function of the location x_i and the time t_j written as in Equation (7), where i and $j = 1, 2, 3, \dots$

$$c_i^j = (x_i, t_j) \quad (7)$$

Specifically, x_i represents the distance between the location where feedwater starts entering the membrane module, and the middle point of the i^{th} control volume along the horizontal axis. When Δx is set to be considerably small, the solute concentration at the middle point of each control volume can represent the bulk solute concentration inside that control volume. t_j refers to the time after desalination operation has been started for j seconds. Therefore, c_i^j is the solute concentration inside the i^{th} control volume, at time t_j after desalination has been started.

The illustration of a single control volume is shown as in Fig 4. v refers to the permeate velocity shown as the arrow pointing downwards in the diagram, which is a function of the bulk concentration c , and it can be calculated using the following equation.

$$v = \frac{\Delta p - \Delta \pi}{R_m} \quad (8)$$

Where Δp , $\Delta \pi$ and R_m refers to the applied pressure, osmosis pressure difference across the membrane surface, and membrane resistance, respectively. $\Delta \pi$ is proportional to the bulk concentration c , ion numbers in a single solute molecule n ,

Fig 4.11: Illustration of a single control volume in the membrane desalination solute concentration modelling

gas constant R , absolute temperature T_a , and solute rejection r . Equation (8) is the same as Equation (1), it is renamed here for caption consistency.

$$\Delta\pi = n \cdot R \cdot T_a \cdot r \cdot c \quad (9)$$

As mentioned earlier, the cross-flow velocity u is also a function of the location x . Based on the law of mass conservation for water molecules within each control volume, the water volume decline equals to the volume of the permeate outflow in a time unit,

$$-\frac{\partial u}{\partial x} \cdot A_v \cdot \Delta x - v \cdot w \cdot \Delta x = 0 \quad (10)$$

Rearranging Equation (10), the declining rate of the cross-flow velocity u with the location x can therefore be written as,

$$\frac{\partial u}{\partial x} = -\frac{v}{H} \quad (11)$$

On the other hand, the conservation of mass for the solute implies that the change of the solute occurs in each control volume in a time unit, equals to the sum of the mass transfer induced by both the advective and permeate flux.

$$(\Delta x \cdot A_v) \cdot \frac{\partial c}{\partial t} = -A_v \cdot \frac{\partial(cu)}{\partial t} \cdot (\Delta x) - (v \cdot \Delta x \cdot w) \cdot (1-r) \cdot c \quad (12)$$

After substituting Equation (11) into Equation (12) and rearranging, it can be derived that:

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x} \left\{ \left[\int_0^x -\frac{v}{H} \cdot dx + u_o(t) \right] \cdot c \right\} - \frac{v}{H} \cdot (1-r) \cdot c \quad (13)$$

With the following transformation result of the permeate velocity Equation (14),

$$\frac{v}{H} = \frac{\Delta p}{H \cdot R_m} - \frac{n \cdot R \cdot T_a \cdot r}{H \cdot R_m} \cdot c \quad (14)$$

as well as the following first order discretization schemes:

The solute concentration changes with both the time t_j and location x_i as discussed earlier and can be formulated as follows.

$$\frac{\partial c}{\partial t} = \frac{c_i^{j+1} - c_i^j}{\Delta t} \quad (15)$$

$$\frac{\partial c}{\partial x} = \frac{c_{i+1}^j - c_i^j}{\Delta x} \quad (16)$$

In addition, equation (13) can be managed separately into part (a) and part (b) indicated as follows.

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x} \left\{ \left[\int_0^x -\frac{v}{H} \cdot dx + u_o(t) \right] \cdot c \right\} - \frac{v}{H} \cdot (1-r) \cdot c \quad (17)$$

(a)
(b)

Part (a) can then be derived into part (a.1) and (a.2):

$$(a) = - \left[\int_0^x -\frac{v}{H} \cdot dx + u_o(t) \right] \cdot \frac{\partial c}{\partial x} + c \cdot \left(\frac{v}{H} \right) \quad (18)$$

(1)
(2)

After substituting Equation (14) into part (a.1), (a.2), and part (b), they can be derived that:

$$(a.1) = - \sum_{n=1}^i \left[\int_0^x - \left(\frac{\Delta p}{H \cdot R_m} - \frac{n \cdot R \cdot T_a \cdot r}{H \cdot R_m} \cdot c_n^j \right) \cdot \Delta x + u_o(t) \right] \cdot \frac{c_{i+1}^j - c_i^j}{\Delta x} \quad (19)$$

$$(a.2) = c_i^j \cdot \left(\frac{\Delta p}{H \cdot R_m} - \frac{n \cdot R \cdot T_a \cdot r}{H \cdot R_m} \cdot c_i^j \right) \quad (20)$$

$$(b) = \left(\frac{\Delta p}{H \cdot R_m} - \frac{n \cdot R \cdot T_a \cdot r}{H \cdot R_m} \cdot c_i^j \right) \cdot (1 - r) \cdot c_i^j \quad (21)$$

The final derived equation for the solute concentration at a certain location and after a certain time of the membrane desalination operation is as follows.

$$c_i^{j+1} = \left\{ \left[\sum_{n=1}^i \left(\frac{\Delta p}{H \cdot R_m} - \frac{n \cdot R \cdot T_a \cdot r}{H \cdot R_m} \cdot c_n^j \right) \cdot \Delta x - u_o^j \right] \cdot \frac{c_{i+1}^j - c_i^j}{\Delta x} + \left(\frac{\Delta p}{H \cdot R_m} - \frac{n \cdot R \cdot T_a \cdot r}{H \cdot R_m} \cdot c_i^j \right) \cdot c_i^j \cdot r \right\} \cdot \Delta t + c_i^j \quad (22)$$

In addition, the total permeate flowrate is the sum of the permeate production of each control volume along the membrane length at any point in time. The equation of the permeate flowrate is written as follows.

$$Q = \sum_{n=1}^N (v_n^j \cdot \Delta x) \cdot w \quad (23)$$

The variables required for using the model can be divided into two groups, the membrane specifications and the operating conditions. Once the membrane specifications are set, the operating conditions including the feedwater concentration in mol/L, applied pressure in pascal, feed flowrate in m³/s, and solute rejection are the essential information to perform the prediction of the concentration profile within the membrane module.

4.3.2 Comparison between the Experimental and Modelling Results for Cross-Flow Filtration (CFF)

The comparison between experimental and modelling results for experiments run under the CFF mode with both NF90-2540 and NF90-4040 were conducted and

Table 4.13: Comparison between experimental and modelling results in the permeate flowrate at steady state for NF90-2540 cross-flow filtration

Test	Feed Conc. (g/L)	Pressure (Bar)	Inflow rate (L/min)	Recovery (%)	Rejection (%)	Exp. Q (L/min)	Mod. Q (L/min)	ΔQ	ΔQ in %
NaCl									
CN1	30	20.3	2.43	10.4	65.5	0.25	0.38	-0.13	-52 *
CN2	30	25.3	1.84	24.1	69.3	0.44	0.47	-0.03	-7
CN3	30	25.2	1.88	24.8	69.3	0.47	0.51	-0.04	-9 *
CN4	30	25.3	1.86	24.7	69.3	0.46	0.51	-0.05	-11 *
CN5	30	24.9	2.28	23.7	69.0	0.54	0.60	-0.06	-11
CN6	30	30.2	1.79	32.7	74.9	0.59	0.52	0.07	12
CN7	30	30.2	1.81	33.9	74.9	0.61	0.56	0.05	8 *
CN8	30	32.6	1.78	31.2	73.1	0.56	0.61	-0.05	-9
CN9	35	24.8	1.85	15.9	63.0	0.29	0.45	-0.16	-55 *
CN10	35	24.8	1.87	16.9	63.0	0.32	0.45	-0.13	-41 *
CN11	35	25.4	1.86	15.9	63.6	0.30	0.47	-0.17	-57
CN12	35	30.2	1.79	23.6	68.2	0.42	0.54	-0.12	-29
MgSO4									
CNM1	1	4.5	2.54	43.89	98.4	1.11	0.9	0.21	19
CNM2	1	9.0	2.49	70.35	97.8	1.75	1.68	0.07	4
CNM3	3	6.6	2.52	51.45	99.0	1.30	1.05	0.25	19
CNM4	10	20.9	2.34	67.67	98.0	1.09	1.25	-0.16	-15

results are shown in Table 4.13 and Table 4.14, respectively. The names, operating conditions, and the permeate recovery and salt rejection rates of these experiments are listed on the left part of the tables. The permeate flowrate from the experimental and modelling results at the steady state, and the difference between the two values in both magnitude and percentage are listed on the right. For laboratory experiments, the steady state refers to when the initial membrane compaction is completed, and thus no

further permeate flux decline can be observed. However, no initial compaction for all experiments conducted in part 1 of the study were purposely performed, the permeate flowrate at the end of the experiments was therefore adopted so that the compaction effect which has already formed can be taken into consideration. For the modelling process, the steady state is reached when the solute concentrations of all control volumes are stabilized, so that no more change in the permeate flux would occur. Some of the experiments are annotated with a *. The solute rejection values for these tests are not available, the rejection result of an experiment with the same or considerably similar operating conditions was therefore used instead.

