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Hydraulic Fracturing Water Recycle through Optimal Ultrafiltration and Nanofiltration Membranes System Design

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Hydraulic Fracturing Water Recycle through Optimal Ultrafiltration and Nanofiltration Membranes System Design

Hydraulic Fracturing Water Recycle through Optimal Ultrafiltration and Nanofiltration Membranes System Design

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By

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Abstract

Innovations in hydraulic fracturing technology have created opportunities for petroleum and natural gas production. This technology injects water, sand, and additives to create fissures in rock formations and discharge oil and gas to the surface. The average amount of water used per well is approximately 4.4 million gallons. The large water demand and the complexities involved in wastewater treatment make this process very expensive and not sustainable as far as water use is concerned. Flexible membrane technology has not been developed to process fracking water for re-use across the U.S. The objective of this project is to compare and analyze the recovery of contaminated fracking water through different types of ultrafiltration and nanofiltration membranes.

Through ultrafiltration, the hydraulic fracture water is pretreated to remove the majority of total suspended solids (TSS) and turbidity. The water flux, chemical oxygen demand (COD), turbidity, TSS, and salt level concentrations are then measured. Afterwards, the treated water is filtered using flat sheet nanofiltration membranes of Osmonics and SEPA Membrane Element Cell Equipment. The process is repeated with different membranes to determine optimal operating pressure, flux, and salt rejection. This study reveals that the highest performing membranes could remove 70 percent of divalent ions with an 85 percent water recovery in the permeate. Therefore, the process reduces significant amount of wastewater, which is disposed to the deep wells injection. With these promising results, our process can recycle water for reuse in hydraulic fracturing while minimizing environmental damage due to water contamination. Through this project, we are confident that hydraulic fracking can become a more sustainable process.

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1. Introduction

An increase in demands for freshwater sources, stricter local legislation on the use of hydraulic fracturing, and the unpredictability of drought conditions conspire the ability to recycle flow back water as an important objective in today's shale gas field. There has been an increase in reports of public concerns that hydraulic fracturing poses a potential risk to water wells and domestic drinking water supplies. Previous research has shown that more than 40 percent of private water wells in Pennsylvania fail to meet federal drinking water standards (1). In Ohio, the state regulators said a dozen earthquakes were induced by the injection of gas drilling waste water (2). Strict enforcement of the Safe Drinking Water Act and the Clean Water Act impose regulations on hydraulic fracturing process and its waste disposals (3). Under these restrictions, the discharge and dilution of flowback water become an inadequate or unsustainable approach to managing waste water.

Research shows promising advancement in utilizing natural gas contained in various unconventional shale formations as an important energy source. The Society of Petroleum Engineers describes unconventional gas shale as fine grained, organic rich, and entrapped in sedimentary rocks (4). According to the Energy Information Administration (EIA), the estimated reserves of shale gas in the United State are about 716 trillion cubic meters, which is the equivalent of approximately 102 billion barrels of crude oil (5). The reserves may secure the worldwide fuel supply for more than 25 years (5). In recent decades, the utilization of hydraulic fracturing and horizontal drilling has dramatically increased the gas production from shale gases. In 2011, about 2,000 shale gas wells were drilled in Pennsylvania, almost 20 times the number of wells drilled in 2007 (6). The advent of hydraulic fracturing technologies in combination with horizontal drilling has allowed gas companies to explore previously untapped gas reserves.

Hydraulic fracturing requires fracturing fluids, which uses freshwater drawn from local water sources and mixed with chemical additives. Local water sources include streams, wells, ponds, and lakes. Table 1 lists different types of fracturing fluid additives and their main components. A single well hydro fracture may require one to five million gallons of fracturing fluid. After hydraulic fracturing, about 10- 40 percent of hydro fracture water will return to the surface as flow back water. The percent return varies upon the geology of the formation (7). The flow back water composition tremendously depends on several factors, such as location of the formation, chemicals used during stimulation, and age of the well. Flow back water typically contains high levels of total dissolved solids (TDS) (ranging from 70,000 to 300,000 mg/L), hydrocarbon, and heavy metals (7). In addition, the water can contain a variety of different salts, causing variation among the different flowback water. This contaminated water can impact human health and affect the environment if it is re-injected or direct discharged onto land or into receiving streams (8,44).

Table 1: Fracturing Fluid Additive Types and Their Main Components (9)

Main components	Purpose
Hydrochloric acid	Helps dissolve minerals and initiate cracks in the rock
Glutaraldehyde	Eliminates bacteria in the water that produce corrosive by-products
Ammonium persulfate	Allows a delayed breakdown of the gel polymer chains
n-dimethyl formamide	Prevents corrosion of the pipe
Borate slats	Maintains fluid viscosity as temperature increases
Polyacrylamide	Slicks the water to minimize friction
Hydroxyethyl cellulose	Thickens the water in order to suspend the sand
Citric acid	Prevents precipitation of metal oxides
Potassium chloride	Creates a brine carrier fluid
Ammonium bisulfite	Removes oxygen from water to protect the pipe from corrosion
Sodium carbonate	Maintains the effectiveness of other components such as cross linkers
Silica, quartz sand	Allows the fractures to remain open so the gas can escape
Ethylene glycol	Prevents scale deposits in the pipe
Isopropanol	Increase the viscosity of the fracture fluid

Managing and disposing of flow back water are becoming more costly due to the increase in trucking costs and disposal fees. Hence, the demand for water conditioning and reuse have increased dramatically this past decade. The waste water treatment industry was estimated to be worth up to $100 billion in the United States (10,45). Furthermore, the complexity of global water management is significantly magnified when contemplating local concern like government regulations, water volumes, and water quality.

When deciding on a method to treat flow back water, it is important to consider the end use and its specific requirements. The composition of the water, the cost of treatment chemicals, type of equipment and maintenance, ease of process mobility, personnel, and disposal of treatment waste should also be considered. Studies of recycling fracturing water are few due to oil and gas companies’ unwillingness to publish their information. It is a major hindrance in determining the economics and standards for recycling fracturing water.

This research paper will discuss different existing treatments of hydraulic fracturing water from shale gas production. However, its emphasis will be the sustainable advance treatments of flowback water using Ultrafiltration (UF) and Nanofiltration (NF) membranes. To fulfill this objective, the flowback water from four locations are first comprehensively characterized. Based on the characterization, research focuses on applying membranes to treat these flowback waters. Furthermore, the specific effects of different types of membranes are investigated. The results were compared to conventional treatments such as coagulation, flocculation, and granular activated carbon. Finally, a preliminary cost estimation of the proposed treatment process was conducted.

2. Literature Review

2.1. Flowback Water

Shale gas wells are not hard to drill, but they are difficult to complete. In almost every case, the rock around the wellbore must be hydraulically fractured before the well can produce a significant amount of gas. The pumped fluid, under pressure up to 8,000 psi, is enough to crack shale as much as 3,000 feet deep in each direction from the wellbore (11). The hydraulic fracture consumes a large amount of water. Up to 40 percent of consumed water will return to surface as flowback water (11, 39). For example, the Fayetteville Shale produces 500,000 to 600,000 gallons of water per well in the first 10 days. It is estimated that 95,000 barrels of flowback water per day are discharged to the surface (12, 43). That is a significant volume of water requiring treatment.

The feasibility of reusing flowback water is dependent on three major factors. The first factor is the volume of the flowback water. The second is the duration in time of flowback water generation. This includes the rate at which water is generated and how it declines over time. The third major factor is the quality of flowback water. Total dissolved solids (TDS), total suspended solids (TSS), and scale causing compounds (calcium, magnesium, barium, and sulfate) all are contributors to the quality of flowback water. High TDS can increase friction in the fluid, which causes problems in the hydraulic fracturing process. Plus, high TSS can increase plugs in well. Therefore, the ideal for reusable flowback water is having low TDS, TSS, and scale causing compounds.

Sustainable or readily available water is very important for wells that use and produce large quantities of water. Their flowback water will require disposal or reuse options. The unit of measurement used for comparison of long term water production is gallon of water per million cubic feet (MMCF) of gas or hydrocarbon liquid equivalent. For example, Barnett Shale generates the largest volume of contaminated water. It is estimated to be 1,000 gallons per MMCF. The lowest long term producer comes from Marcellus Shale which is less than 200 gallons per MMCF (13).

2.2. Shale Formation

There are various shale gas formations in the United States. Four most popular formations are Barnett, Haynesville, Fayetteville, and Marcellus Shale which are located and spread throughout multiples states.

