


12-2014

Recycling wastewater for hydraulic fracturing by use of nanofiltration membranes

Haley D. Cleous

University of Arkansas, Fayetteville

Follow this and additional works at: <http://scholarworks.uark.edu/cheguht>

 Part of the [Hydraulic Engineering Commons](#), [Membrane Science Commons](#), and the [Nanoscience and Nanotechnology Commons](#)

Recommended Citation

Cleous, Haley D., "Recycling wastewater for hydraulic fracturing by use of nanofiltration membranes" (2014). *Chemical Engineering Undergraduate Honors Theses*. 108.
<http://scholarworks.uark.edu/cheguht/108>

This Thesis is brought to you for free and open access by the Chemical Engineering at ScholarWorks@UARK. It has been accepted for inclusion in Chemical Engineering Undergraduate Honors Theses by an authorized administrator of ScholarWorks@UARK. For more information, please contact scholar@uark.edu, ccmiddle@uark.edu.

Recycling Produced Water for Hydraulic Fracturing using Nanofiltration Membranes

An Undergraduate Honors College Thesis

in the

Ralph E. Martin Department of Chemical Engineering
College of Engineering
University of Arkansas
Fayetteville, AR

by
Haley Cleous

12/5/2014

Table of Contents

Introduction	4
Hydraulic Fracturing Process	4
Water Treatment.....	4
Water Characteristics.....	5
Nanofiltration	6
Materials and Methods	7
Commercial Nanofiltration Membranes	7
Membrane Rejection	8
Membrane Titration	10
Evaporimetry	10
Results and Discussion	12
Rejection	12
Charge	13
Pore Sizes	14
Economics	15
Conclusions and Recommendations	17
References	19
Appendix	21

Introduction

Hydraulic Fracturing Process

Hydraulic fracturing has become a controversial topic in the United States with the natural gas boom in recent years. Previously unattainable reserves of shale gas are now accessible due to horizontal drilling. Hydraulic fracturing accompanies horizontal drilling to maximize the extraction of natural gas and oil from fissures in the rock.

Hydraulic fracturing occurs after a well has been drilled but before it begins producing fuel. A mixture of fluids including water, sand, and chemicals are pumped into the well under extremely high pressures. The fluids open or enlarge fractures in the rock. This maximizes the extraction possible of the underground resources. Each well requires approximately 5 million gallons of water. Up to 80% of this water may return to the ground's surface over the lifetime of the well. ^[1] The water returns to the surface heavily contaminated and is ineligible for direct discharge to surface water bodies. Water contamination by fossil fuel production is not a new problem. Globally, approximately 15-18 billion m³ of freshwater is contaminated in correlation with fuel production. ^[2] Unconventional extraction methods such as fracking require more water than conventional methods.

Water Treatment

The water that returns to the surface from hydraulic fracturing wells must be treated or disposed of in Class II injection wells. Disposal to injection wells, although

viewed as the simplest solution, is harmful to the environment. The carbon dioxide emissions from trucks driving the massive amounts of water from the well site to the disposal well can add up to 8,000 tons per year. ^[3] Water treatment and reuse is a far superior alternative to deep well injection.

The extent that water must be treated depends on what it is used for. Water can be recycled and used for future hydraulic fracturing wells, irrigation, livestock or wildlife watering, or industrial purposes. The water will not generally be treated to a potable level because it is not economical. Reusing water for future hydraulic fracturing wells is preferable and the objective of this research study.

Water Characteristics

Water returned from a hydraulic fracturing well contains three categories of containments: organics, suspended solids, and dissolved solids. The water characteristics and concentrations vary widely based on well location and time. The water returned is divided into two categories: flowback and produced water.

Flowback is the term for water that comes up 10-14 days after fracking, before gas production. The water characteristics are related to the chemicals used in hydraulic fracturing and the containments are in low concentrations.

Produced water is the water that comes up accompanying gas production for the duration of the well. This may be up to 40 years, or however long the well is in service. The volume of water increases with time and can range from two to ten barrels per day. ^[4] The water characteristics are related to the geochemistry of the formation and the containments are in high concentrations. For this research, produced water was used because it is the more difficult target for treatment.

It was determined that the containments with the highest concentrations and the most significance in produced water are sodium and calcium. Table 1 displays concentrations of these two minerals in waters tested in our lab.

Table 1: Major Ion Concentration in Produced Water

	Sodium (ppm)	Calcium (ppm)
TX	50,000	16,000
OK	43,000	8,100
UT	17,200	113
ND	18,200	8,700

Salinity may range from 1,500 – 205,000 ppm depending on the location, with the Marcellus, Barnett, and Haynesville shale locations always greater than 40,000 ppm. [5] This is higher than the concentration of seawater, which has a salinity of 35,000 ppm. Although the concentration of sodium is very high, there are not major impacts on the frac fluid performance due to sodium reported. Therefore, it can be assumed that sodium removal is not a top priority in order to reuse water in hydraulic fracturing.

Calcium may be found in concentrations ranging from 454 – 23,500 ppm. [6] Calcium and magnesium cause scale, which impacts frac fluid performance by interfering with breakers. Concentrations of these contaminants should be reduced to less than 2,000 ppm in order to reuse produced water in future hydraulic fracturing wells. [7]

Nanofiltration

Nanofiltration (NF) membranes are ideal for treatment of produced water for hydraulic fracturing because they are designed to remove divalent ions but not monovalent ions. Like ultrafiltration (UF), microfiltration (MF), and reverse osmosis (RO), NF uses pressure as a driving force to push water across the membrane. Membranes are often thought of as dense, but unlike reverse osmosis (RO) membranes there are small pores that allow components to pass through. Small monovalent ions travel through the pores or diffuse across the membrane with the water, but anything too large is rejected. Operating pressures and costs are lower for nanofiltration than reverse osmosis.