Table 4.14: Comparison between experimental and modelling results in the permeate flowrate at steady state for NF90-4040 cross-flow filtration

Test	Feed Conc. (g/L)	Pressure (Bar)	Inflow rate (L/min)	Recovery (%)	Rejection (%)	Exp. Q (L/min)	Mod. Q (L/min)	ΔQ	ΔQ in %
NaCl									
CN14	10	11.1	2.45	34.2	71.8	0.84	1.22	-0.38	-45
CN15	30	16.8	2.4	18.2	53.2	0.44	0.7	-0.26	-59
CN16	30	20.2	2.39	26.7	58.9	0.64	0.87	-0.23	-36
CN17	30	20.5	2.35	26.4	59.2	0.62	0.88	-0.26	-42
CN18	30	25.6	2.33	37.4	64.6	0.87	1.06	-0.19	-22
CN19	30	26.5	2.27	38.4	64	0.87	1.06	-0.19	-22
CN20	30	30.3	2.25	45.7	64.6	1.03	1.23	-0.20	-19
CN21	30	30.2	2.24	46.3	61.7	1.04	1.31	-0.27	-26
CN22	45	25.7	2.29	21.7	51.7	0.50	0.85	-0.35	-70
MgSO ₄									
CNM6	2.4	3.24	2.55	37.4	99	0.95	1.03	-0.08	-8
CNM7	3	3.14	2.55	39.5	99	1.01	0.85	0.16	-16
CNM8	3	5.46	2.52	62.1	99	1.56	1.68	-0.12	-8
CNM9	4.5	3.17	2.54	25.4	99	0.65	0.56	0.09	14

*Plots for test CNM8&9 are not available in the appendix, however, the performance indicators are available for the modelling prediction.

4.3.2.1 Comparison between the Experimental and Modelling Results for NaCl Experiments

For NaCl CFF experiments run with NF90-2540, experimental results in the permeate flowrate at the steady states mostly agree with modelling results as shown in Table 4.13. However, experimental results are found to be smaller than modelling results except for test CN6 and CN7. The difference range between the modelling and experimental results in magnitude and in percentage for experiments run with NF90-2540 is -0.17 to 0.07 L/min and -57 to 12%, respectively. The model predictions are more accurate in experiments CN2-CN8 compared with CN1, CN9-12. The difference range in percentage for these two groups of experiments is -11 to 12%, and -57 to -29%, respectively. Likewise, experimental results are smaller than modelling results for NaCl CFF experiments run with NF90-4040 as well, as shown in Table 4.14. The difference range in magnitude and in percentage for experiments run with NF90-4040 is -0.19 to -0.38 L/min and -19 to -70%, respectively. For NF90-4040 experiments, the model predictions are more accurate for CN18-21 compared with the rest. The difference range for these two groups of experiments is -19 to -26%, and -70 to -36%, respectively. In addition, the differences observed between the experimental and modelling results in both magnitude and percentage tend to be larger as well as more consistent for the NF90-4040 model.

One possible explanation for the above observations is that the levels of membrane compaction completeness are different for these tests. As mentioned earlier, permeate flux decline is often seen during the initial membrane compaction process, which is resulted from the denser membrane structure induced by the applied pressure. The compaction effect increases the membrane resistance as well as the salt rejection ratio during the initial compaction stage. These effects together lead to a lower permeate flux in real applications, and thus explains the over-prediction of the modelling results in which the membrane compaction effect is not considered. For tests CN2-8 and CN18-21, the feed concentration is 30 g/L and the applied pressure range is ~25-30 bar. The experiments with lower prediction accuracy were conducted with either lower concentration and lower pressure or higher concentration and intermediate pressure. These combinations are expected to result

in a relatively low permeate recovery. However, the decline in the permeate recovery is found not to change proportionally with the feed concentration and applied pressure in the experiments under the conditions described above. Therefore, the model over-predicts in the experiments conducted with intermediate feed concentration and applied pressure. Due to the better awareness of the significance in the effect of the membrane compaction after analyzing the reasons for the permeate flux drop observed from the FFFR experiments run with NF90-2540 in part 1 of the study, the initial membrane compaction process has been performed until the permeate flux became stable for all experiments run with NF90-4040 in part 2 of the study. Therefore, the completeness of the compaction process should be higher for the NF90-4040 experiments compared with NF90-2540, which resulted in the larger differences between the experimental and modelling results shown in Table 4.14.

The compaction effect is in fact not incorporated in the development of the mathematical model. As a result, the modelling prediction on the solute concentration profile and permeate flowrate should be more accurate for those experiments conducted prior to performing the membrane compaction, which agrees with the smaller differences observed between the experimental and modelling results for the NF90-2540 experiments, owing to the lower compaction completeness levels.

4.3.2.2 Comparison between the Experimental and Modelling Results for MgSO_4 Experiments

For MgSO_4 CFF experiments run with NF90-2540, difference between experimental and modelling results for permeate flux at steady states are positive in three out of the four tests. The difference range between the modelling and experimental results in magnitude and in percentage for experiments run with NF90-2540 is -0.16 to 0.25 L/min and -15 to 19%, respectively. The value deviations for the four MgSO_4 experiments with NF90-4040 are more evenly distributed centered around zero. The difference range between the modelling and experimental results in magnitude and in percentage for experiments run with NF90-4040 is -0.12 to 0.16 L/min and -16 to 14%, respectively. In addition, modelling results in the MgSO_4 experiments showed more consistency with experimental results compared with NaCl experiments.

The setup used in this study was originally designed for RO membrane desalination, onto which pressure applied is often much higher than that of NF membranes. It was observed in the present study that, the system often became unstable when lower pressures, especially under 20 bar were applied, and the readings also became incorrect after the system has been running for a while. As a result, the durations of MgSO_4 tests were much shorter compared with NaCl tests due to this operational issue, and compaction process was therefore less completed for MgSO_4 tests. Consequently, the lower levels of compaction completeness resulted in higher permeate flux values than expected. Therefore, modelling results would be closer to experimental results owing to the exclusion of compaction factor in developing the mathematical model, which agrees with the findings from the analysis on NaCl CFF experiments.

Another reason which might have contributed to the differences between experimental and modelling results is that, rejection for MgSO_4 was mostly between 98-99%, which is much higher and more stable compared with NaCl in the above experiments. To obtain the rejection values, the permeate conductivity was manually collected and measured during the experiments. Human errors could have occurred during the measuring process especially for NaCl tests, of which rejection can fall within a much larger range compared with the stable and high rejection rate for feedwater containing divalent ions like MgSO_4 , using NF membranes.

4.3.2.3 Summary for the Comparison between Experimental and Modelling Results for CFF Experiments

Although the modelling results in the permeate flowrate at the steady state agrees with the experimental results in most of the CFF tests, differences between the two values still exist and were found to follow a certain pattern. The important findings from this section are as follows.

- (a) The differences between the experimental and modelling results are mostly negative for both the NF90-2540 and NF90-4040 NaCl experiments, due to the lower experimental permeate flowrates resulted from the membrane compaction compared with the results obtained from the mathematical model, in which the compaction effect was not involved.

- (b) The differences are generally larger for the NF90-4040 NaCl tests compared with NF90-2540, mainly due to the higher level of the compaction completeness for the NF90-4040 tests, resulted from the comprehensive compaction preparation for these tests. The compaction completeness ranking is as follows, MgSO_4 with NF90-2540 $\approx$ MgSO_4 with NF90-4040 $<$ NaCl with NF90-2540 $<$ MgSO_4 with NF90-4040.
- (c) For the MgSO_4 tests, the experimental results are found to be closer to the modelling results compared with the NaCl tests, and the differences are more concentrated around the center of zero. This observation is due to the lower compaction completeness levels caused by the shortened experimental durations in the cases of unstable operation of the system.
- (d) Human errors might be present in the intermittent measurements of the permeate conductivities for obtaining the salt rejection rate, especially for the NaCl experiments, of which the rejection rate can fall within a much wider range compared with MgSO_4 .