2.2.1. Barnett Shale

Barnett Shale formation is a Mississippian age black shale that has a high organic content. It underlines 5,000 square miles of the Dallas/ Fort Worth area of Texas. It is the most active natural gas location in the United States with as many as 173 new drilling rigs in 2011 (13). Gas production increased from 94 million cubic feet per day in 1998 to over 3 billion cubic feet per day in 2007 (13). Barnett Shale requires approximately 4 million gallons of water per well. This amount includes 250,000 gallons used for drilling and 3.8 million gallons used for fracturing. The flowback water has high levels of TDS (50,000 to 140,000 ppm), low TSS and moderate scaling tendency. Also, the shale generates high volumes of flowback water (13).

2.2.2. Marcellus Shale

Marcellus Shale is a sedimentary rock formation deposited over 350 million year ago during the middle Devonian period (15). Most of the shale lies beneath West Virginia, western and northeastern Pennsylvania, southern New York, eastern Ohio, and parts of Maryland. It is an estimated 95,000 square miles (15). It represents one of the largest reserves of on shore natural gas. The shale gas requires 5.6 million gallons of water per well. This amount includes 85,000 used for drilling and approximately 5.5 million gallons used for fracturing (13).The quality of flowback water is manageable with low TSS (160 ppm), high TDS (40,000- 90,000 ppm), and moderate scaling tendency (16). It had generated a significant volume of flowback water within the first few weeks. Fortunately, its waste water production has decreased dramatically.

2.2.3. Fayetteville Shale

Fayetteville Shale requires 4.9 million gallons of water per well. The amount includes 65,000 gallons used for drilling and approximately 4.9 million gallons used for fracturing. The flowback water has very low TDS (15,000 ppm), low TSS, and low scaling tendency (16). It is an ideal candidate for recycling, because it has a good flowback water quality.

2.2.4. Haynesville Shale

Haynesville Shale covers southwestern Arkansas, northwestern Louisiana and east Texas. The shale gas requires 5.6 million gallons of water per well including 600,000 gallons used for drilling and 5 million gallons used for fracturing (13). The flowback water has high TDS levels, high TSS (350 ppm), and high scaling tendency (10,000 ppm of calcium, 1,000 ppm of magnesium). Plus, the flowback water sometimes contains high levels of chlorides (16).

2.2.5. Efficiency of Water Usage per Well

Table 2 summarizes the water usage and gas production of the selected four shale formations. It shows that Barnett has utilized the least amount of water per well. Yet, it is not the most efficient in its water usage. On average, Barnett Shale needs 1.3 gallons of water to produce 1MMBtu of gas. Haynesville uses the highest volume of water and produces the highest amount of gas (17). It is the most efficient in its water usage. It needs less than 1 gallon of water to produce 1MMBtu of gas. Fayetteville Shale produces the least amount of gas and is the least efficient in using its water.

Table 2: Water Use Efficiency of Four Major Shale Gases Formations (17)

Shale Play	Average Water Use Per Well (million gallons)	Average Gas Production Over Well Lifetime (billion cubic feet)	Water Use Efficiency (in gallons per MMBtu)
Haynesville	5.6	6.5	0.84
Marcellus	5.6	5.2	1.05
Barnett	4.0	3.0	1.30
Fayetteville	4.9	2.6	1.84

2.3. Common Methods of Disposal and Discharge

There are three common methods of flowback waste water management. Surface discharge via wastewater treatment plants has historically been a common method in the northeast United State (18, 41, 42). However, these options have been generally phased out due to stricter discharge regulations. Another common technique is where waste water is diluted and disposed of into Publically Owned Treatment Works (POTW). However, the transportation costs are extremely high, and POTWs are limited in how much water they can accept and treat. Fall 2008, the Pennsylvania Department of Environmental Protection ordered a restriction on the amount of produced water disposal to POTWs (18).

The most common method of flowback water disposal is injected into Class II deep wells. Class II wells are built to inject various substances including brine, water, stream, polymers, and carbon dioxide. The technique is favorable due to tis cheap disposal cost of $2 per barrel of water, excluding the offsite transportation cost of $3 per barrel (Flexible Water Solution). Class II wells are regulated under the Underground Injection Control Program. One disadvantage of these wells is that they could result in a leakage of fluids that can reach an Underground Source of Drinking Water (USDW). If an injection well is not constructed and cased properly, it might allow contaminated water to compromise the drinking water sources. Currently, only four injection wells operate for this purpose in Pennsylvania. More than 60 permit applications for injection wells are pending in New York, according to the Congressional Research Service (19).

One important note is that the service companies adjust the proportion of fracturing fluid additives to the unique conditions of each well. Although Occupational Safety and Hazard Administration (OSHA) requires that material safety data sheets (MSDS) accompany each chemical used on the drill site, the proportion of each chemical additive may be kept proprietary (20).

2.4. Sustainable Treatments of Flowback Water

The application of hydraulic fracturing in shale gas drilling requires an enormous volume of water. The increasing consumption of surface and ground water for hydraulic fracturing is a great concern for the public. Stricter regulations and higher costs of transporting water offsite have forced the industry to find suitable solutions. Two classifications of treatment technologies are available for sustaining and recycling flowback water. The classification is divided into convention treatment and advanced treatment technologies. Both classes have energy, environmental, and economic impacts that are directly affected by the quality of flowback water (40).

2.4.1. Conventional Treatments

Conventional treatments include flocculation, coagulation, sedimentation, filtration, and multiple distillation processes. These treatment processes are generally effective in removing water quality contaminants such as solids, oil and grease, as well as hardness compounds. These conventional water treatment processes can be energy intensive and utilize large amounts of chemicals. Often, they are used in conjunction with each other to reach desired specifications. For conventional filtration treatment, sand and activated carbon filtration is the most common method used in the waste water industry. Flowback water runs through a well packed bed and as the water moves through pathways in the porous bed, the hydrocarbons and particles in flowback water are captured by different mechanisms such as diffusion, direct collision, and Van der Waals attraction (21). The depth of the packed bed is designed at a given feed flow rate and the desired final contaminant concentration. To take full advantage of the different adsorption ability between breakthrough and saturation, the filtration is built in a series. However, this method requires a massive amount of sand or activated carbon, and frequent amount of cleaning (21).

This simple filtration treatment is only sufficient for large particles. If particles are smaller or less dense, additional methods must be used. This filtration treatment is often made more effective by adding flocculent and coagulant chemicals to the feed. Flocculants such as lime (calcium hydroxide) and biodegradable polymers can enhance the formation of insoluble precipitates. Dissolved solids will be converted to insoluble forms and can be removed as suspended solids through coagulation, settling, and filtration systems.

Centrifugation and cyclones can also be used to segregate materials by density. Light oils and organic compounds will separate from heavier water and suspended solids. Surfactant can be added to flowback water to create foam, which causes hydrophobic compounds to preferentially attach to foam bubbles. These separated foam bubbles will rise and overflow the vessel and then are allowed to disassociate. However, it requires a large volume of foam, which causes water loss, and large vessel volume to break the foam (34).

Multiple distillation involves a network of horizontal heating coils, which are arranged in the chambers that each have successively lower pressure. Waste water is fed vertically through chambers and a portion of that water is vaporized. This process continues until there is no water left to vaporize (23, 36, 38).

2.4.2. Advantage Treatments

Advantage treatment technologies include evaporation, electrocoagulation, thermal distillation, and membrane separation. These technologies are used to treat dissolved solids, primarily consisting of multivalent ion salts. They also remove dissolved barium, strontium, and some dissolved radionuclides. Dissolved solids are much more difficult and energy intensive to treat and can only be separated with advanced membrane and thermal technologies. However, the fouling and the efficiency still remain concerns. These technologies are sensitive and costly to maintain; hence, pretreating the feed is necessary. Previously listed conventional treatments are initially needed to ensure that most of the suspend solids and organic compounds are removed. Multiple evaporation and thermal distillation processes demand heat to evaporate water. For effective evaporation treatment, water is evaporated in a series of stages. Each downstream stage is held at a lower pressure than the previous one. Because the boiling point of water decreases as the pressure decreases, the vapor from preceding high pressure stages can be used to provide the heat required for the next low pressure stage. These heat-demanded processes are expensive due to high energy and capital costs.

Electrocoagulation is an electrical process that has the capacity to destabilize and coagulate suspended colloidal matter in water. When contaminated water passes through the electrocoagulation cell, the anodic process releases positively charged ions, which bind onto negatively charged colloidal particles in water resulting in coagulation. At the same time, gas bubbles, produced at the cathode, attach to the coagulated matter causing it to float to the surface where it is removed by a surface skimmer. This method is not feasible due to its sizable energy requirements and design of the electrocoagulation reactors (24, 30, 37).