Nanofiltration is used as a secondary treatment step to remove the dissolved components in the water. It is not a good target to remove organics and suspended solids because they would cause fouling on the membrane surface. Fouling reduces flux and requires replacement membranes more frequently. A primary treatment step to remove organics and suspended solids is required before the water can be sent to a nanofiltration membrane. The pretreatment step used in this study was UF.

Materials and Methods

Commercial Nanofiltration Membranes

Five commercial Sepro Membranes were obtained from ULTURA Water. NF membranes are asymmetric in design, with a porous support structure and a dense top layer that controls separation. The active layer of the membranes is made of trimesoyl chloride and piperazine chemistry. The reaction is depicted in Figure 1.

Each membrane had an unknown ratio of TMC and PIP, which changes the number and size of the pores. Additionally, unknown additives were added to some of the membranes to change the hydrophobicity and surface characteristics.

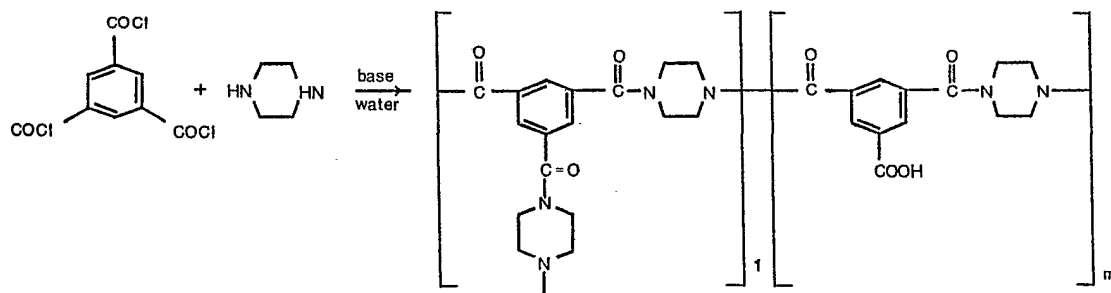


Figure 1: Trimesoyl chloride and piperazine chemical reaction.

Membrane Rejection

These membranes were tested using simulated fracking water and produced fracking water obtained from a frac site in Texas. A lab scale, cross-flow membrane filtration system was used for the experiments. Figure 2 displays the experimental apparatus. Figure 3 is a photograph of the Osmonics unit used in the experiments. Membranes were loaded one at a time into the filtration cell. Pressure was set and water was recycled through the system until steady state was achieved. At steady state, approximately 5 mL of permeate was collected. Samples were analyzed for calcium and sodium using ion-selective electrodes. Probes were used according to the procedure in the user manual. A calibration curve was created each time probes were used to ensure accuracy.

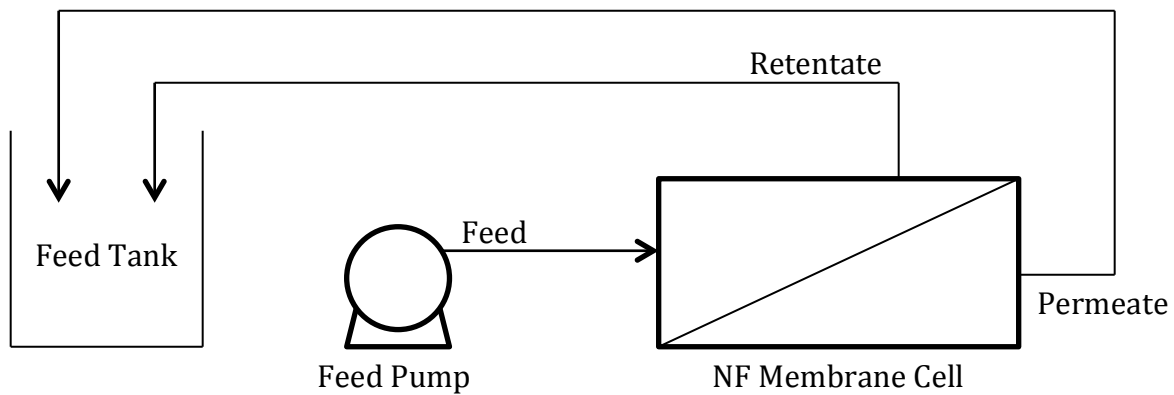


Figure 2: Nanofiltration cell experimental apparatus.