4.3.3 Comparison between the Experimental and Modelling Results for Fast Feed Flow Reversal (FFFR) Operation

To understand if the mathematical model developed in this study is also applicable in predicting the concentration and permeate flux values for the FFFR operations, the modelling predictions were also conducted using the real situations in the laboratory FFFR experiments. When applying the mathematical model in the FFFR operations, the idea is to simulate the real operation by conducting the modelling process for each half cycle and use the reversed end concentrations at all control volumes as the starting concentrations for the consecutive half cycle. In other words, the technique used in achieving the flow reversal for each half cycle in applying the mathematical model is to reverse the starting concentration profile obtained from the previous half cycle.

4.3.3.1 Discrepancy of the Modelling and Experimental Results in the NF90-4040 FFFR operations

To predict the concentration profile and permeate flowrate for each half cycle in the

laboratory FFFR operations using the mathematical model, the operating variables used, i.e., the applied pressure and feed flowrate strictly follow the experimental conditions. However, most of the modelling results are found to be unreasonably large compared with the experimental results. Besides the exclusion of the membrane compaction process in designing the model as discussed earlier, this higher than expected permeate flowrate was also partially caused by the lower than expected rejection rate, which will be discussed later in this section. In addition, the permeate flux decline observed in the laboratory experiments was not reflected in the modelling results.

The modelling results of cycles 1-15 from test RN13 shown in Table 4.15 are within the acceptable range of discrepancy between the experimental and modelling results, and is therefore given as an example to show the absence of the permeate flux decline in the modelling results. In addition, the comparison results of test RNM15 is listed in Appendix B, which is an example for the MgSO_4 test. $Q_{P(M)}$ and $Q_{P(E)}$ are the predicted permeate flowrate for each half cycle obtained from the modelling results almost constant even with the T_H values being twice as much of the T_R values. This finding suggests two possibilities:

- (a) No permeate flux decline has occurred if the modelling result is correct.
- (b) Permeate flux decline has occurred and the modelling results is incorrect.

Since the other factors which might have led to permeate flux decline were already eliminated before commencing the experiment, including the fully performed initial membrane compaction, the second possibility is more likely to be true, which indicating the incapability of the mathematical model in predicting the desalination performance for the FFFR operations with ratio $R > 1$. In addition, for the permeate flowrate of test RN13, the modelling values are twice as much of the experimental values. The differences between the two are even larger than the cross-flow filtration (CFF) NaCl experiments run with the NF90-4040 model. Two main contributors were found to be responsible for this larger difference:

- (a) the difference in the compaction completeness levels as discussed in the last section; and

Table 4.15: Modelling result of cycles 1-15 from FFFR test RN13

Cycles	$Q_{P(M)}$ (L/min)	$Q_{P(E)}$ (L/min)	T_R (s)	T_H (s)	Q_{in} (L/min)	Q_B (L/min)
1	1.06	0.54	64	129	2.24	1.18
2	1.03	0.53	64	128	2.22	1.19
3	1.05	0.54	64	128	2.23	1.18
4	1.04	0.53	64	129	2.22	1.18
5	1.06	0.54	64	127	2.25	1.19
6	1.02	0.53	63	125	2.24	1.22
7	1.06	0.52	63	127	2.25	1.19
8	1.02	0.52	64	124	2.24	1.22
9	1.04	0.52	63	129	2.22	1.18
10	1.04	0.52	62	127	2.23	1.19
11	1.04	0.51	63	129	2.22	1.18
12	1.06	0.51	64	128	2.24	1.18
13	1.05	0.52	62	127	2.24	1.19
14	1.05	0.51	63	126	2.25	1.20
15	1.04	0.51	63	127	2.24	1.20

(b) the unexpected lower rejection rate from test RN13.

The rejection rate in test RN13 was found to be 25%, with feedwater containing 40g/L of NaCl and average applied pressure of 27.8 bar. Although such condition was not tested for the FFR mode, the rejection rate for an experiment with feedwater containing 40g/L of NaCl and average applied pressure of 25.7 bar is 56% based on the linear regression approach. The rejection rate for test RN13 is smaller than half of the result obtained from the linear regression. One possible reason for the big difference in the rejection rate is that during the FFFR operation, the effect of concentration accumulation has been building up throughout the experiment, which consequently resulted in the lower rejection rate at the end. The rejection rates for the NF90-4040 experiments were measured approaching the end of the operations

instead of throughout the experiments, which is an inappropriate experimental design in considering the concentration accumulation factor. It is suggested for the future FFFR experiments conducted under the condition of $R > 1$ to monitor the rejection rates closely throughout the experiments to see how the concentration accumulation would affect the rejection rate. On the other hand, this lower than expected rejection rate supports the theory of the negative effect on the permeate flux due to the ratio $R > 1$.

To further verify the theory of the lower than expected rejection rate due to the concentration accumulation, the comparison between the experimental and modelling results in treating the FFFR operation as CFF operation were conducted, and the results are shown in Table 4.17. Based on the values of ΔQ , the difference between the experimental and modelling results were found to be larger compared with the results for the CFF operations shown in Table 4.13 and Table 4.14, which indicates

Fig 4.12: Modelling and experimental results for cycles 1-15 from test RN13

that some other factors in addition to the compaction completeness level has also contributed to the differences of the two values. In addition, ΔQ with the largest magnitude are found in tests RN15-17, which coincides with the largest magnitude of the permeate flux decline in percentage observed in these tests. The reason for the modelling results being so much higher than expected is due to the lower experimental rejection rates applied, which were resulted from the concentration accumulation. The modelling results for test RN18&19 were found to be errors probably due to the even lower rejection rates for these two tests.

Therefore, the much higher modelling results in comparison to the experimental results for the FFFR operations with ratio $R > 1$ were mainly caused by the

Table 4.16: Comparison between experimental and modelling results in the permeate flowrate at steady state for NF90-4040 FFFR operations with $R > 1$

Test	Feed Conc. (g/L)	Pressure (Bar)	Inflow rate (L/min)	Rejection (%)	Δ Permeate flux (%)	Exp. Q (L/min)	Mod. Q (L/min)	ΔQ
RN11	10	11.6	2.4	72	11.9	0.71	1.29	-0.58
RN12	30	17.4	2.4	60	0.6	0.45	0.41	0.04
RN13	40	27.8	2.2	55	(-) 11.1	0.51	1.06	-0.55
RN14	45	27.0	2.3	52	2.5	0.45	0.94	-0.49
RN15	50	28.8	2.2	43	(-) 16.9	0.41	1.34	-0.93
RN16	60	21.6	2.3	25	(-) 18.5	0.29	1.96	-1.67
RN17	60	28.3	2.2	25	(-) 14.0	0.34	2.10	-1.76
RN18	80	33.4	2.2	21	(-) 16.2	-	-	-
RN19	80	34.0	2.2	19	(-) 8.7	-	-	-
RNM15	3	3.9	2.5	99	(-) 2.2	0.75	1.15	-0.40
RNM16	2.4	3.4	2.5	99	(-) 6.5	0.73	1.08	-0.35
RNM17	4.5	4.9	2.5	99	(-) 0.6	0.61	1.11	-0.50
RNC1	45	33.2	2.2	83	(-) 12.5	0.26	0.56	-0.30
RNC2	45	33.1	2.2	82	(-) 12.1	0.23	0.60	-0.37

following two factors:

- (a) the exclusion of the membrane compaction effect; and
- (b) the fail in detecting the concentration accumulation effect.

The modelling results presented above were obtained using the values of Δx and Δt in (0.1L) m and 1s. After observing the incapability of the model in predicting the concentration accumulation effect in the FFR operations with $R > 1$, smaller values of Δx and Δt were also applied to see how they would affect the modelling results.

4.3.3.2 Effect of the Value of Δx on the Modelling Results

To understand how the length of each control volume would affect the modelling result, smaller values of Δx in 0.05L and 0.02L were tested with the mathematical model as well. With Δx equals to 0.1L, the concentration profile had only 10 measurement points with one at each of the control volumes, which might be too few to reflect the factual desalination situation within the membrane module. With Δx equals to 0.05L and 0.02L, 20 and 50 measurement points can be established from the increasing numbers of the control volumes with a smaller length.