In recent years, membrane filtration technologies have shown an increasing effectiveness in surface water treatment when compared to conventional treatment technologies. In membrane separation technology, small porous and dense membranes are used to treat flowback water. However, these membranes do not perform well alone when the feed water has a high level of turbidity or high fouling tendencies. For example, microfiltration and ultrafiltration membranes should be used to diminish TSS in flowback water before directing it to nanofiltration or reverse osmosis membranes. This will significantly reduce fouling due to large particles.

2.5. Research Emphases Methods

2.5.1. Coagulation

This experiment is conducted to evaluate the effectiveness of the polymer (provided by Flexible Water Solution) and optimum dosage for destabilization, optimum pH, and the most effective mixing time. The polymers (polyamphotype) are long-chained carbon compounds of high molecular weight that have many active sites. The active sites adhere to floc, joining them together and producing a larger, tougher floc that settles better (25). This process is called bridging. The dose and point of addition must be determined for each water sample.

At the point of polymer addition, intense mixing will ensure uniform dispersion of the polymer throughout the raw wastewater. The mixing intensity of agitation required for optimum rapid mixing and flocculation is measured by the G value. The G value concept is defined by this equation (26):

$$G = \sqrt{\frac{P}{\mu * V}} \qquad (2.1)$$

Where G: velocity gradient (sec^{-1})
P: power input (W)
μ: dynamic viscosity (Pa*s)
V: volume of water (m^3)

The intensity and duration of mixing must be controlled to avoid overmixing or undermixing. Overmixing will shear the floc particle so that the floc is small and finely dispersed. Undermixing disperses the polymer, increases chemical use, and reduces the removal efficiency. Adequate mixing must be provided to bring the floc into contact and keep the floc from settling in the flocculation basin.

Also, some unit-less geometric ratios for intensive mixing are shown in Table 3. These values can be used to select the proper basin depth, surface area, and the propeller diameter. The objective of flocculation is to bring the particles into contact so that they will collide, stick together, and grow to a size that will readily settle.

Table 3: Tank and Impeller Geometries for Mixing (26)

Geometric Ratio	Allowed Range
D/T (radial)	0.14-0.5
D/T (axial)	0.17-0.4
H/D (either)	2-4
H/T (axial)	0.34-1.6
H/T (radial)	0.28-2
B/D (either)	0.7-1.6

Where D: propeller diameter

T: equivalent tank diameter

H: water depth

B: water depth below impeller

2.5.2. Water Softening

Hardness in water is caused by the ions of calcium and magnesium. In this research, lime $Ca(OH)_2$ and soda ash Na_2CO_3 are used. However, this precipitation softening process cannot produce water completely free of hardness because of solubility of calcium carbonate and magnesium hydroxide. Furthermore, the completion of chemical reactions is limited by physical considerations, such as adequate mixing and limited detention time in settling basins. All the chemical reactions are explained below:

Removing carbonate hardness from lime

$Ca(HCO_3)_2 + Ca(OH)_2 = 2\ CaCO_3 + 2\ H_2O$ (2.2)

$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3 + Mg(CO_3) + 2\ H_2O$ (2.3)

$MgCO_3 + Ca(OH)_2 = CaCO_3 + Mg(OH)_2$ (2.4)

Removing non-carbonate hardness from lime

$MgSO_4 + Ca(OH)_2 = CaSO_4 + Mg(OH)_2$ (2.5)

$MgCl_2 + Ca(OH)_2 = CaCl_2 + Mg(OH)_2$ (2.6)

Removing non-carbonate hardness from soda ash

$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ (2.7)

2.5.3. Activated Carbon Filtering

Activated carbon is available in two different forms: powdered (PAC) and granular (GAC). In this research, the PAC is used. Cabot Norit Activated Carbon provides three PAC types: Hydrodarco B (iodine 500, molasses 75), Hydrodarco C (iodine 500, molasses 90), and Norit 200 (iodine 900, molasses 230). The apparent density of PAC ranges from 23-46 lb/ft^3 depending on the type of material and the manufacturing process (27, 30, 35). Iodine and molasses numbers are often used to characterize PAC. In general, higher iodine and molasses numbers indicate greater absorbency.

2.5.4. Membrane Separation

Membrane separation treatments use less energy than conventional thermal separation. They are cost efficient, easy to operate, and environment friendly. Membranes come with a wide array of porous sizes and make-up materials to accommodate various contaminants. It is important to select the right membrane to prevent the occurrence of fouling.

Membrane filtration processes are categorized by the size of the molecules they retain. There are Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO) processes.

Selection of the appropriate membrane suitable to address the desired separation is determined by the feed composition of the treated water and the final objective of purification. Besides the shape, size, and charge of particles in flowback water, compatibility of contaminants and materials of membranes must also be considered. Most membranes are made up of synthetic organic polymers. Typical UF polymers include poly vinylidene fluoride, polyether-sulfone, and poly acrylonitrile (28, 32, 33). NF membranes are from cellulose acetate blends or polyamide composites. Membranes can be constructed from inorganic materials such as ceramics or metals. Ceramic membranes are micro-porous, thermally stable, and chemical resistant.

Membranes have several modules. Four main types of modules are plate and frame, tubular, spiral wound, and hollow fiber. The most popular module in the industry for NF and RO membranes is the spiral wound. This module has a flat sheet membrane wrapped around a perforated permeate collection tube. The feed flows on one side of the membrane, and permeate is collected on the other side in towards the center collection tube.

- **Ultrafiltration (UF)**

UF membranes have the membrane pore radius size ranging from 2 to 100 nm and lower permeability than microfiltration membranes. The UF process requires operating pressures from 0.5 to 5 bar. Hollow fibers are a very common module for MF and UF. The hollow fibers resemble a thin straw with holes in the side and at both ends. The open section in the center of the straw is called the lumen. The holes along the side are the pores through which the water passes during filtration, the hole at the end is used to distribute the influent or collect the effluent, depending upon the flow path used. The advantage of hollow fiber membranes is that they have more surface area per unit volume than flat sheet membrane (28, 31, 32). Also, they are easy to backwash due to theirs self-supporting nature.

- **Nanofiltration (NF)**

NF, which has recently been developed, presents significant advantages when compared with other membrane processes. NF process is an intermediate technique between UF and RO. NF membranes have the membrane pore radius size smaller than 2 nm. Most NF membranes are negatively charged and capable of removing divalent ad multivalent ions. It is difficult for divalent metal ions such as calcium, barium, strontium, magnesium, copper, zinc, and iron multivalent anions to diffuse their way through the negative charge membrane matrix structure. NF membranes have a specific size rejection capability known as molecular weight cut off.

The spiral wound module is common design for NF. This module consists of flat sheets that are placed together with their active side facing away from each other. It is one of the most compact and inexpensive configurations available. Each pair of sheets is separated by a mesh-like material and then glued together on three sides. The remaining side is then fixed in place around a perforated center tube. The feed is pumped lengthwise along the unit. The treated permeate is forced through the membrane sheets into the channel and flows in the direction of the perforated center collection tube.

2.5.5. Fouling and Cleaning

- **Fouling**

Successful utilization of membrane technology has been greatly limited by membrane fouling. In filtration systems, fouling causes a loss in flux over time. Fouling reduces the permeability of the membrane. Consequently, fouling increases operation and maintenance costs by deteriorating membrane performance and ultimately shortening membrane life. Numerous studies in recent years have investigated the causes and control of membrane fouling, and substantial progress has been made.

Fouling can be characterized into three fouling mechanisms: 1) standard blocking, 2) complete blocking, and 3) cake-layer blocking. Standard blocking is due to particles that are smaller than membrane pore size getting into the pores and constricting pore channels. Complete blocking is caused by the particles whose size is similar to the size of membrane pore blocking the entrance to pore channels. Once the membrane pores are blocked, particles will accumulate on the surface and form a cake layer, which further contributes to membrane fouling. The sequence of fouling during the filtration process starts with pore constriction (standard blocking), followed by pore blocking (complete blocking), and then cake-layer blocking.

- **Cleaning**

Cleaning methods include mechanical cleaning, hydraulic cleaning, electric cleaning, and chemical cleaning. The choice of the cleaning method mainly depends on the module configuration, the type of membranes, the chemical resistance of membranes and the type of fouling encountered.