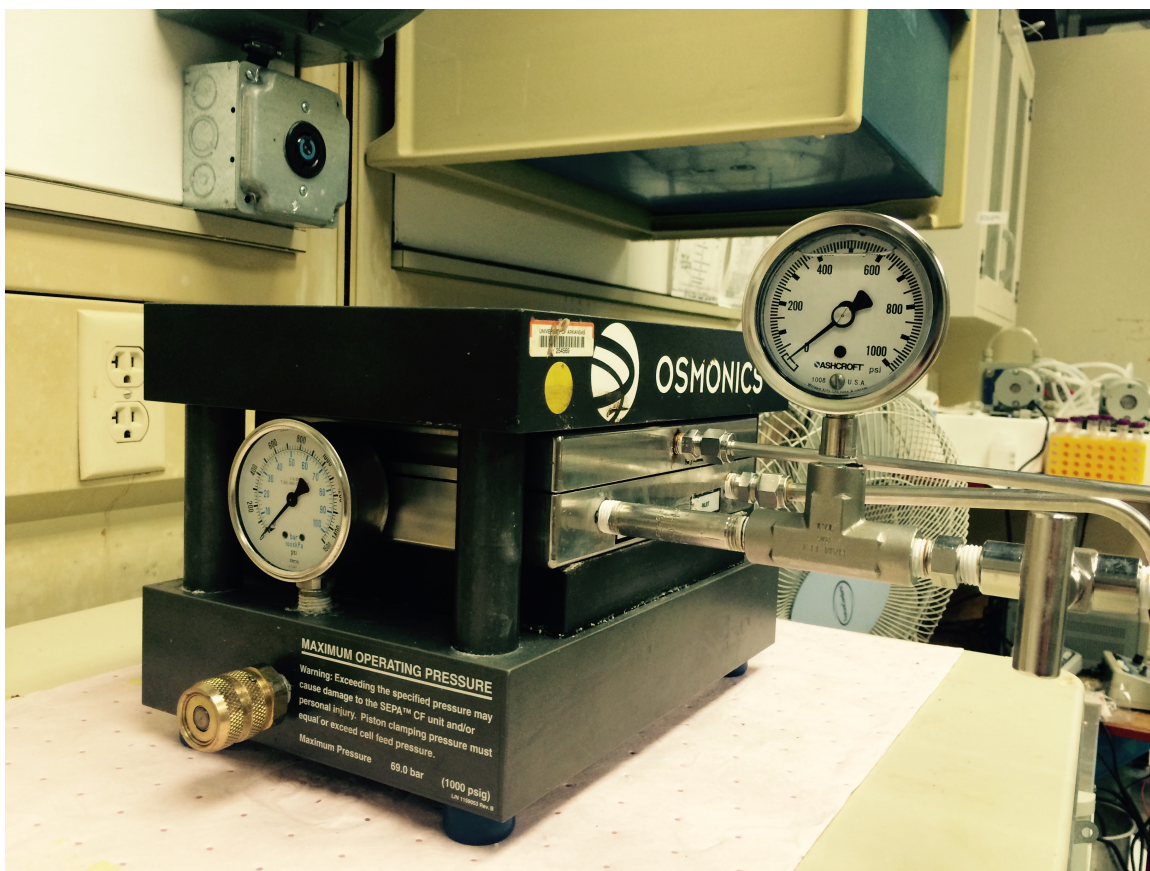


Figure 3: Photograph of NF membrane cell.

Membrane Titration

In order to determine the charge on the commercial membranes, a titration was carried out. The titration procedure used loosely follows that of Schaep published in 2001. First, the amount of negative charge was tested. Solutions of 0.1 M NaCl and 0.1 M MgCl were prepared. Samples of 3 cm by 3 cm were cut from each of the Sepro membranes. Samples were immersed in 50 mL of the NaCl solution for one hour so that all original counter-ions are replaced with sodium. Membrane samples were removed from the solution and rinsed thoroughly with demineralized water. Next, samples were immersed in 50 mL of the MgCl solution for one hour. It is assumed that after one hour the magnesium ions replaced the sodium ions. The solution was then tested for sodium concentration using atomic absorption spectroscopy (AA). The concentration of sodium ions is translated into equivalents per square meter of membrane area. This is the amount of negative charge on the membrane.

Second, the amount of positive charge was tested. The same procedure was used as that for negative charge except that NaCl and Na₂SO₄ were used. A chloride electrode was used to determine the amount of charge instead of AA.

Evaporimetry

Evaporimetry was used to determine the pore sizes of each commercial membrane. Figure 4 shows the experimental apparatus. This apparatus exactly matches that of Mirriam et. al.^[8] A circular section of membrane was placed in a diffusion chamber and edges were sealed tightly. This apparatus was placed on an

analytical scale, set to measure in milligrams. Approximately 1-2 mL of isopropyl alcohol was added so that it just covered the membrane surface. The experiment was left to run overnight for approximately ten hours. A data-logger program linked to Excel was set up that took measurements of mass every 30 seconds. A temperature probe was also utilized to record temperature at 30-second intervals. The experiment was performed at night with the air conditioning turned off to minimize variations in evaporation related to airflow mixing in the room.