Fig 4.13: Modelling results of the permeate flowrate for cycles 1-6 with Δx in 0.1L, 0.05L, and 0.02L

The modelling results for cycles 1-6 under the conditions of $\Delta x = 0.1L$, 0.05L, and 0.02L are shown in Fig 4.13. As shown in the plot, the effect of the concentration

accumulation is still not present even with the smaller values of Δx . The values of the permeate flowrate tended to stabilize with even faster rates for the modelling prediction with smaller Δx . Therefore, it can be concluded that the absence of permeate flux decline is not affected by the value of Δx . In addition, the permeate flowrate value tended to become larger with decreasing values of Δx . Theoretically, the smaller the control values are set, the more accurate the modelling results would be. Therefore, setting the Δx too large can lead to lower than the accurate permeate flowrate values using the mathematical model developed in this study, in which the membrane compaction effect is not considered.

4.3.3.3 Effect of the Value of Δt on the Modelling Results

The effect of Δt was also investigated to see how it would affect the modelling result in the permeate flowrate. Δt used in the modelling prediction for test RN13 presented above was 1 s. For each half cycle, the duration is fixed for the modelling prediction based on the real experimental situation. To shorten the value of Δt , the number of measurement points would become larger since the time interval used is smaller. For example, the reversal interval for the first half cycle in test RN13 was 64s, the number of measurement points was 64 with Δt equaled to 1s. To shorten Δt from 1s to 0.5s and 0.2s, the number of measurement points would become twice and five times, which are 128 and 320, respectively.

Fig 4.14: Modelling results of the permeate flowrate for cycles 1-6 with Δt in 1s, 0.5s, and 0.2s

The results for all Δt values tested are shown in Fig 4.14. As shown in the plot, no sign of the presence in the permeate flowrate decline can be seen when shortening the value of Δt . Same to the result on investigating the effect of Δx , the permeate flowrate value tended to stabilize even more quickly for smaller Δt . However, the stabilized values for different Δt are found to be the same, which are ~ 1.04 L/min. Therefore, changing the value of Δt would accelerate the stabilization of the permeate flowrate but would not affect the final stabilized value.

4.3.3.4 Summary for the Comparison between Experimental and Modelling Results for the FFFR Experiments

Contrary to the expectation, no permeate flowrate decline was observed in the modelling results. Since comprehensive preparations have been performed prior to conducting the FFFR experiments using NF90-4040, it is concluded that the modelling results failed to predict the real situation for the FFFR operations with $R > 1$. Investigations were conducted to understand how the control volume's length Δx and time interval Δt would affect the modelling results. The results showed no presence of permeate flowrate decline even with smaller values of Δx and Δt . Therefore, the mathematical model developed in the current study is by far not suitable to predict the operating performance for the FFFR operations with ratio $R > 1$. Further amendment and improvement in the model are expected for its wider applications other than the cross-flow filtration (CFF).

4.3.4 Summary for the Mathematical Model Developed in Predicting the Concentration and Permeate Flowrate for Membrane Desalination Processes

The most significant findings obtained from this section are listed as follows.

- (a) The mathematical model worked well for most of the CFF experiments for both the NF90-2540 and NF90-4040 models.
- (b) The mathematical model was found to give predictions excluding the effect of the initial membrane compaction, and it would therefore result in higher permeate flowrate values when comparing with the post-compaction experimental results.
- (c) The model is by far not capable of predicting the desalination performance

for the FFFR operations with ratio $R > 1$.

Although the modelling results showed no permeate flowrate decline for the FFFR experiments run under the situation of $R > 1$, the experimental results are reliable for the following reasons:

- (a) The membrane used in these tests was fully compacted prior to conducting the experiments, the effect of the initial compaction is therefore eliminated.
- (b) Consistent permeate flux decline was observed in numerous experiments even with an increase in the applied pressure from a few of the tests.
- (c) Lower than expected salt rejection rates were observed at the end of the FFFR experiments, indicating the presence of the concentration accumulation build-up throughout the experiments.

Chapter 5 Conclusions

The appropriate management of the highly polluted wastewater produced by the ever-growing industrial applications such as the shale gas production and RO desalination is of the primary importance in protecting the health and safety of the surrounding population and ecosystems of the industrial sites' location. In addition, with future implementation of the ZLD concept owing to regulatory requirements regarding the reduction of wastewater discharge to the environment, the advancement in technologies with the ability to manage wastewaters with exceptionally high concentration produced from various industrial applications is imperative. One efficient and effective way to help in resolving the above issues is to dewater the wastewater streams to the largest extent prior to entering the final treatment step, of which the cost is often high and largely associated with influent volume.

The prevailing membrane technologies in treating the domestic and industrial wastewaters have been recognized as a potential solution for ameliorating the existing ZLD systems. However, the fouling/scaling phenomenon has so far limited the potential of membrane technology in treating the highly concentrated wastewaters. Facing the above issues, the feed flow reversal (FFR) technique has been proven in several studies to be effective in mitigating the fouling/scaling issues in the membrane desalination processes. However, the concentration of the synthetic solutions used in these studies was comparatively low. Therefore, the focus of this study is on investigating the feasibility of the fast feed flow reversal (FFFR) concept in dealing with wastewaters with remarkably high concentrations. In addition, NF membrane was chosen to be incorporated with the FFFR technique in this study due to its satisfying desalination efficiency as a potential intermediate or pre-treatment step, together with its moderate energy consumption compared with other membrane modules and the thermal-based technologies.

Desalination performance indicators of the FFFR application using the NF90-2540 membrane in treating feedwater with a wide range of TDS levels are for the first time, investigated in the current study. Various levels of the permeate recovery and salt rejection rates in dealing with feedwater containing TDS from ~30g/L up to 70g/L with different mixtures of chemicals added into the feedwater are presented. Since

NF membranes can provide moderate desalination performance among all membrane technologies, NF desalination systems incorporating the FFFR technique can be considered as an intermediate or pre-treatment step which has the potential to improve the dewatering efficiency when dealing with highly concentrated wastewaters such as the shale gas produced water, RO brine, and the downstream of the ZLD systems as discussed in the earlier sections. Results from this study can be used as a reference for the future FFFR applications, especially when incorporated in the NF membrane desalination systems. For practical applications, the best operating conditions depend on various aspects such as the operating cost, permeate flux requirement, and desired permeate quality, etc.

The effect of the ratio R between the hydraulic retention time (T_H) and the feed flow reversal time (T_R) on the permeate flux of desalination incorporated with the FFFR technique was investigated in part 2 of the study. It was proved that when incorporating the FFR technique into the conventional membrane desalination processes to eliminate the fouling/scaling issues, it is critical to ensure that T_R is larger than T_H , or $R < 1$ so that gradual accumulation of the highly concentrated brine which might deteriorate the permeate flux can therefore be avoided. The negative effect of the ratio $R > 1$ on a FFFR-incorporated NF desalination system was for the first time, verified to be a real issue through observing permeate flux decline in numerous experiments. The tested range of the ratio R was 1.16-1.43 limited by the design specifications of the setup used in this study. Nevertheless, the percentage of the permeate flux decline was found to be as high as 18.5%, which would be a significant issue in the larger scale pilot or industrial applications. In addition, it was found that the permeate flux would decrease under the condition of $R > 1$ only if the average bulk concentration within the membrane module reaches a certain level. The threshold value was found to be 34 g/L of NaCl in this study, however, is not recommended to be used as a reference since the gaps between the NaCl concentrations tested were too large to result in an accurate threshold value.

A mathematical model was developed in predicting the concentration profile and the permeate flux values for membrane desalination operations. The modelling results mostly agreed with the cross-flow filtration (CFF) experiments. However, it was

found that the initial membrane compaction effect is not reflected in the model, based on the better agreement of the modelling results to those experiments with lower compaction completeness levels. The mathematical model was found to be incapable of predicting the desalination performance for the operations with $R > 1$. The modelling results of the permeate flowrate tended to stabilize with time unlike the obvious permeate flowrate decline found in the laboratory experiments. Due to the limited time available in this study, further modification and amelioration to the model cannot be accomplished. Nevertheless, deterioration in the permeate flux of the desalination systems incorporated with FFFR due to the concentration accumulation effect, was for the first time experimentally confirmed. Nevertheless, future amendment and improvement of the mathematical model is expected to provide accurate prediction results for the FFFR systems, in hoping to contribute in the designing stage of the future applications to avoid any operating issues, i.e., the negative effect of the concentration accumulation on the desalination permeate flux.