Mechanical cleaning uses oversized sponge balls and can only be applied in tubular systems. The hydraulic cleaning method includes back flushing (only applicable to MF and UF membranes), alternate pressurizing and depressurizing and changing the flow direction at a given frequency. The process includes reversing the direction of water flow through the filter using permeate. The permeate removes the material deposited on the surface of the membrane and the waste stream is collected and removed from the module. Electric cleaning: is a very special method of cleaning. By applying an electric field across a membrane, charged particles or molecules will migrate in the direction of the electric field. This method of removing particles or molecules from interphase can be applied without interrupting the process. The application of an electric cleaning is very effective for the protein removal. All the charge protein molecules can be separated by an electric field.

The most used method for cleaning membranes is chemical cleaning. Different chemicals are used individually or in combination to reduce fouling in membranes. The concentration of the chemical and cleaning time duration are very important depending upon the chemical resistance of the membrane. A number of chemicals can be used for cleaning. They are acids, alkali, detergents, enzymes, complexion agents, disinfectants, etc. Cleaning solutions can be heated to enhance their impact. When cleaning, the chemical solution is allowed to soak through or is circulated through the membrane. It is important to buffer the tolerance of membranes when using strong corrosive chemicals such as chlorine, acid, and basic solutions.

The effectiveness of the cleaning can be quantified by calculating the systems' loss of original specific flux (28)

$$Loss\ of\ specific\ flux\ = 100 * \left(1 - \frac{Jsi}{Jsio}\right) \qquad (2.8)$$

Where Jsi: specific flux when the system restarted after cleaning ($\frac{gfd}{psi}$)

Jsio: specific flux at time zero point of membrane testing ($\frac{gfd}{psi}$)

2.6.Common Membrane Process's Terminologies and Definitions

Flux is the flow rate through an individual membrane filter module expressed in terms of gallons of flow per square foot of membrane filter surface area per time.

Permeate is the filtrate from a membrane filter. It is called permeate due to the way that the feed water permeates through the membrane.

Permeate flux is defined as the volume of permeate obtained per unit time and unit membrane area

$$J\ = \frac{Q}{A} \qquad (2.9)$$

Where J: permeate flux ($\frac{gal}{ft^2 * hr}$)

Q: permeate flow rate ($\frac{gal}{hr}$)

A: membrane surface area (ft^2)

Specific flux is the flux of the membrane divided by the transmembrane pressure of the membrane itself. The lower the specific flux, the more pressure loss through the system and the more expensive it is to operate the system.

Water flux and **salt flux** depend on each other.

$$\frac{C_w}{C_{permeate}} = \frac{N_{Aw}}{N_s} \qquad (2.10)$$

Where C_W: the water concentration in the permeate

$C_{permeate}$: the salt concentration in the permeate

N_{Aw}: the water flux

N_s: the salt flux

Osmosis is a naturally occurring phenomenon that describes the tendency of clean water to dilute dirty water when they are placed across a permeable membrane with each other.

Osmotic pressure of the feed and permeate solutions play a role in the separation. Osmotic pressure is the pressure needed to cause a solvent to leave a solution and permeate through the membrane.

$$\pi \ = i * M * R * T \quad (2.11)$$

Where π is the osmotic pressure

i: the van’t Hoff factor

M: the molarity of the solution

R: the ideal gas constant

T: the solution temperature.

Transmembrane pressure is the change in the pressure of the water as it passes through the membrane. Transmembrane pressure is referred to as TMP by the industry. If the feed has a high salt content, it will require a greater transmembrane pressure. Therefore, the process consumes more energy.

Salt rejection R is the term used to define the salt concentration reduction percentage of permeate water relative to the feed water in the membrane filtration process.

$$R = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) * 100\% \qquad (2.12)$$

Where C_{feed}: the salt concentration in the feed solution

$C_{permeate}$: the salt concentration in the permeate solution

Percent recovery of a membrane system is the percent of feed water that actually passes through the membrane. It is determined by dividing the permeate to the feed, then times 100. It often refers to the efficiency of the treatment process.

COD is Chemical Oxygen Demand test that is commonly used to measure the amount of organic compounds in water. The test procedure requires the addition of potassium dichromate and sulfuric acid reagents. The mixture of chromic and sulfuric acids converts organic matters to CO_2 and water. It is one of the procedures to determine the quality of water.

TSS is total suspended solids. It is a variable in analyzing the quality of water.

TDS is total dissolved solids. It is another variable in analyzing the quality of water.

Turbidity is the cloudiness of water caused by TSS and TDS. It is a key test in determining water quality.

Conductivity measurement is used to detect the concentration of ions in a solution. The amount of ions is measured in micro Siemens unit (µS). The micro Siemens value increases with higher concentrations of dissolved salt ions in flowback water.

Water hardness is a high content of minerals such as calcium and magnesium in water. Although ions of iron, manganese, and strontium also produce hardness, they are not present in significant quantities.

3. Experimental Methods

The objective of this research is to explore the recycling of hydraulic fracturing water through optimal ultrafiltation and nanoflitration systems. Fracturing water from Shale gas production is treated through many membrane filtration processes. The optimal system is then compared with conventional treatment methods to determine its feasibility. The ultimate goal is to design a recycling system that is suitable to treat fracturing water for reuse purposes and obtains at least 75% water recovery.

Flowback water from four shale formations were analyzed and characterized. The quality of the flowback water was examined with TDS, TSS, turbidity, and hardness tests. Flowback waters were then sent through a separation method. Coagulation, water softening, activated carbon filtration, and membrane filtration methods were performed. The quality of produced water is then evaluated.

The result of this research is significant in helping to solve both the water demand and economic problems. It also will help minimize pollution to the environment. The research found that the ultimate goal can be fulfilled by integrating both conventional and advanced treatments. The next step is to optimize the recycling process of hydraulic fracturing water, while making the entire process scalable for onsite treatment.

The research was proceeded with the following expectations:

1) Analyzed and characterized the chemical constituents in flowback water. Water samples were provided by Flexible Water Solution Inc. for one year. Fracturing waters were expected to vary in composition, TSS, TDS, and COD.

2) Evaluated conventional treatment processes for TSS, TDS, and COD removal. Based on the

characteristic of the flowback water, determined the quantity of lime/soda ash and polymer aid. An adequate amount of chemical usage was crucial to optimize the treatment cost. These processes were expected to be ineffective in the removal of contaminants.

3) Developed advance treatment system to recycle flowback water for reuse purposes. System design was to pretreat water with UF and polish with NF to meet reuse specifications. Explored various membrane materials that can accompany different qualities of flowback water. Expected some flowback water will require extra passes through membrane system.

4) Estimated capital cost and operating cost of treatment for the mobile onsite unit, seeking to optimize the cost of recycling treatment system. The designed system was expected to cost less than current practices.

3.1. Characterization of Flowback Water

There was limited information regarding to the constituents of flowback water. Therefore, tests must be performed to analyze the water contaminants. Flowback water from four locations was provided by Flexible Water Solution Inc. The waters were well mixed before collected for testing to ensure generating data accurately. Figure 1 displays water samples from Oklahoma, Texas, North Dakota, and Utah. These flowback waters were tested for COD, TSS, turbidity, pH, conductivity, and hardness levels.