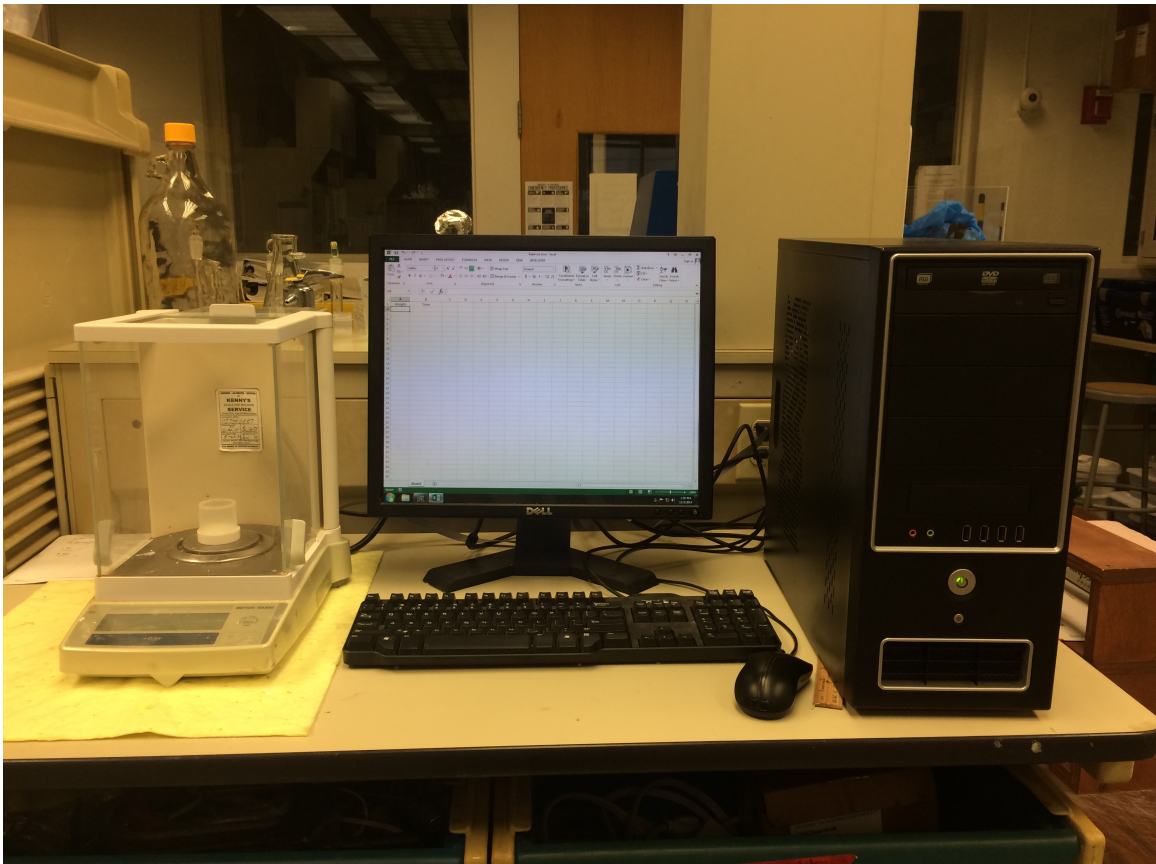


Figure 4: Evaporometry experimental set-up.

Results and Discussion

Rejection

The objective of this experiment was to have the highest possible rejection of calcium and the lowest possible rejection of sodium. Of the five membranes tested, NF3A best met this objective with a 69.8% rejection of calcium and a 4% rejection of sodium at 700 psi. Unfortunately this rejection of calcium is not enough to reduce TX water from 16,000 ppm to <2,000 ppm in one pass. It is desired to improve the membrane performance to 90% calcium rejection.

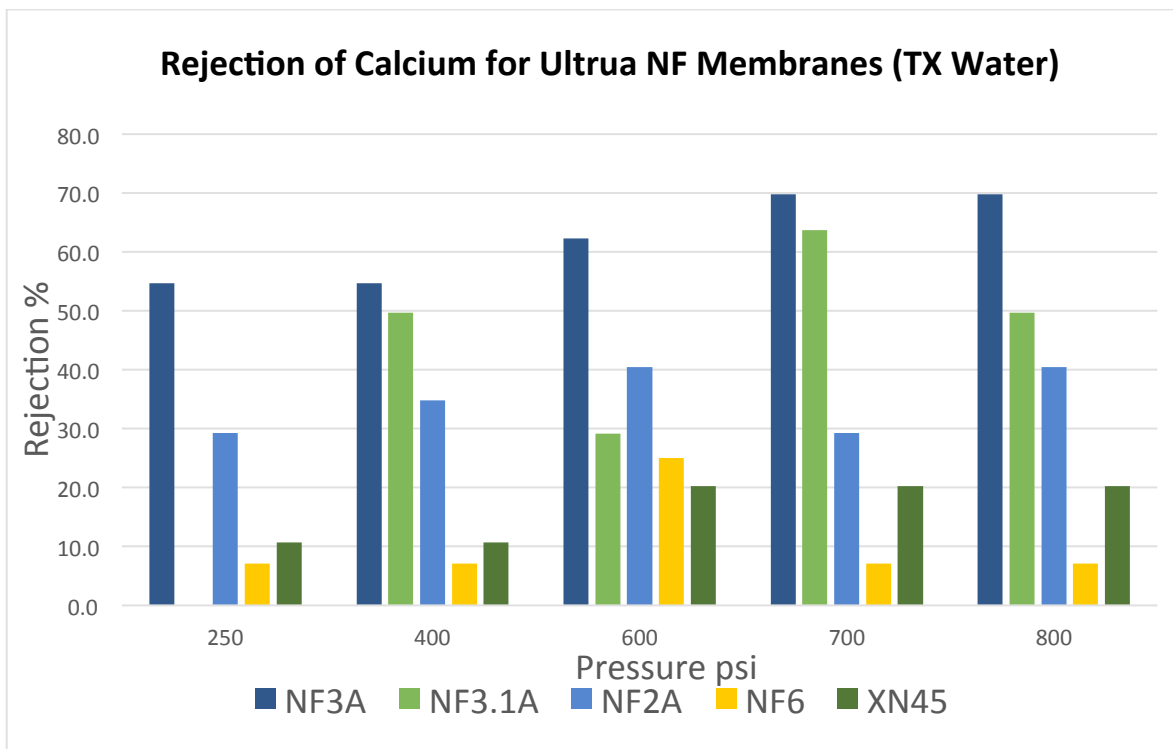


Figure 5: Calcium rejection at pressures ranging from 250 to 800 psi.