To summarize:

- Laboratory experiments implementing the concept of FFFR for treatment of highly concentrated feedwaters with the TDS level up to 70 g/L, are performed for the first time and presented with the desalination performance in this study. The operations are found to be stable up to ~4 hours.
- The significance of the ratio R on the desalination permeate flux has been experimentally proved in applying the FFR concept. Negative impacts of $R > 1$ on the permeate production can be observed in numerous experiments conducted in this study. No experimental data on this issue can be found in the literature so far to the best of our knowledge.
- A mathematical model is developed to simulate the concentration profile and permeate flux values for desalination processes using spiral wound membrane modules. The modelling results greatly agree with the experiments in which the membrane compaction completeness level is low.

References

- Alzahrani, S., Jaafar, O., Mohammad, A. W., Hilal, N., and Abdullah, P. (2013). "Comparative study of NF and RO membranes in the treatment of produced water II: Toxicity removal efficiency", Desalination, Vol. 315, pp. 27-32.
- Bartman, A. R., McFall, C. W., Christofides, P. D., and Cohen, Y. (2009). "Model-predictive control of feed flow reversal in a reverse osmosis desalination process", Journal of Process Control, Vol. 19, pp. 433-442.
- Boerlage, S. F. (2001). Scaling and particulate fouling in membrane filtration systems, Swets & Zeitlinger [etc.], Lisse etc.
- Çakmakce, M., Kayaalp, N., and Koyuncu, I. (2008). "Desalination of produced water from oil production fields by membrane processes", Desalination, Vol. 222, pp. 176-186.
- Chang, O., Kinzel, M., Dilmore, R., and Wang, J. Y. (2018). "Physics of Proppant Transport Through Hydraulic Fracture Network", Journal of Energy Resources Technology, Vol. 140, No. 3, pp. 1-11.
- Christofides, P. (2009). "Brackish water reverse osmosis (BWRO) operation in feed flow reversal mode using an ex situ scale observation detector (EXSOD)", Journal Of Membrane Science, Vol. 341, pp. 60-66.
- Clark, C., and Veil, J. (2009). "Produced Water Volumes and Management Practices in the United States", United States Department of Energy, Argonne, IL : Argonne National Laboratory .
- Coday, B. D., Cath, T. Y., Xu, P., Beaudry, E. G., Herron, J., Lampi, K., and Hancock, N. T. (2014). "The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams", Desalination, Vol. 333, No. 1, pp. 23-35.
- Deng, S., Yu, G., Chen, Z., Wu, D., Xia, F., and Jiang, N. (2009). "Characterization of suspended solids in produced water in Daqing oilfield", Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 332, pp. 63-69.
- Dolan, F. C., Cath, T. Y., and Hogue, T. S. (2018). "Assessing the feasibility of using produced water for irrigation in Colorado", Science of the Total Environment, Vol. 640-641, pp. 619-628.
- Ebrahimi, P. and Vilcaez, J. (2018). "Petroleum produced water disposal: Mobility and transport of barium in sandstone and dolomite rocks", Science of the Total Environment, Vol. 634, pp. 1054-1063.
- Echchelh, A., Hess, T., and Sakrabani, R. (2018). "Review: Reusing oil and gas produced water for irrigation of food crops in drylands", Agricultural Water Management, Vol. 206, pp. 124-134.

- Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., and Abidin, Z. Z. (2009). "Review: Review of technologies for oil and gas produced water treatment", Journal of Hazardous Materials, Vol. 170, pp. 530-551.
- Faouzi, A., and Victoria, Z. (2016). TODAY IN ENERGY. Retrieved from U.S. Energy Information Administration: <https://www.eia.gov/todayinenergy/detail.php?id=27512>
- Feng, G., Guo, Y., and Tan, W. (2015). "Effects of thermal hydrolysis temperature on physical characteristics of municipal sludge", Water Science and Technology, Vol. 72, No. 11, pp. 2018-2026.
- Fillo, J. P., Koraido, S. M., and Evans, J. M. (1992). "Sources, Characteristics, and Management of Produced Waters from Natural Gas Production and Storage Operations", Environmental Science Research, Vol. 46, pp. 151-161.
- Gagnon, G. A., Krkosek, W., Anderson, L., McBean, E., Mohseni, M., Bazri, M., and Mauro, I. (2016). "Impacts of hydraulic fracturing on water quality: a review of literature, regulatory frameworks and an analysis of information gaps", Environmental Reviews, Vol. 24, No. 2, pp. 122-131.
- Gilron, J., Waisman, M., Daltrophe, N., Pomerantz, N., Milman, M., Ladizhansky, I., and Korin, E. (2006). "Prevention of precipitation fouling in NF/RO by reverse flow operation", Desalination, Vol. 199, pp. 29-30.
- Hu, G., Liu, T., Hager, J., Hewage, K., and Sadiq, R. (2018). "Hazard assessment of hydraulic fracturing chemicals using an indexing method", Science of the Total Environment, Vol. 619-620, pp. 281-290.
- Istirokhatun, T., Dewi, M.N., Ilma, H.I., Susanto, H. (2018). "Separation of antiscalants from reverse osmosis concentrates using nanofiltration", Desalination, Vol. 429, pp. 105-110.
- Jack, P. and Troy, C. (2016). TODAY IN ENERGY. Retrieved from U.S. Energy Information Administration: <https://www.eia.gov/todayinenergy/detail.php?id=26112>
- Jia, F. and Wang, J. (2018). "Treatment of flue gas desulfurization wastewater with near-zero liquid discharge by nanofiltration-membrane distillation process", Separation Science and Technology (Philadelphia), Vol.53, No. 1, pp. 146-153.
- Jiménez, S., Micó, M. M., Arnaldos, M., Medina, F., and Contreras, S. (2018, February). "Review: State of the art of produced water treatment", Chemosphere, Vol. 192, pp. 186-208.
- Khedr, M. G. (2012), "Processing of desalination reject brine for optimization of process efficiency, cost effectiveness and environmental safety", Advancing Desalination, InTech, Rijeka, pp. Ch. 06.

Kim, E.-S., Liu, Y., and Gamal El-Din, M. (2011). "The effects of pretreatment on nanofiltration and reverse osmosis membrane filtration for desalination of oil sands process-affected water", Separation and Purification Technology, Vol. 81, pp. 418-428.

Li, T., Tang, D., Song, J., and Law, A. W-K. (2019) "Reverse osmosis desalination process with feed flow reversal operation: experimental studies." Desalination and Water Treatment, Vol. 144, pp. 339-344.

Loganathan, K., Chelme-Ayala, P., and Gamal El-Din, M. (2015). "Effects of different pretreatments on the performance of ceramic ultrafiltration membrane during the treatment of oil sands tailings pond recycle water: A pilot-scale study", Journal of Environmental Management, Vol. 151, pp. 540-549.

Lu, X., Kujundzic, E., Mizrahi, G., Wang, J., Cobry, K., Peterson, M., . . . Greenberg, A. R. (2012). "Ultrasonic sensor control of flow reversal in RO desalination-Part 1: Mitigation of calcium sulfate scaling", Journal of Membrane Science, Vol. 419-420, pp. 20-32.

Lutz, B. D., Lewis, A. N., and Doyle, M. W. (2013). "Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development", Water Resources Research, Vol. 49, No. 2, pp. 647-656.

Maule, A. L., Makey, C. M., Benson, E. B., Burrows, I. J., and Scammell, M. K. (2013). "Disclosure of hydraulic fracturing fluid chemical additives: analysis of regulations", New solutions : a journal of environmental and occupational health policy : NS, Vol. 23, No. 1, pp. 167-187.

Md, A. A., Subir, B., David, P, Mohtada, S. (2017). "Colloidal Fouling of Nanofiltration Membranes: Development of a Standard Operating Procedure", Membranes, Vol. 7, No. 1, pp. 4.

Mccurdy, R. (2018). EIA ENERGY CONFERENCE. Retrieved from U.S. Energy Information Administration: <https://www.eia.gov/conference/2018/>

Mohammadi, T., Kazemi Moghadam, M., and Madaeni, S. S. (2003). "Hydrodynamic factors affecting flux and fouling during reverse osmosis of seawater", Desalination, Vol. 151, No. 3, pp. 239-245.

Mondal, S., Hsiao, C.-l., and Wickramasinghe, S. R. (2008). "Nanofiltration/Reverse Osmosis for Treatment of Coproduced Waters", Environmental Progress, Vol. 27, No. 2, pp. 173-179.

Motta, A., Borges, C., Esquerre, K., and Kiperstok, A. (2014). "Oil Produced Water treatment for oil removal by an integration of coalescer bed and microfiltration membrane processes", Journal of Membrane Science, Vol. 469, pp. 371-378.