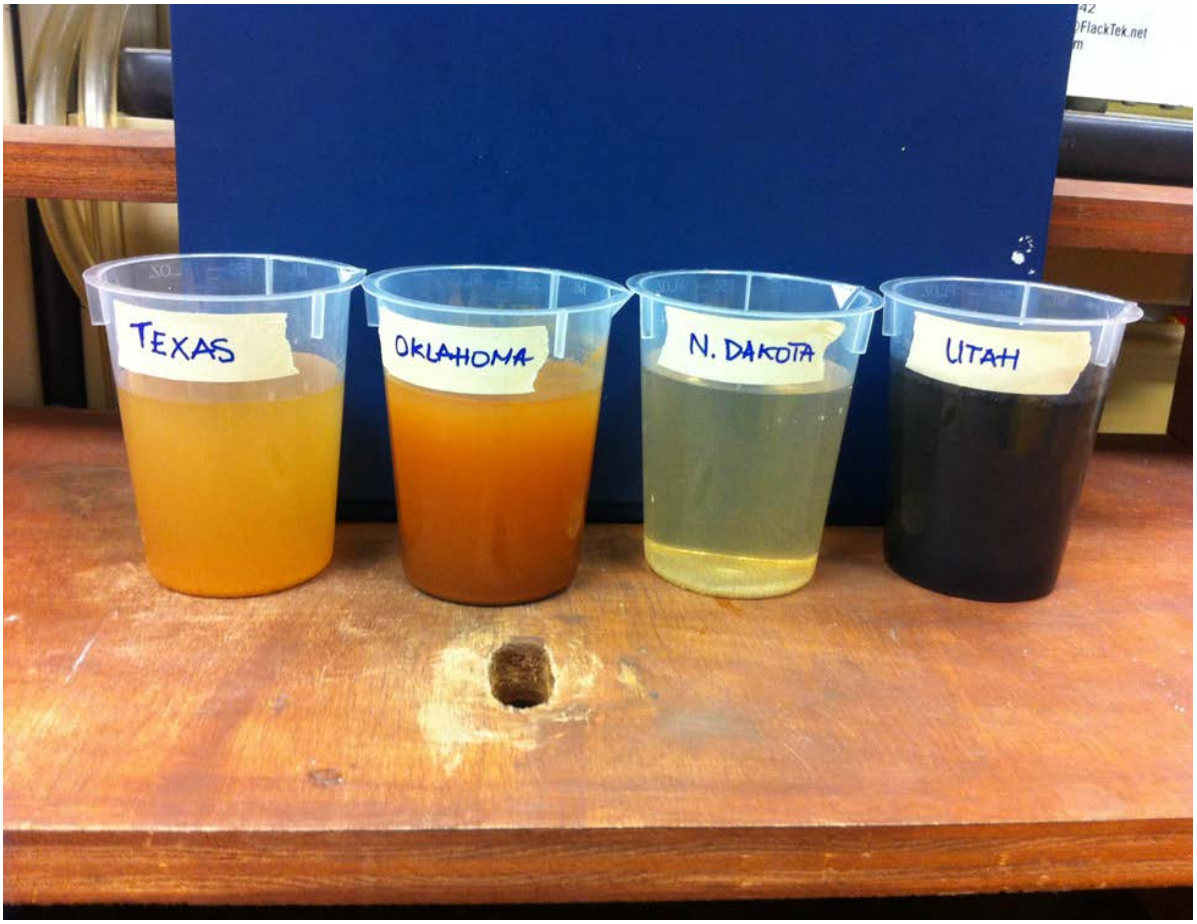

Figure 1: Samples of Flowback from Four Shale Formation Locations (photo by author)

3.1.1. Chemical Oxygen Demand (COD)

COD tests measured the oxygen demand of equivalent organic matter susceptible to oxidation by a strong chemical oxidant. Addition potassium dichromate and sulfuric acid reagents destroyed organic matter and converted them into CO_2 and water. In this experiment, COD was measured using manganese III digestion method without chloride removal. The prepackaged tests were purchased from Hach Company. The trivalent manganese is a strong, non-carcinogenic chemical oxidant that changed quantitatively from purple to colorless when it reacted with organic matter. It typically oxidized about 80% of the organic compounds. A calibration was based on the oxidation of Potassium Acid Phthalate (KHP). The KHP calibration was adequate for this application.

The following procedure was used to determine COD.

- Prepared 800 ppm COD standard, by mixing 0.68g of dried KHP with 1 L of deionized water (DI water). Used 0.5 mL of this solution as the sample volume.
- Pipetted 0.5 mL of standards and flowback water into a Mn III COD vial, include the blank sample. Caped and inverted several times to mix.
- Placed the vials in the DRB 200 reactor (Figure 4) that is preheated to 150^0C. Digested for 1 hour.
- Removed the vials and placed them in cooling rack for 10 minutes. Allowed the vials to cool down to room temperature.
- Used Spectrophotometer Unico 1100 (Figure 5) to observe the absorbance values.
- Calculated COD concentration (ppm) based on the calibration curve.

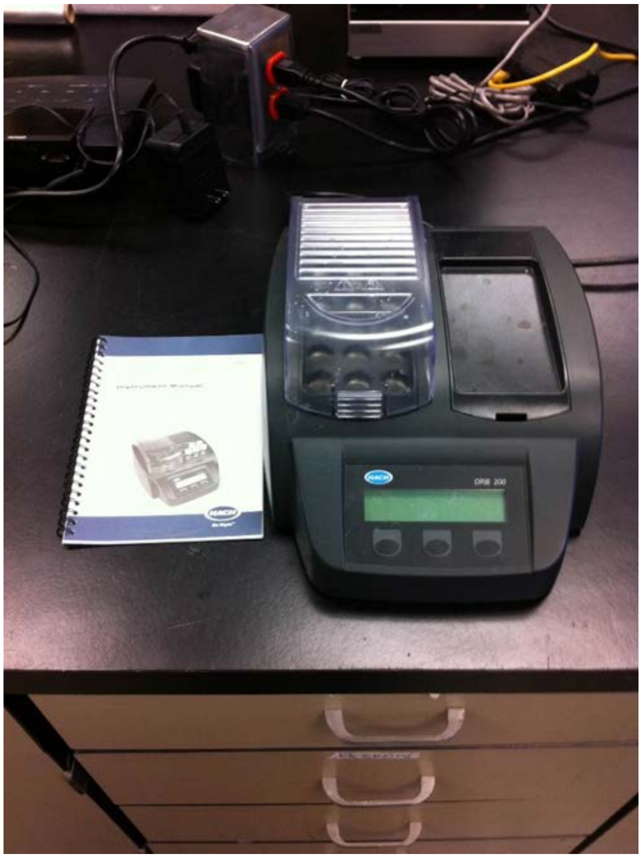

Figure 2: Digital Reactor Block 200 Hach (DRB) (photo by author)

Figure 3: Spectrophotometer Unico 1100 (photo by author)

3.1.2. Total Suspend Solids (TSS)

A measured portion of a sample was draw through a glass fiber filer by applying a vacuum to the suction flask under the filer. The filter was transferred from the filtration apparatus to an aluminum dish as a support. Caution must be taken when increasing the diameter of the filter or decreasing the volume of the sample due to suspended materials clogging the filter and prolonging filtration. After drying at 103^0C in the Thermo Scientific Lindberg Blue M oven for one hour, the filter with the dry suspended solids was weighed. The temperature at which the residue was dried had an important bearing on results. After drying, each sample required close attention to desiccation. Opening the desiccator was minimized to limit moist air exposure.

The weight of suspended solids is equal to the difference between their weight and the original weight of the clean filter (29).

$$mg\ total\ suspended\ solids\ = \frac{(A-B)*1000}{sample\ volume\ (mL)} \qquad (3.1)$$

Where A: weight of filter and dried residue (mg)

B: weight of clean filter (mg)

3.1.3. Turbidity

This turbidity test measured an optical property of the sample with results from scattering and absorption of light by particles in the sample. The amount of turbidity measured depends on variables such as size, shape, color, and refractive properties of the particles. This procedure is calibrated using turbidity standards and the readings are in terms of Nephelometric Turbidity Unit (NTU).

The procedure below was used to calibrate and measure turbidity of samples.

- Prepared four standard solutions using a 4000 NTU standard (purchased from VWR).

- Pipetted 3 mL of standards and flowback water into vials.
- Used the Spectrophotometer Unico 1100 to observe the absorbance values.
- Calculated the turbidity level (NTU) of flowback water based on the calibration curve.

3.1.4. Conductivity

Conductivity is used to describe the amount of ions in a solution. The concentration of ions is presented in micro Siemens unit (μS). The micro Siemens value increases with higher concentrations of dissolved salt ions. The conductivity meter, Traceable VWR (Figure 4), is easy to use. However, it only gives an approximate concentration and is not very accurate.

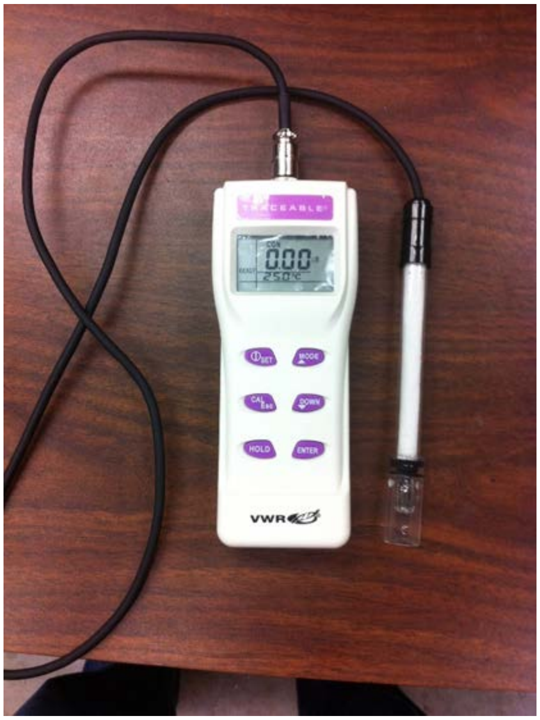

Figure 4: The Conductivity Meter Traceable VWR (photo by author)

3.1.5. Water Hardness

For measuring calcium concentrations, the ISE Electrode and Orion Model 330 are used. Also, Ionic Strength Adjuster (ISA) solution is used to enhance the accuracy of probes. 1mL of ISA solution is added for each 50 mL of water samples. However, the probes have a limitation in their concentration range. Therefore, all flowback waters are diluted by a factor of 100.