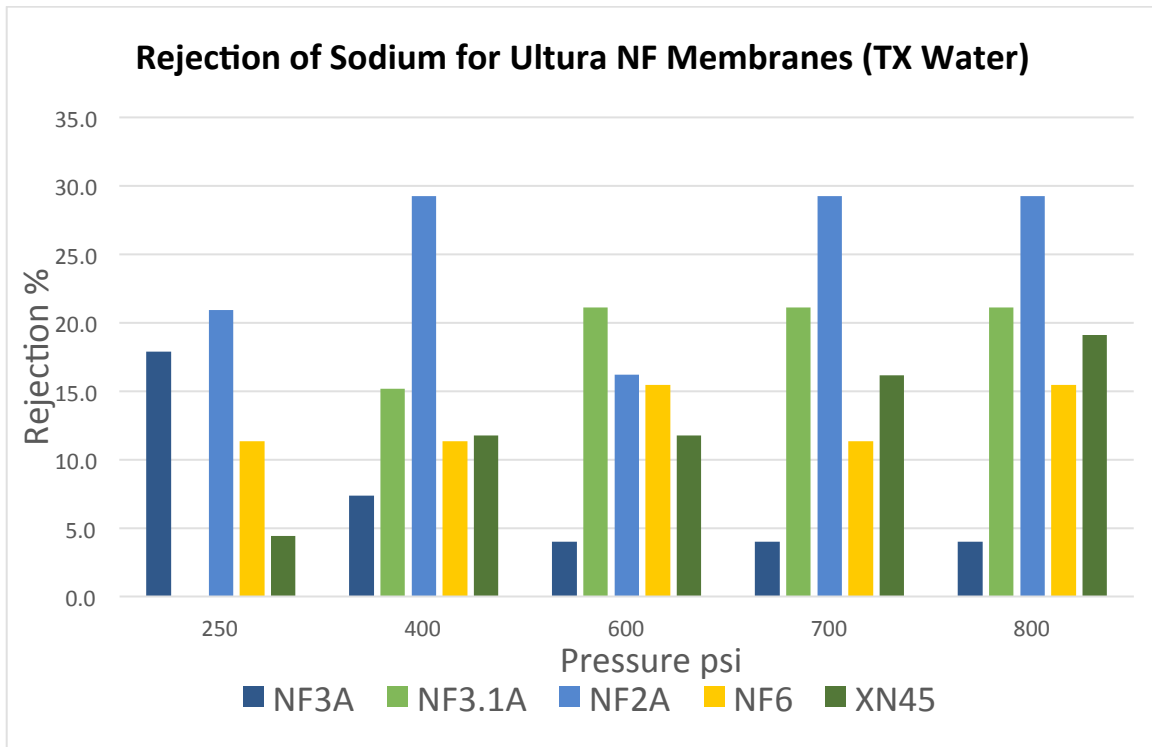


Figure 6: Sodium rejection at pressures ranging from 250 to 800 psi.

Charge

Results from membrane titrations show that the amount of charge on the membranes is very low but quantifiable. When determining the amount of negative charge, the atomic absorption standards used were between zero and 500 ppm. Results showed values that were approximately zero. It is assumed that there is a slight charge, but results from the test are not conclusive. In order to get a better estimate about the amount of negative charge, samples should be analyzed using a different AA procedure and standards an order of magnitude smaller. When measuring positive charge, smaller standards were used. All five commercial membranes were found to have a positive charge in the range of 2.72 to 3.11 milli-equivalents per square meter.

Table 2: Positive charge on nanofiltration membranes.

Sample	Cl Concentration (ppm)	Charge (meq/m ²)
NF2A	1.901446772	2.979857032
NF3A	1.739199417	2.725590686
NF3.1A	1.818514536	2.849889572
NF6	1.739199417	2.725590686
XN4	1.988161082	3.115751578

Pore Sizes

Evaporometry relates evaporation rate, W (measured in the experiment) to vapor pressure, P using the Irving Langmuir's Equation.

$$W = (P_v - P_p) \sqrt{\frac{m}{2\pi RT}} \quad (1)$$

The vapor pressure can then be used in the Kelvin Equation to solve for the pore radius, r .^[9]

$$\ln \frac{P'}{P} = -\frac{2 \sigma V}{R T r \cos \theta} \quad (2)$$

The evaporation rate was fairly constant initially, dropped suddenly, and then went to zero. Figure 6 shows the evaporation rate curve for one of the evaporometry runs performed. Using this evaporation curve, pore sizes can be determined.

It was assumed that only results below 15 nanometers are actually pores in the membrane. Evaporometry has been proven down to a minimum size of two nanometers, however it has been stated that this technique can be used for all nanofiltration membranes. Therefore, histograms were created for each NF membrane of the pore size distribution from 1-15 nm. The histograms are located in the Appendix.

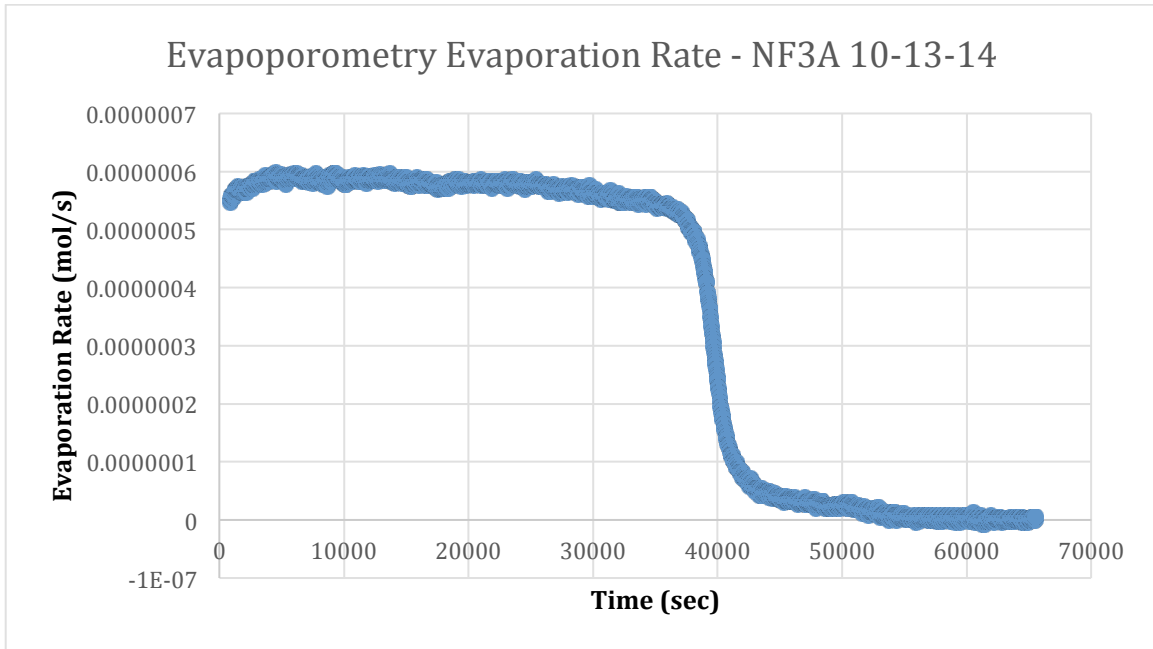


Figure 7: Evaporation rate curve from sample evaporoporometry experiment.