Mumford, A. C., Akob, D. M., Klinges, J. G., and Cozzarelli, I. M. (2018). "Common Hydraulic Fracturing Fluid Additives Alter the Structure and Function of Anaerobic

Microbial Communities”, Applied And Environmental Microbiology, Vol. 84, No. 8, pp. 1-16.

Munirasu, S., Haija, M. A., and Banat, F. (2016). “Use of membrane technology for oil field and refinery produced water treatment—A review”, Process Safety and Environmental Protection, Vol. 100, pp. 183-202.

Nasiri, M. and Jafari, I. (2017). “Produced Water from Oil-Gas Plants: A Short Review on Challenges and Opportunities”, Polytechnica-Chemical Engineering, Vol. 61, No. 2, pp. 73-81.

Oetjen, K., Chan, K. E., Spear, J. R., Cath, T. Y., Higgins, C. P., Gulmark, K., Borch, T. (2018). “Temporal characterization and statistical analysis of flowback and produced waters and their potential for reuse”, Science of the Total Environment, Vol. 619-620, pp. 654-664.

Pérez -González, A., Ibáñez, R., Gómez, P., Urtiaga, A.M., Ortiz, I., Irabien, J.A. (2015). “Nanofiltration separation of polyvalent and monovalent anions in desalination brines”, Journal of Membrane Science, Vol. 473, No. C, pp. 16-27.

Pica, N. E., Carlson, K., Steiner, J. J., and Waskom, R. (2017). “Produced water reuse for irrigation of non-food biofuel crops: Effects on switchgrass and rapeseed germination, physiology and biomass yield”, Industrial Crops & Products, Vol. 100, pp. 65-76.

Pomerantz, N., Ladizhansky, Y., Korin, E., Waisman, M., Daltrophe, N., and Gilron, J. (2006). “Prevention of scaling of reverse osmosis membranes by "zeroing" the elapsed nucleation time. Part I. Calcium sulfate”, Industrial and Engineering Chemistry Research, Vol. 45, No. 6, pp. 2008-2016.

Qian, Z., Liu, X., Yu, Z., Zhang, H., and JÜ, Y. (2012). “Energy, Resources and Environmental Technology: A Pilot-scale Demonstration of Reverse Osmosis Unit for Treatment of Coal-bed Methane Co-produced Water and Its Modeling”, Chinese Journal of Chemical Engineering, Vol. 20, pp. 302-311.

Qin, J. J., Wai, M. N., Oo, M. H., Kekre, K. A., and Seah, H. (2009). “Impact of anti-scalant on fouling of reverse osmosis membranes in reclamation of secondary effluent”, Water Science and Technology, Vol. 60, No. 11, pp. 2767-2774.

Reinjection, P. W. (n.d.). Produced Water Discharge and Reinjection. Retrieved from Oil&Gas UK:
https://oilandgasukenvironmentallegislation.co.uk/contents/topic_files/offshore/produced_water.htm

Rosenblum, J., Nelson, A. W., Ruyle, B., Schultz, M. K., Ryan, J. N., and Linden, K. G. (2017). “Temporal characterization of flowback and produced water quality from a hydraulically fractured oil and gas well”, Science Of The Total Environment, Vol. 596, pp. 369-377.

- Rouina, M., Kariminia, H.-R., Mousavi, S. A., and Shahryari, E. (2016). "Effect of electromagnetic field on membrane fouling in reverse osmosis process", Desalination, Vol. 395, pp. 41-45.
- Salahi, A., Mohammadi, T., Nikbakht, M., Golshenas, M., and Noshadi, I. (2012). "Purification of biologically treated Tehran refinery oily wastewater using reverse osmosis", Desalination & Water Treatment, Vol. 48, No. 1-3, pp. 27.
- Sauvet-Goichon, B. (2007). "Ashkelon desalination plant - A successful challenge." Desalination, Vol. 203, No. 1-3, pp. 75-81.
- Scanlon, B. R., Reedy, R. C., and Nicot, J. P. (2014). "Comparison of Water Use for Hydraulic Fracturing for Unconventional Oil and Gas versus Conventional Oil", Environmental Science & Technology, Vol. 48, No. 20, pp. 12386-12393.
- Semblante, G. U., Lee, J. Z., Lee, L. Y., Ong, S. L., and Ng, H. Y. (2018). "Brine pre-treatment technologies for zero liquid discharge systems", Desalination, Vol. 441, pp. 96-111.
- Seyed Shahabadi, S. M., and Reyhani, A. (2014). "Optimization of operating conditions in ultrafiltration process for produced water treatment via the full factorial design methodology", Separation and Purification Technology, Vol. 132, pp. 50-61.
- Shaffer, D. L., Arias Chavez, L. H., Moshe, B.-S., Romero-Vargas Castrillón, S., Ngai Yin, Y., and Elimelech, M. (2013). "Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions", Environmental Science & Technology, Vol. 47, No. 17, pp. 9569-9583.
- She, Q., Wang, R., Fane, A. G., and Tang, C. Y. (2016). "Membrane fouling in osmotically driven membrane processes: A review", Journal of Membrane Science, Vol. 499, pp. 201-233.
- Shrestha, N., Chilkoor, G., Wilder, J., Gadhamshetty, V., and Stone, J. J. (2017). "Potential water resource impacts of hydraulic fracturing from unconventional oil production in the Bakken shale", Water Research, Vol. 108, pp. 1-24.
- Siagian Utjok, W. R., Widodo, S., Khoiruddin, Wardani Anita, K., and Wenten, I. G. (2018). "Oilfield Produced Water Reuse and Reinjection with Membrane", MATEC Web of Conferences, Vol. 156, pp. 08005.
- STATISTA (2018). Annual water consumption per capita worldwide in 2016, by select country (in cubic meters)*. Retrieved from STATISTA: <https://www.statista.com/statistics/263156/water-consumption-in-selected-countries/>
- Stringfellow, W. T., Camarillo, M. K., Domen, J. K., Sandelin, W. L., Varadharajan, C., Jordan, P. D., Birkholzer, J. T. (2017). "Identifying chemicals of concern in hydraulic fracturing fluids used for oil production", Environmental Pollution, Vol. 220 (Part A), pp. 413-420.

Struchtemeyer, C. G., and Elshahed, M. S. (2012). “Bacterial communities associated with hydraulic fracturing fluids in thermogenic natural gas wells in North Central Texas, USA”, Fems Microbiology Ecology, Vol. 81, No. 1, pp. 13-25.

Subramani, A., and Jacangelo, J. G. (2014). “Review: Treatment technologies for reverse osmosis concentrate volume minimization: A review”, Separation and Purification Technology, Vol. 122, pp. 472-489.

Sullivan Graham, E. J., Dean, C. A., Yoshida, T. M., Twary, S. N., Teshima, M., Alvarez, M. A., Laur, P. M. (2017). “Oil and gas produced water as a growth medium for microalgae cultivation: A review and feasibility analysis”, Algal Research, Vol. 24(Part B), pp. 492-504.

Sweity, A., Zere, T. R., David, I., Bason, S., Oren, Y., Ronen, Z., and Herzberg, M. (2015). “Side effects of antiscalants on biofouling of reverse osmosis membranes in brackish water desalination”, Journal of Membrane Science, Vol. 481, pp. 172-187.

Tibbetts, P. J. C., Buchanan, I. T., Gawel, L. J., and Large, R. (1992). “A Comprehensive Determination of Produced Water Composition”, In J. P. Ray (Ed.), Produced Water: Technological/Environmental Issues and Solutions, pp. 97-112, Boston, MA: Springer US.

Tong, T., and Elimelech, M. (2016). “The Global Rise of Zero Liquid Discharge for Wastewater Management: Drivers, Technologies, and Future Directions”, Environmental Science & Technology, Vol. 50, No. 13, pp. 6846-6855.

Torres, L., Yadav, O. P., and Khan, E. (2016). Review: “A review on risk assessment techniques for hydraulic fracturing water and produced water management implemented in onshore unconventional oil and gas production”, Science of the Total Environment, Vol. 539, pp. 478-493.

Troy, C. and Jack, P. (2016). U.S. Energy Information Administration. Retrieved from Today In Energy: <https://www.eia.gov/todayinenergy/detail.php?id=25372>

Tsai, J.-H., Macedonio, F., Drioli, E., Giorno, L., Chou, C.-Y., Hu, F.-C., . . . Tung, K.-L. (2017). “Membrane-based zero liquid discharge: Myth or reality?”, Journal of The Taiwan Institute of Chemical Engineers, Vol. 80, pp. 192–202.