For measuring strontium and barium, the Atomic Absorption Spectrometer AA GBC933 is used (Figure 5). This equipment is very accurate for a highly soluble and small quantity of ions such as strontium and barium. Each ion requires a lamp which is made from GBC.

Figure 5: The Atomic Absorption Spectrometers GBC 933 (photo by author)

3.2. Conventional Treatment

3.2.1. Coagulation

This experiment was conducted to evaluate the effectiveness of the polymer (provided by Flexible Water Solution) and optimum dosage for destabilization, optimum pH, and the most effective mixing time. The axial flow was investigated using the jar test technique (Figure 6).

The axial flow was considered because the flow has lower shear stress then the radial flow. The jar test was widely used to simulate a full scale coagulation process to determine optimum chemical dosages. The apparatus consists of 4 agitator propellers to operate at the same rotational speed (rpm). The laboratory containers were 500 mL beakers.

The following steps were taken to analyze the sample.

- Filled 4 beakers with a measured amount of the water to be treated.
- Added the coagulant to each sample.
- Flash mixed the samples by agitating at designed speed for period of time.
- Recorded the time of flocculation and settling characteristics of flocculation.
- Tested the quality of water (include COD, turbidity, and hardness level).

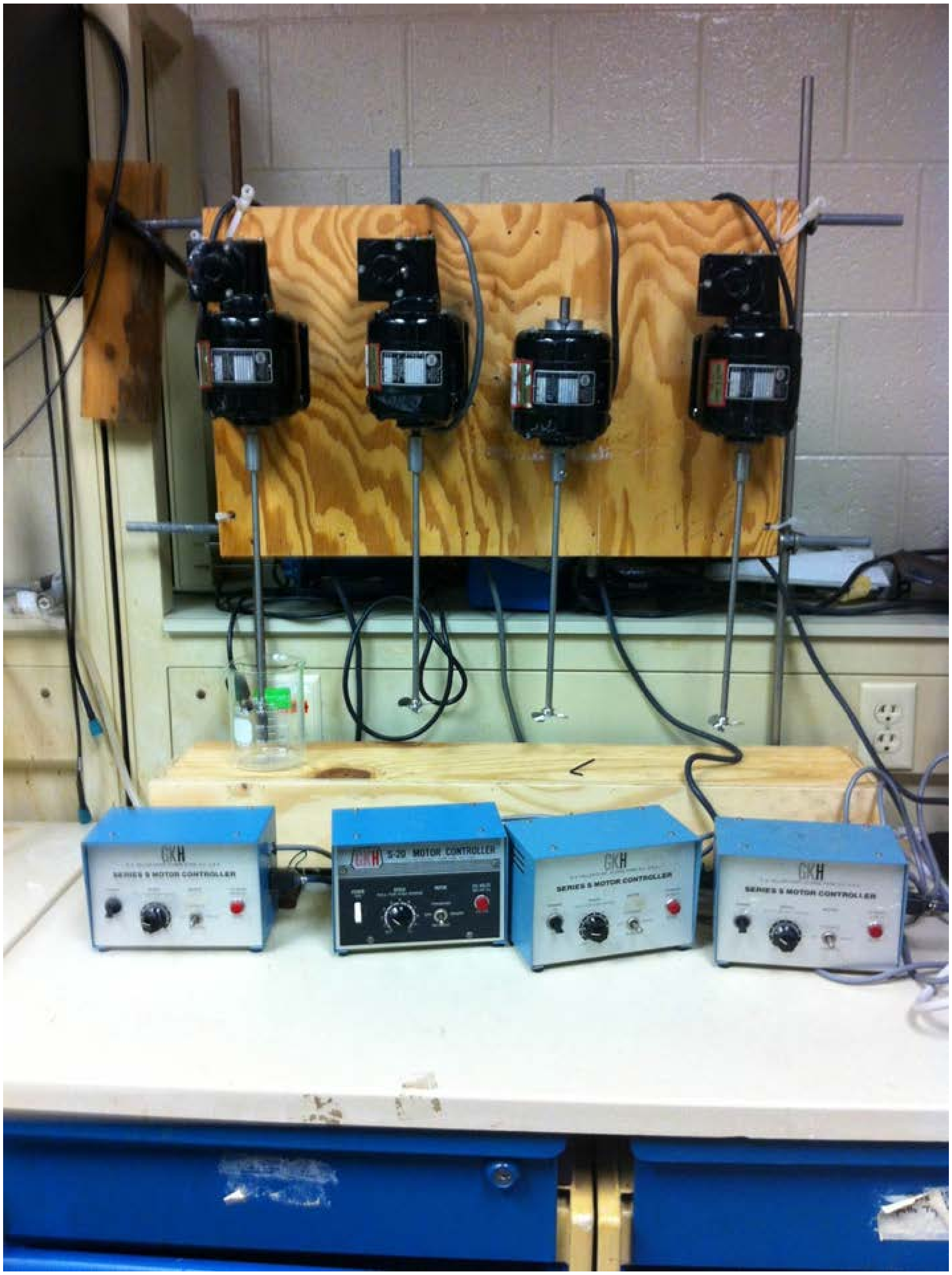

Figure 6: Coagulation Experimental Setup (photo by author)

3.2.2. Water Softening

The experiment was performed following these steps:

- Used 100 mL of three flowback water location
- Added lime slowly into the sample with mixing using the magnitude mixing plate
- Added sodium hydroxide NaOH to bring the pH of solution to 10
- Mixed the solution for 10 minutes
- Removed the solid precipitate at the bottom using vacuum filter
- Measured the filtered water’s calcium and sodium levels. Also, dried the solid in an oven and weighted
- Repeated the experiment with soda ash
- Recorded all the data carefully

3.2.3. Activated Carbon

The experiment was performed using 100 mL of flowback water. 100 mg of powder activated carbon (PAC) was added to the sample and allowed to mix for 20 minutes. Then, the solution was vacuum filtered. COD concentration was tested and recorded.

According to Cabot Norit, the best location for PAC addition is usually at the beginning of the water treatment process. Applying PAC at the earliest point in the treatment process allows the longest contact time possible before the application of other chemicals, which prevents interference from other chemicals, such as coagulants and chlorine.

3.3. Advanced Treatments

3.3.1. UF

In this research, the UF membrane was used as the pretreatment step before NF membrane. The setup is shown in Figure 7 below. First, the 6 L of flowback water were pumped through a standard filter Whirlpool (from Home Depot) dimension 10”- 5”. This 5 micron sediment cartridge is made from pure polypropylene microfiber. It is a grooved series extended surface area module. This step protects the UF hollow fiber. Then, the water was followed through a UF, which is a hollow fiber cartridge unit from KOCH PM 50. The rejected is allowed to recycled back in the feed tank. The permeate was collected separately for further NF treatment. The permeate flow rate was monitored and timed every 10 minutes. Finally, the amount of remaining water in the feed tank was measured for water recovery calculation.