Results were summarized in percent of pores at or below two nanometers and compared to rejection in Table 3. Results show that when there are too many small pores, the sodium is rejected. When there are larger pores there is not enough calcium rejected. The best membrane from this study, NF3A had 63% of pores in the range of two nm or less.

Table 3: Correlation between percent of pores below 2nm and rejection of Na & Ca.

Membrane	% of Pores at or Below 2 nm	Na Rejection at 700 psi	Ca Rejection at 700 psi
NF2A	68.94 %	29.2 %	29.2 %
NF3A	63.35 %	4.00 %	69.8 %
NF3.1A	44.53 %	21.1 %	63.6 %
NF6	41.06 %	11.3 %	7.10 %
XN45	43.16 %	16.2 %	20.2 %

Economics

Fracking companies spend approximately \$5 per barrel for disposal to deep well injection. Of the \$5, \$2 is spent on injecting the water into the ground and \$3 is

spent on transportation. In order for companies to consider treating water, the treatment cost must be less than the cost for injection. NF is desirable because treatment costs are only \$1.31 per barrel compared to RO, which costs \$4.28 per barrel.

The high sodium concentration is the reason it is not economical to treat produced water to a potable level. If one had to remove all of the sodium, treatment technologies would be limited to reverse osmosis, evaporation, or distillation. These options require either high pressure or temperatures, which make them more expensive.

The main determination of treatment cost is the water recovery attainable. In order to calculate treatment cost, the water recovered by NF and RO membranes was estimated using the Van't Hoff Equation.

$$\Delta\pi = iCRT \quad (3)$$

The Van't Hoff equation is intended for dilute ion concentrations, but with high concentrations it is an appropriate estimation. This equation uses only the molar concentration of the species removed to calculate an osmotic pressure. The osmotic pressure must be overcome in order for permeate to penetrate the membrane. Table 4 displays the theoretical water recovery for RO and NF based on the concentrations of sodium and calcium measured in the lab. Water recovery is the amount of water that can be reused. All water that is not recovered still has to be disposed of by deep well injection. RO is not an applicable treatment for produced water because the osmotic pressure is sometimes so large that normal operating

pressures cannot overcome it to generate clean water. NF, however, has water recoveries ranging from 86 – 98%.

Table 4: Theoretical water recoveries of produced water by RO and NF.

Maximum Water Recoveries				
	RO - 99.9 % Rejection of Ca & Na - 1,500 psi	High Pressure RO - 99.9 % Rejection of Ca & Na - 3,000 psi	NF - 67% Rejection of Ca & 5% Rejection of Na - 700 psi	NF - 67% Rejection of Ca & 5% Rejection of Na - 1,500 psi
TX Water	0%	25%	86%	88%
OK Water	0%	42%	90%	92%
ND Water	35%	70%	86%	90%
UT Water	55%	80%	97%	98%

When calculating treatment costs, the following assumptions were made.

Pretreatment cost before the water reaches NF or RO is \$0.50 per barrel. RO and NF treatment costs are based on calculations from Al-Sahali et. al. It is assumed that NF cost is approximately the same as RO except that NF membranes are approximately double the cost of RO membranes due to demand. A water recovery of 25% for RO and 86% for NF was selected based on the Texas water concentrations.

Conclusions and Recommendations

It is concluded that the treatment and reuse of produced water from hydraulic fracturing has both environmental and economic advantages. Treatment requires a primary step to remove organics and suspended solids. Nanofiltration membranes remove divalent ions but retain monovalent ions. The result is lower osmotic pressures and higher water recoveries.