U.S. Energy Information Administration. (2017). INTERNATIONAL ENERGY OUTLOOK 2017. Retrieved from U.S. Energy Information Administration: <https://www.eia.gov/outlooks/ieo/index.php>

Uchymiak, M., Lyster, E., Glater, J., and Cohen, Y. (2008). “Kinetics of gypsum crystal growth on a reverse osmosis membrane”, Journal of Membrane Science, Vol. 314, No. 1, pp. 163-172.

United Nations Population Division (2017). Population, total. Retrieved from THE WORLD BANK: <https://data.worldbank.org/indicator/SP.POP.TOTL>

United States Environmental Protection Agency. (n.d.). TENORM: Oil and Gas Production Wastes. Retrieved from EPA: <https://www.epa.gov/radiation/tenorm-oil-and-gas-production-wastes#tab-1>

Warsinger, D. M., Swaminathan, J., Guillen-Burrieza, E., Arafat, H. A., and Lienhard V, J. H. (2015). "Scaling and fouling in membrane distillation for desalination applications: A review", Desalination, Vol. 356, pp. 294-313.

Xiong, R., and Wei, C. (2017). "Review: Current status and technology trends of zero liquid discharge at coal chemical industry in China", Journal of Water Process Engineering, Vol. 19, pp. 346-351.

Xu, P., and Drewes, J. E. (2006). "Viability of nanofiltration and ultra-low pressure reverse osmosis membranes for multi-beneficial use of methane produced water", Separation and Purification Technology, Vol. 52, pp. 67-76.

Yost, E. E., Stanek, J., and Burgoon, L. D. (2017). "A decision analysis framework for estimating the potential hazards for drinking water resources of chemicals used in hydraulic fracturing fluids", Science Of The Total Environment, Vol. 574, pp. 1544-1558.

Zhao, S., Huang, G., Cheng, G., Wang, Y., and Fu, H. (2014). "Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to Reverse Osmosis membranes", Desalination, Vol. 344, pp. 454-462.

Appendix A. Experimental Results arranged according to Table x-z

Table A.1: Experimental results of FFFR operation with NaCl added in feedwater

Test	Membrane model	NaCl concentration (g/L)	Pressure (bar)	Feed flowrate (L/min)	Duration (hours)	T _H (s)	T _R (s)	Ratio R
RN1	2540	30	19	2.4	2.0	52	58	0.90
RN2	2540	30	25	2.3	1.1	59	61	0.97
RN3	2540	35	28	2.1	2.0	65	67	0.97
RN4	2540	50	24	1.7	2.0	69	70	0.99
RN5	2540	50	29	1.8	4.0	71	72	0.99
RN6	2540	60	29	2.1	1.8	57	56	1.02
RN7	2540	70	35	2.6	1.6	46	47	0.98
RN8	2540	60	35	2.2	1.8	57	57	1.00
RN9	2540	60	35	2.2	2.0	58	59	0.98
RN10	2540	70	34	2.8	1.5	42	44	0.95
RN11	4040	10	12	2.4	3.2	87	68	1.50
RN12	4040	30	17	2.4	2.0	78	63	1.24
RN13	4040	40	28	2.2	2.7	88	63	1.40
RN14	4040	45	27	2.3	2.0	83	68	1.22
RN15	4040	50	29	2.2	2.6	84	59	1.42
RN16	4040	60	22	2.3	2.6	74	58	1.28
RN17	4040	60	28	2.2	1.8	80	56	1.43
RN18	4040	80	33	2.2	2.0	82	59	1.39
RN19	4040	80	34	2.2	2.7	77	55	1.40

Table A.2: Experimental results of FFFR operation with NaCl & MgSO₄ added in feedwater

Test	Membrane model	NaCl + MgSO ₄ concentration (g/L)	Pressure (bar)	Feed flowrate (L/min)	Duration (hours)	T _H (s)	T _R (s)	Ratio R
RNM1	2540	0+1	5	2.5	0.5	85	88	0.97
RNM2	2540	0+1	5	2.5	0.6	81	103	0.79
RNM3	2540	0+4.5	6	2.5	2.1	80	66	1.21
RNM4	2540	30+1	20	1.9	1.3	67	72	0.93
RNM5	2540	30+1	20	2.4	2.1	52	55	0.95
RNM6	2540	30+1	21	2.8	0.9	44	47	0.94
RNM7	2540	35+3	23	2.1	1.9	64	64	1.00
RNM8	2540	35+3	25	2.3	1.8	57	57	1.00
RNM9	2540	35+3	29	2.2	1.8	66	67	0.99
RNM10	2540	35+3	33	2.2	2.0	67	68	0.99
RNM11	2540	35+6	29	2.1	1.8	66	66	1.00
RNM12	2540	50+3	28	2.2	2.1	55	54	1.02
RNM13	2540	50+3	30	1.8	3.4	69	70	0.99
RNM14	2540	50+3	36	1.9	2.0	70	70	1.00
RNM15	4040	0+3	4	2.5	0.8	85	73	1.16
RNM16	4040	0+2.4	3	2.5	0.6	85	63	1.35
RNM17	4040	0+4.5	5	2.5	1.7	82	66	1.24
RNM18	4040	0+3	3	2.6	2.2	85	73	1.16
RNM19	4040	0+2.4	3	2.6	2.4	85	63	1.35

Table A.3: Experimental results of FFFR operation with NaCl & CaCl₂ added in feedwater

Test	Membrane model	NaCl + CaCl ₂ concentration (g/L)	Pressure (bar)	Feed flowrate (L/min)	Duration (hours)	T _H (s)	T _R (s)	Ratio R
RNC1	4040	0+60	33	2.2	2.8	79	62	1.27
RNC2	4040	0+60	33	2.2	2.4	78	61	1.28
RNC3	2540	30+1.11	24	2.3	2.1	47	59	0.80
RNC4	2540	30+1	25	2.3	3.1	55	54	1.02
RNC5	2540	30+3	25	2.3	2.7	59	60	0.98
RNC6	2540	30+3	26	2.3	2.0	58	59	0.98
RNC7	2540	35+1	24	2.3	2.0	55	54	1.02
RNC8	2540	35+1	25	2.3	3.1	56	58	0.97
RNC9	2540	35+3	25	2.3	2.6	55	54	1.02

Table A.4: Experimental results of cross-flow filtration with NaCl added in feedwater

Test	Membrane model	NaCl concentration (g/L)	Pressure (bar)	Feed flowrate (L/min)	Duration (hours)
CN1	2540	30	20	2.4	1.6
CN2	2540	30	25	1.8	1.9
CN3	2540	30	25	1.9	2.7
CN4	2540	30	25	1.9	2.7
CN5	2540	30	25	2.3	2.8
CN6	2540	30	30	1.8	2.1
CN7	2540	30	30	1.8	2.9
CN8	2540	30	31	1.8	5.3
CN9	2540	35	25	1.9	2.4
CN10	2540	35	25	1.9	2.8
CN11	2540	35	25	1.9	3.1
CN12	2540	35	30	1.8	3.3
CN13	4040	0	2	2.6	1.8
CN14	4040	10	11	2.5	2.3
CN15	4040	30	17	2.4	4.6
CN16	4040	30	20	2.4	3.0
CN17	4040	30	21	2.4	2.4
CN18	4040	30	26	2.3	2.9
CN19	4040	30	27	2.3	2.6
CN20	4040	30	30	2.2	2.5
CN21	4040	30	30	2.3	2.4
CN22	4040	45	26	2.3	2.3

Table A.5: Experimental results of cross-flow filtration with NaCl & MgSO₄ added in feedwater

Test	Membrane model	NaCl + MgSO ₄ concentration (g/L)	Pressure (bar)	Feed flowrate (L/min)	Duration (hours)
CNM1	2540	0+1	4	2.5	0.5
CNM2	2540	0+1	9	2.5	1.1
CNM3	2540	0+3	7	2.5	0.7
CNM4	2540	0+10	21	2.3	1.0
CNM5	2540	30+1	20	2	1.0
CNM6	4040	0+3	3	2.6	2.2
CNM7	4040	0+2.4	3	2.6	2.4

Table A.6: Experimental results of cross-flow filtration with NaCl & CaCl₂ added in feedwater

Test	Membrane model	NaCl + CaCl ₂ concentration (g/L)	Pressure (bar)	Feed flowrate (L/min)	Duration (hours)
CNC1	4040	30+1	25	2.3	1.0
CNC2	4040	30+1	25	2.3	1.0
CNC3	4040	30+3	26	2.3	1.0