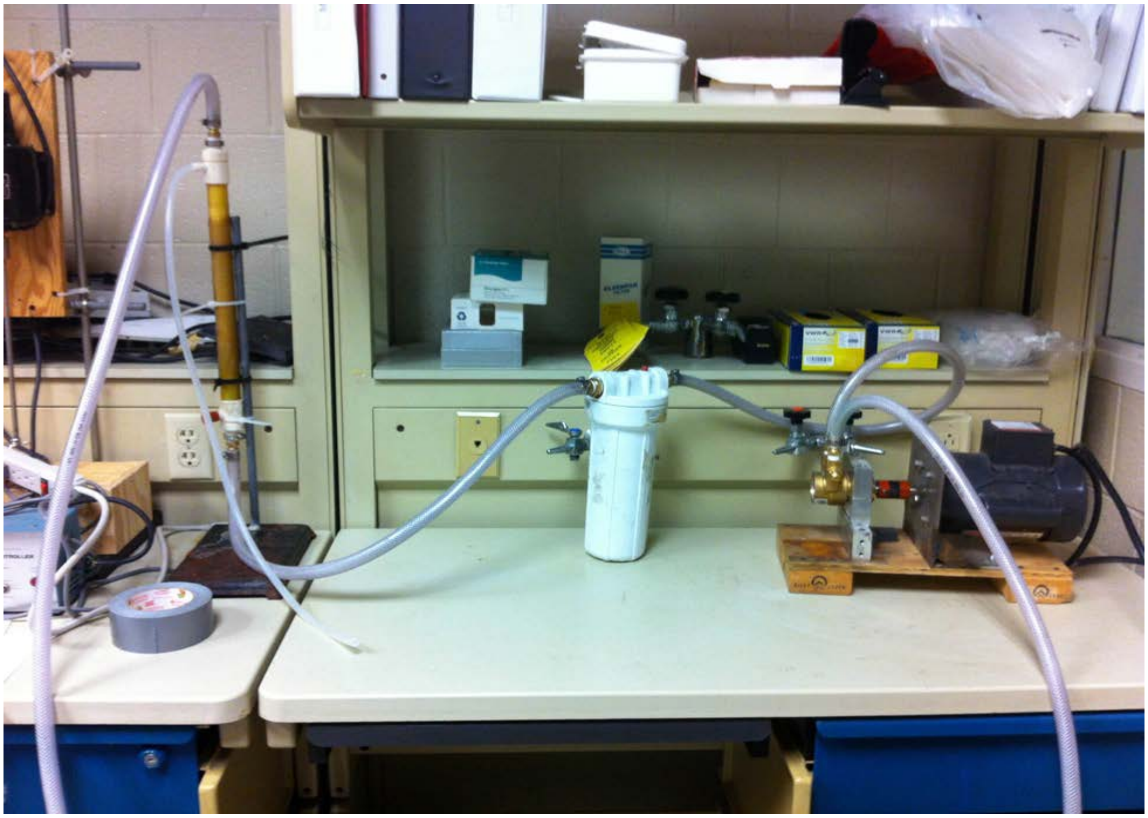

Figure 7: The UF Experimental Setup (photo by author)

3.3.2. NF

In this experiment, five membranes from Ultura (NF 2A, NF 3A, NF3.1A, NF 6, and XN 45) were investigated. The membranes were exposed to flowback water in a SEPA CF II cell manufactured by GE Osmonics. The cell had an effective membrane area of 140 cm^2 with a hold up volume 70 mL. The cell can withstand a pressure of 1000 psig, and therefore is suitable for NF filtration applications. The unit design simulates the cross flow dynamics of full scale operation. It is the most suitable technology for flat sheet membranes. The structure including SEPA CF II cell by GE Osmonics is shown below.

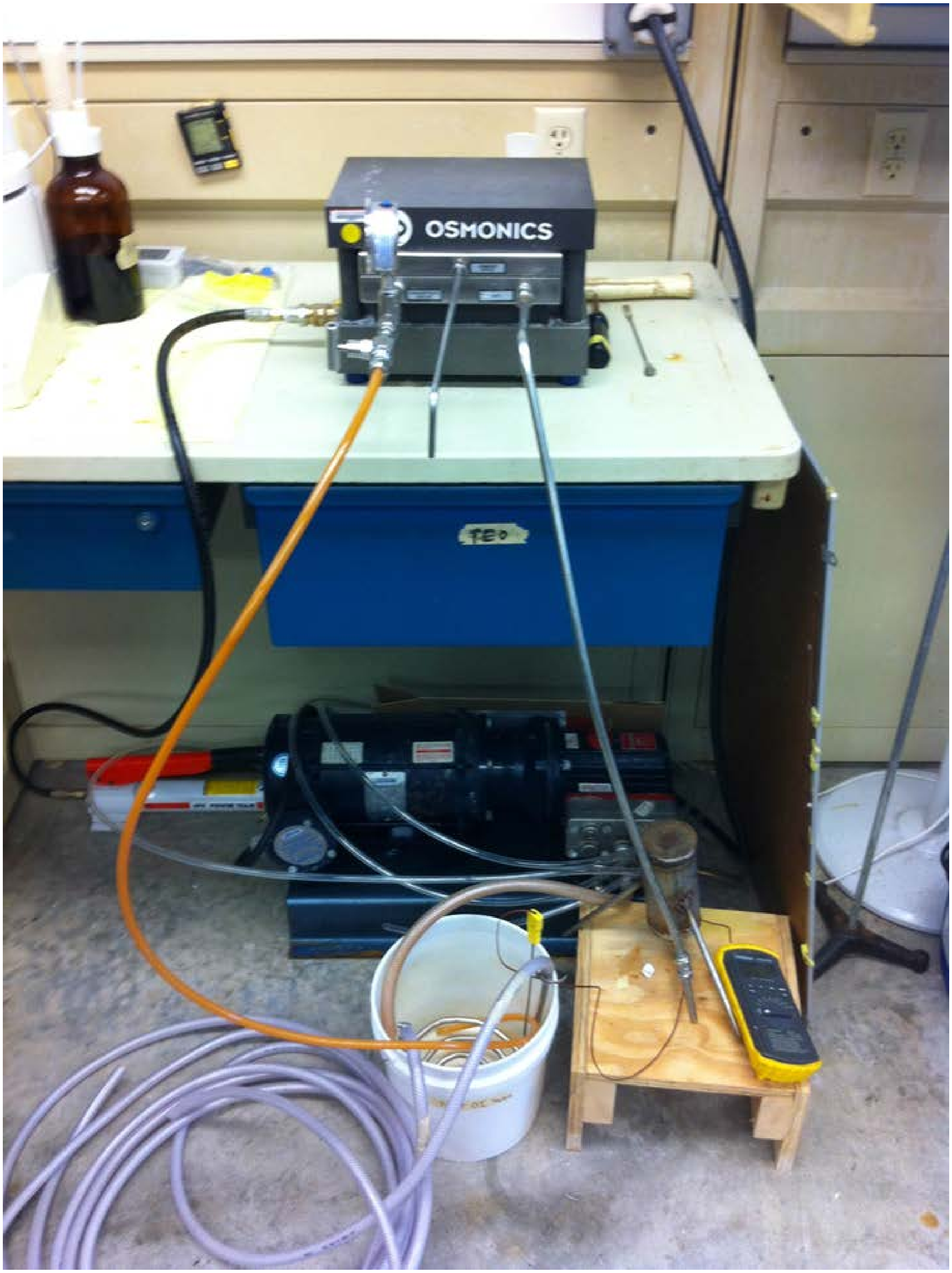

Figure 8: The NF Experimental Setup (photo by author)

The reject water was recycled back into the feed tank to ensure that the membranes are exposed to the same concentration of dissolved solids. The constant pressure was maintained by adjusting a pressure relief valve located at the feed inlet. The feed was pumped through the system using a pressure pump. In order to prevent pulsation, the pressure hole up was designed to ensure that the system pressure is more stable. Also, the cooling coil was immerged in the feed tank to keep the water at room temperature. In the first part of the experiment, each membrane was tested at 5 different pressures. The permeates were collected to measure the calcium and sodium levels. The purpose of this step was to determine the suitable membrane for the specific flowback water based on the rejection and water recovery.

After the right membrane is selected, the chosen membrane was tested again with 3 prepared draw solutions: $CaCl_2$, NaCl, mixed of $CaCl_2$ and NaCl, and flowback water. The system was operated at 700 psig. The permeate flow rate and concentration were monitored every 10 minutes. The remaining water in the feed tank was measured.

The final part of the experiment was testing the membrane durable. The permeate was allowed to recycle back in the feed tank. Therefore, the salt concentrations of the feed remain constant, hence, the osmosis pressure will not change. The test was run for 6 hours and the permeate flux was monitored. All the filtered water was stored for later reference.

3.4. Ethics and Limitations

The biggest challenge in this research is flowback water information. Also, there is a limited amount of water that can be accessed. Moreover, since these membranes are still ongoing research and development, there is limited information. Last, due to restrictions in time and budget, only a few ion in the flowback water were measured.

4. Results and Analysis

4.1. Characterization

The quality of flowback water was evaluated by multiple tests. These tests included pH, TSS, turbidity, COD, and conductivity. Levels of calcium and sodium were also quantified. Table 4 revealed the qualities of flowback water from four locations. Table 4 showed that Oklahoma and Utah water contained higher contents of contaminant than North Dakota and Texas water. This data confirmed the cloudiness visual and strong odors that Oklahoma and Utah water were giving off. Texas water had the highest hardness level based on its conductivity, calcium, and sodium values. All water had close to neutral pH, which is ideal for membrane treatment.