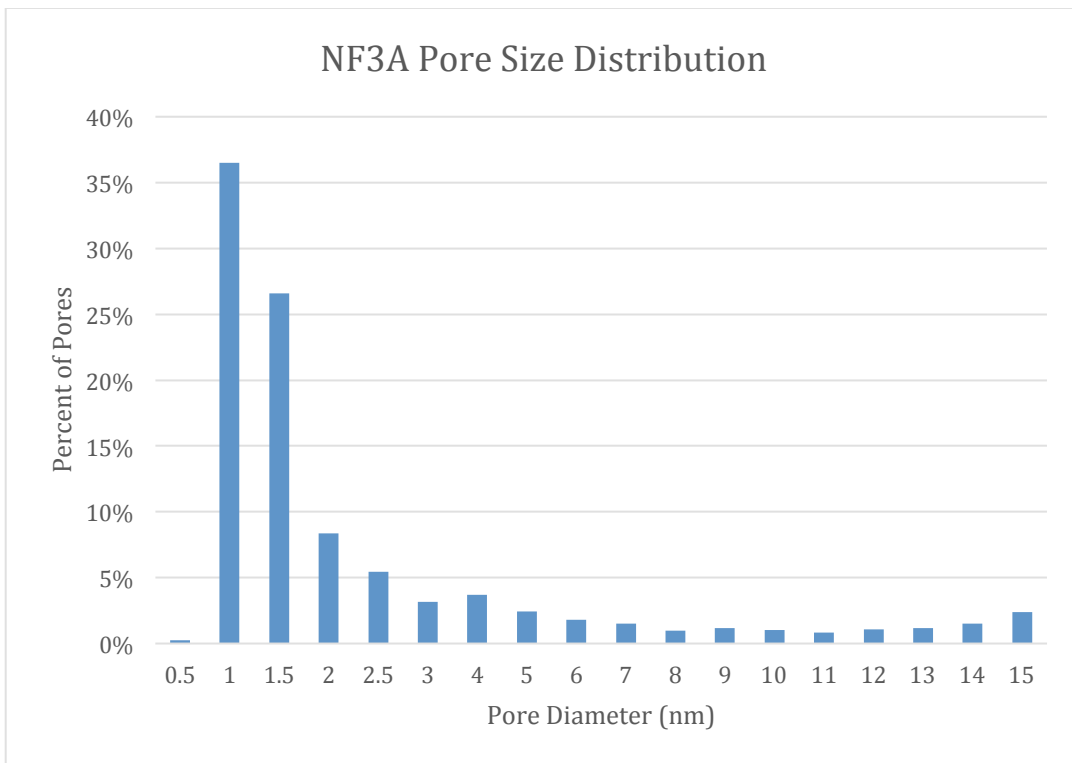
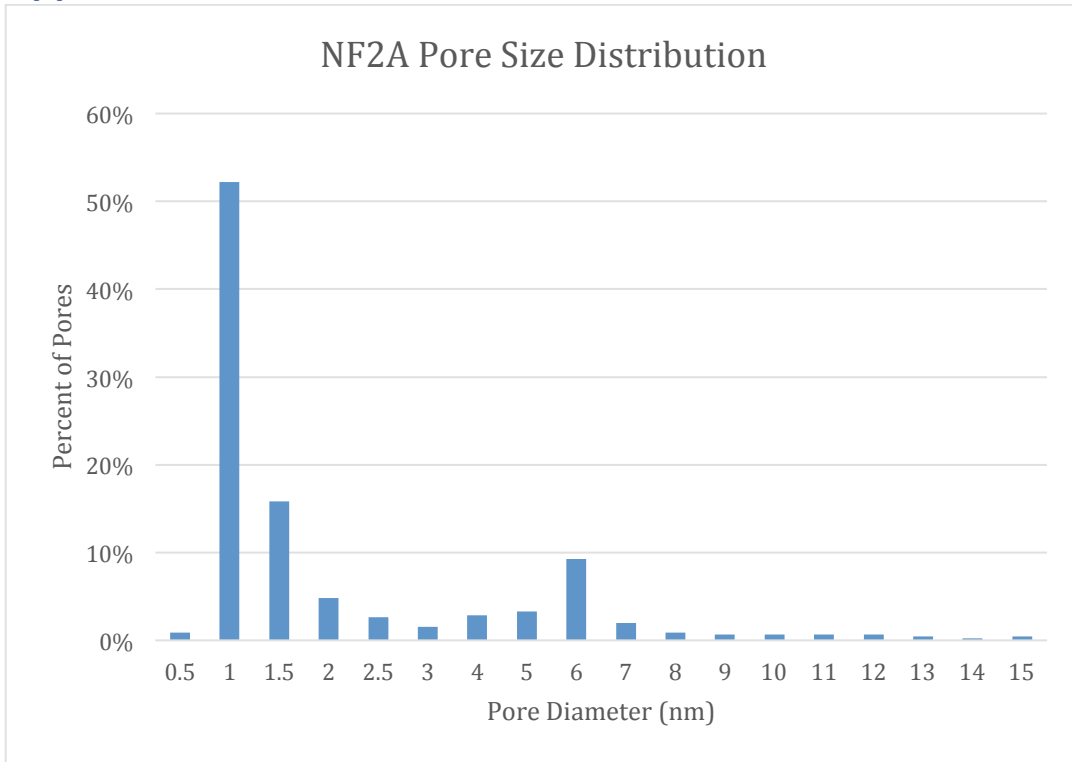
Of the commercial membranes tested, NF3A had the optimum separation, rejecting 4% sodium and 69.8% calcium. This rejection is promising, however in order to reduce ion concentrations below the goal for reuse a membrane with 90% calcium rejection is desired. For future research optimizing membranes, it was necessary to characterize the membranes tested. Membranes were tested for charge and pore size. It was determined that membranes have a low but quantifiable surface charge. Pore size ranged from 1-15 nm. The optimum membrane has a high concentration of pores at or below 2 nm and few pores in the 6-7 nm range. It is recommended that future experiments include creating and testing charged membranes and comparing to the ones used in this study. It is also recommended that a membrane be created with fewer defects and more pores of the optimum size to reject calcium.