Fig A.RN.1: Pressure and recovery trends of test RN1

Fig A.RN.2: Pressure and recovery trends of test RN2

Fig A.RN.3: Permeate conductivity, salt rejection, pressure and recovery trends of test RN3

Fig A.RN.4: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RN4

Fig A.RN.5: Permeate conductivity, salt rejection, pressure and recovery trends of test RN5

Fig A.RN.6: Permeate conductivity, salt rejection, pressure and recovery trends of test RN6

Fig A.RN.7: Permeate conductivity, salt rejection, pressure and recovery trends of test RN7

Fig A.RN.8: Permeate conductivity, salt rejection, pressure and recovery trends of test RN8

Fig A.RN.9: Permeate conductivity, salt rejection, pressure and recovery trends of test RN9

Fig A.RN.10: Pressure and recovery trends of test RN10

Fig A.RN.11: Pressure and recovery trends of test RN11

Fig A.RN.12: Pressure and recovery trends of test RN12

Fig A.RN.13: Pressure and recovery trends of test RN13

Fig A.RN.14: Pressure and recovery trends of test RN14

Fig A.RN.15: Pressure and recovery trends of test RN15

Fig A.RN.16: Pressure and recovery trends of test RN16

Fig A.RN.17: Pressure and recovery trends of test RN17

Fig A.RN.18: Pressure and recovery trends of test RN18

Fig A.RN.19: Pressure and recovery trends of test RN19

Fig A.RNM.1: Pressure and recovery trends of test RNM1

Fig A.RNM.2: Pressure and recovery trends of test RNM2

Fig A.RNM.3: Pressure and recovery trends of test RNM3

Fig A.RNM.4: Pressure and recovery trends of test RNM4

Fig A.RNM.5: Pressure and recovery trends of test RNM5

Fig A.RNM.6: Pressure and recovery trends of test RNM6

Fig A.RNM.7: Pressure and recovery trends of test RNM7

Fig A.RNM.8: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM8

Fig A.RNM.9: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM9

Fig A.RNM.10: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM10

Fig A.RNM.11: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM11

Fig A.RNM.12: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM12

Fig A.RNM.13: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM13

Fig A.RNM.14: Permeate & brine conductivity, salt rejection, pressure and recovery trends of test RNM14

Fig A.RNM.15: pressure and recovery trends of test RNM15

Fig A.RNM.16: pressure and recovery trends of test RNM16

RNM17

Fig A.RNM.17: pressure and recovery trends of test RNM17

Fig A.RNC.1: Pressure and recovery trends of test RNC1

Fig A.RNC.2: Pressure and recovery trends of test RNC2

Fig A.RNC.3: Pressure and recovery trends of test RNC3

Fig A.RNC.4: Pressure and recovery trends of test RNC4

Fig A.RNC.5: Pressure and recovery trends of test RNC5

Fig A.RNC.6: Pressure and recovery trends of test RNC6

Fig A.RNC.7: Pressure and recovery trends of test RNC7

Fig A.RNC.8: Pressure and recovery trends of test RNC8

Fig A.RNC.9: Pressure and recovery trends of test RNC9

Fig A.CN.1: Pressure and recovery trends of test CN1

Fig A.CN.2: Permeate conductivity, salt rejection, pressure and recovery trends of test CN2

Fig A.CN.3: Pressure and recovery trends of test CN3

Fig A.CN.4: Pressure and recovery trends of test CN4

Fig A.CN.5: Pressure and recovery trends of test CN5

Fig A.CN.6: Permeate conductivity, salt rejection, pressure and recovery trends of test CN6

Fig A.CN.7: Pressure and recovery trends of test CN7

Fig A.CN.8: Permeate conductivity, salt rejection, pressure and recovery trends of test CN8

Fig A.CN.9: Pressure and recovery trends of test CN9

Fig A.CN.10: Pressure and recovery trends of test CN10

Fig A.CN.11: Permeate conductivity, salt rejection, pressure and recovery trends of test CN11

Fig A.CN.12: Permeate conductivity, salt rejection, pressure and recovery trends of test CN12

Fig A.CN.13: Pressure trend, recovery trends throughout the experiment and after compaction of test CN13

Fig A.CN.14: Pressure trend, recovery trends throughout the experiment and after compaction of test CN14

Fig A.CN.15: Pressure trend, recovery trends throughout the experiment and after compaction of test CN15

Fig A.CN.16: Pressure trend, recovery trends throughout the experiment and after compaction of test CN16

Fig A.CN.17: Pressure trend, recovery trends throughout the experiment and after compaction of test CN17

Fig A.CN.18: Pressure trend, recovery trends throughout the experiment and after compaction of test CN18

Fig A.CN.19: Pressure trend, recovery trends throughout the experiment and after compaction of test CN19

Fig A.CN.20: Pressure trend, recovery trends throughout the experiment and after compaction of test CN20

Fig A.CN.21: Pressure trend, recovery trends throughout the experiment and after compaction of test CN21

Fig A.CN.22: Pressure trend, recovery trends throughout the experiment and after compaction of test CN22

Fig A.CNM.1: Pressure and recovery trends of test CNM1

Fig A.CNM.2: Pressure and recovery trends of test CNM2

Fig A.CNM.3: Pressure and recovery trends of test CNM3

Fig A.CNM.4: Pressure and recovery trends of test CNM4

Fig A.CNM.5: Pressure and recovery trends of test CNM5

Fig A.CNM.6: Pressure trend, recovery trends throughout the experiment and after compaction of test CNM6

Fig A.CNM.7: Pressure trend, recovery trends throughout the experiment and after compaction of test CNM7

Fig A.CNC.1: Pressure and recovery trends of test CNC1

Fig A.CNC.2: Pressure and recovery trends of test CNC2

Fig A.CNC.3: Pressure and recovery trends of test CNC3

Appendix B. Omitted Results from Averaging the data for those Experiments with the same Operating Conditions

Table B.1: Recovery trend slope of the emitted experiments from Table 4.6

Test	NaCl concentration (g/L)	Pressure (bar)	Duration (hours)	Slope of the Recovery Trend Line (*10000)
RN1	30	19	2.0	-4
RN2	30	25	1.1	-5
RN4	50	24	2.0	-1
RN5	50	29	4.0	-0.3
RN6	60	29	1.8	-3
RN8	60	35	1.8	-5
RN9	60	35	2.0	-9
RN10	70	34	1.5	-2
RN7	70	35	1.6	-2

Table B.2: Recovery trend slope of the emitted experiments from Table 4.7

Test	NaCl + MgSO ₄ concentration (g/L)	Pressure (bar)	Duration (hours)	Slope of the Recovery Trend Line (*10000)
RNM1	0+1	5	0.5	-14
RNM2	0+1	5	0.6	-4
RNM4	30+1	20	1.3	-1
RNM5	30+1	20	2.1	0.6
RNM6	30+1	21	0.9	0.2
RNM7	35+3	23	1.9	-28
RNM8	35+3	25	1.8	-6
RNM9	35+3	28	1.8	-14
RNM10	35+3	33	2.0	4
RNM12	50+3	28	2.1	-2
RNM13	50+3	30	3.4	-6
RNM14	50+3	36	2.0	-10

Table B.3: Recovery trend slope of the emitted experiments from Table 4.8

Test	NaCl concentration (g/L)	Pressure (bar)	Duration (hours)	Slope of the Recovery Trend Line (*10000)
RNC3	30+1.11	24	2.1	-7
RNC4	30+1	25	3.1	-4
RNC5	30+3	25	2.7	-6
RNC6	30+3	26	2.0	-4
RNC7	35+1	24	2.0	-9
RNC8	35+1	25	3.1	-3

Table B.4: Modelling result of cycles 1-15 from FFFR test RNM15

Cycles	$Q_{P(M)}$ (L/min)	$Q_{P(E)}$ (L/min)	T_R (s)	T_H (s)	Q_{in} (L/min)	Q_B (L/min)
1	1.13	0.76	73	108	2.53	1.40
2	1.09	0.76	74	105	2.53	1.44
3	1.08	0.75	73	105	2.53	1.45
4	1.08	0.76	73	104	2.53	1.45
5	1.08	0.75	74	104	2.53	1.45
6	1.08	0.77	74	105	2.53	1.45
7	1.08	0.75	74	105	2.53	1.45
8	1.08	0.75	74	105	2.53	1.45
9	1.08	0.74	74	105	2.53	1.45

Appendix C. Results of the NaCl Conductivity Standard Calibration

Fig C.1: NaCl conductivity standard calibration for concentration between 0-7mol

Fig C.2: NaCl conductivity standard calibration for concentration between 0-0.7Mmol