References

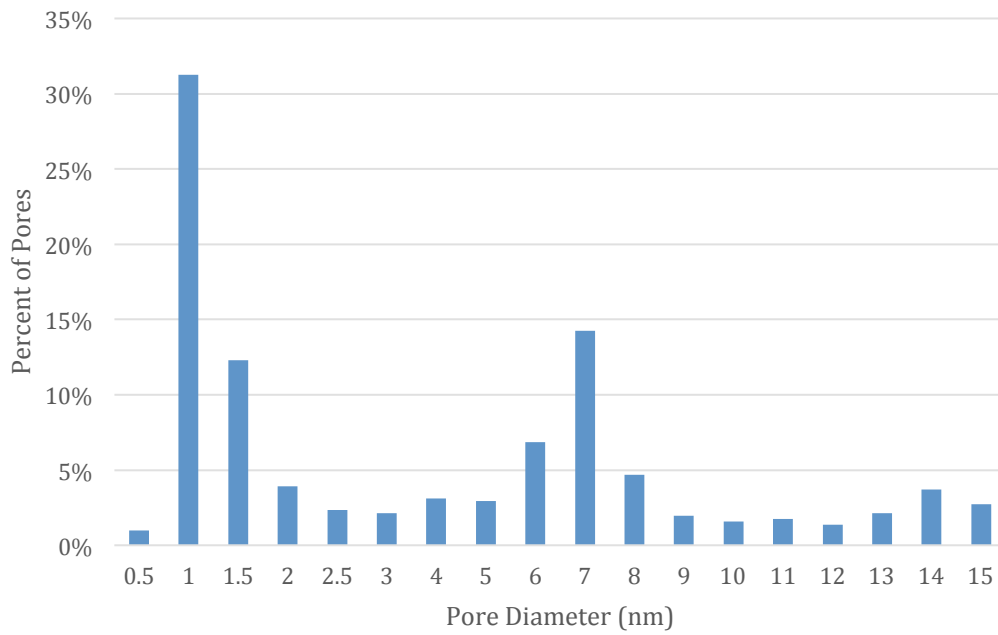
- [1] "Hydraulic Fracturing Study Fact Sheet." *Epa.gov*. US Environmental Protection Agency, June 2010. Web. 4 Apr. 2014.
- [2] "Water and Energy Facts and Figures." *The United Nations World Water Development Report 2014* (n.d.): n. pag. *Unesco.org*. United Nations Educational Scientific and Cultural Organization, 2014. Web. 29 Nov. 2014.
- [3] Ely, John W., Aaron Horn, Robbie Cathey, Michael Fraim, Dr., and Sanjeev Jakhete. "Game Changing Technology for Treating and Recycling Frac Water." *Society of Petroleum Engineers* PP SPE.145454 (2011): n. pag.
- [4] Hammer, Rebecca, and Jeanne VanBriesen, Ph.D, PE. "In Fracking's Wake: New Rules Are Needed to Protect Our Health and Environment from Contaminated Wastewater" *Natural Resources Defence Council*, 2012.
- [5] Dahlen *Journal of Environmental Hydrology*, 2013
- [6] Miller, Daniel J., Xiaofei Huang, Hua Li, Sirirat Kasemset, Albert Lee, Dileep Agnihotri, Thomas Hayes, Donald R. Paul, and Benny D. Freeman. "Fouling-resistant Membranes for the Treatment of Flowback Water from Hydraulic Shale Fracturing: A Pilot Study." *Journal of Membrane Science* 437 (2013): 265-75.
- [7] Katie Guerra, US Bureau of Reclamation.
- [8] Merriam, Lauren, Alex Moix, Robert Beitle, and Jamie Hestekin. "Carbon Dioxide Gas Delivery to Thin-film Aqueous Systems via Hollow Fiber Membranes." *Chemical Engineering Journal* 253 (2014): 165-73.

- [9] Krantz, William B., Alan R. Greenberg, Elmira Kujundzic, Adrian Yeo, and Seyed S. Hosseini. "Evaporometry: A Novel Technique for Determining the Pore-size Distribution of Membranes." *Journal of Membrane Science* 438 (2013): 153-66.
- [10] Al-Sahali, Mohamad, and Samar Al-Qattan. "Performance Analysis of Small Capacity Reverse Osmosis Desalination Plants." *Kuwait J. Science Engineering* 39.2B (2012): 231-53.
- [11] Schaep, Johan, and Carlo Vandecasteele. "Evaluating the Charge of Nanofiltration Membranes." *Journal of Membrane Science* 188.1 (2001): 129-36.

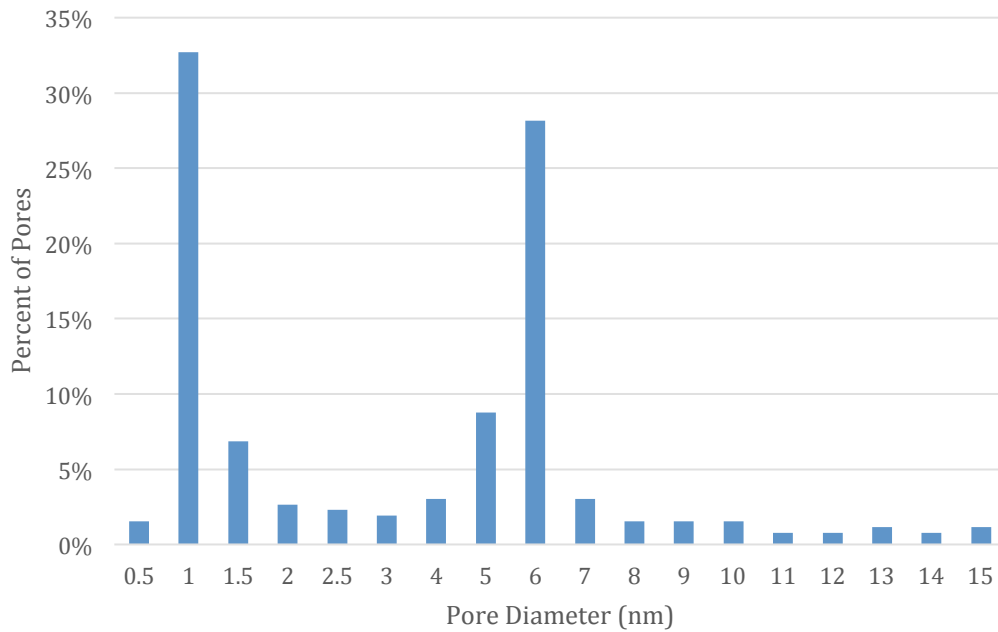
Appendix



NF3.1A Pore Size Distribution



NF6 Pore Size Distribution



XN45 Pore Size Distribution