Table 4: The Quality of Flowback Water from Four Locations

	N. Dakota	Oklahoma	Texas	Utah
pH	6.8	6.15	7	7.2
TSS (ppm)	12,400	21,300	9,900	19,500
Turbidity (NTU)	321	2,200	75	2,900
COD (ppm)	28,000	54,100	21,000	75,600
Conductivity (mS)	130	162	215	59.5
Calcium (ppm)	8,700	8,100	16,000	113
Sodium (ppm)	18,200	43,000	50,000	17,200

4.2. Treatments

4.2.1. Water Softening

As mentioned early in the literature chapter, precipitation of calcium carbonate must be at pH 10. In this experiment, lime or soda ash were added until the water samples reached pH 10. Since the calcium level of Utah water was 113 ppm, which was less than the specification for reuse water, flowback water of the other three locations was tested. Figure 9 compared the removal of calcium by using lime and soda ash for North Dakota, Oklahoma, and Texas flowback water. Lime had proven to perform slightly better than soda ash. This experiment concluded that lime removed calcium more effectively than soda ash in hydraulic fracturing water.

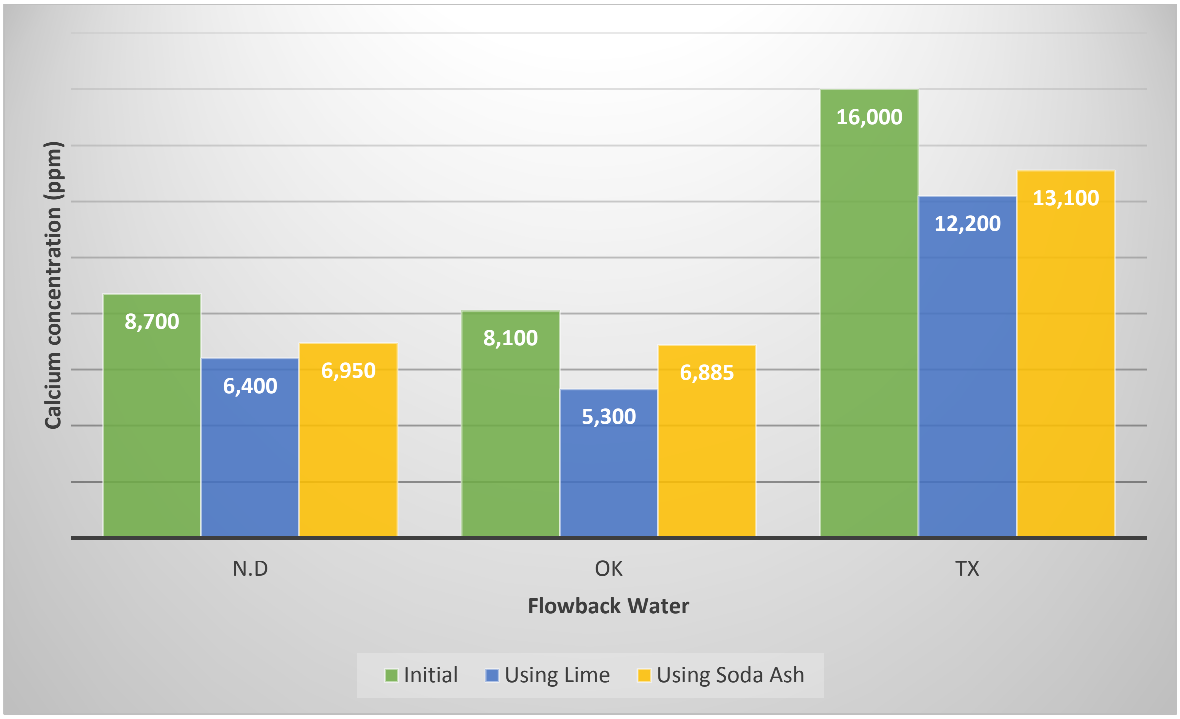

Figure 9: Calcium Concentration Removal using Lime / Soda Ash

For North Dakota and Oklahoma flowback water, 300 mg of lime were needed per 100 mL to reach pH 10. Texas water needed 170 mg per 100 mL of sample. Therefore, North Dakota and Oklahoma have higher carbonate hardness in their flowback water than Texas.

4.2.2. Coagulation

Only Oklahoma flowback water was available at the time of the coagulation experiment. Coagulants were provided by Flexible Water Solution. Two dosages of polymers were tested with water samples agitated at 180 rpm and mixed for 20 minutes. The addition of first dosage was equivalent to 3.7 mL of polymer per gallon of water, according to the manufacture suggestion. Samples were collected to analyze for hardness level. The second dosage was 7.0 mL of polymer per gallon of water, which almost doubled the first dosage amount. Samples were again collected and analyzed. The experiment was performed three times.

The results of this experiment are shown in Table 5. For both dosages of polymer, they could remove 82% of TSS (from 21,300 to 3,850 ppm). Also, the turbidity level was significantly reduced from 2,200 to 350 NTU. However, in Figure 10, the conductivity level only reduced from 162 mS to 135 mS for the first dosage and to 133 mS for the second dosage of polymer. Calcium and sodium removal quantities are shown in Figure 11 and Figure 12.

The addition of polymer raised pH level from 6.15 to 8.5. It also increased the sodium concentration in tested water. Figure 12 showed the sodium concentration results of samples. These results were speculated to be faulty readings. Polymers might have interfered with sodium probe. Further information about the polymer must be explored for explanation. Nevertheless, this experiment proved that purpose of the coagulation is to reduce the overall suspended solid and turbidity levels in hydraulic fracturing water.

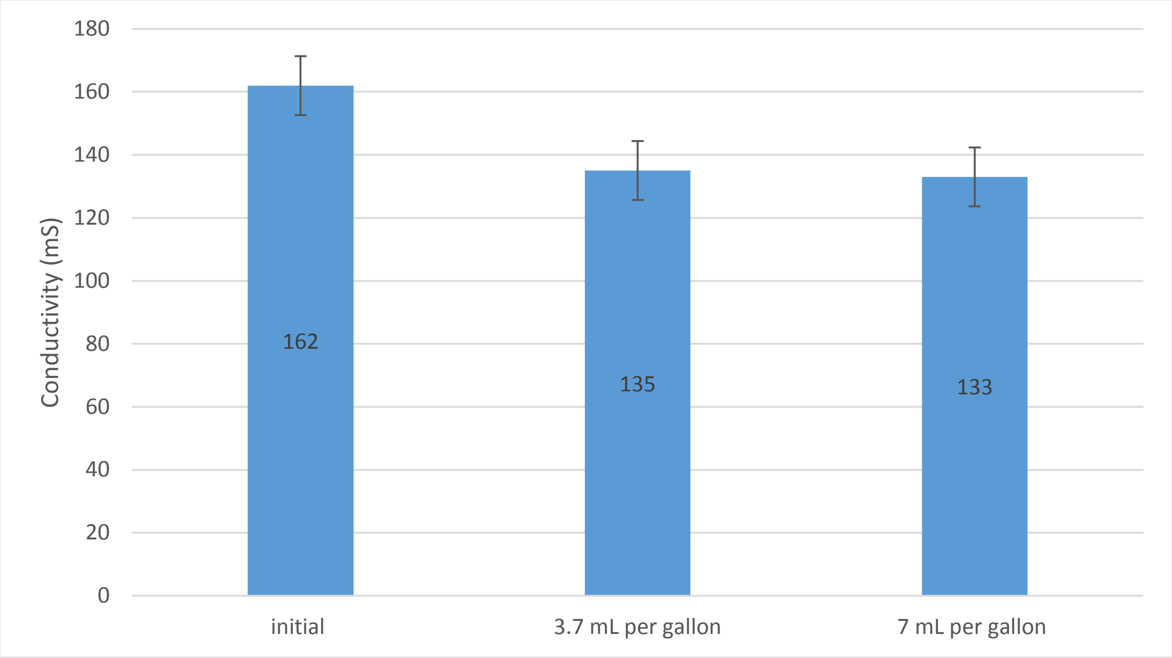

Figure 10: The Conductivity of Coagulation Test

Table 5: Comparing the Quality of Oklahoma Flowback Water between Two Treatments

	Initial Feed	Lime	Polymer aid
TSS (ppm)	21,300	20,600	3,850
Turbidity (NTU)	2,200	2,000	350
COD (ppm)	54,100	46,000	41,200
Conductivity (mS)	162	159	135

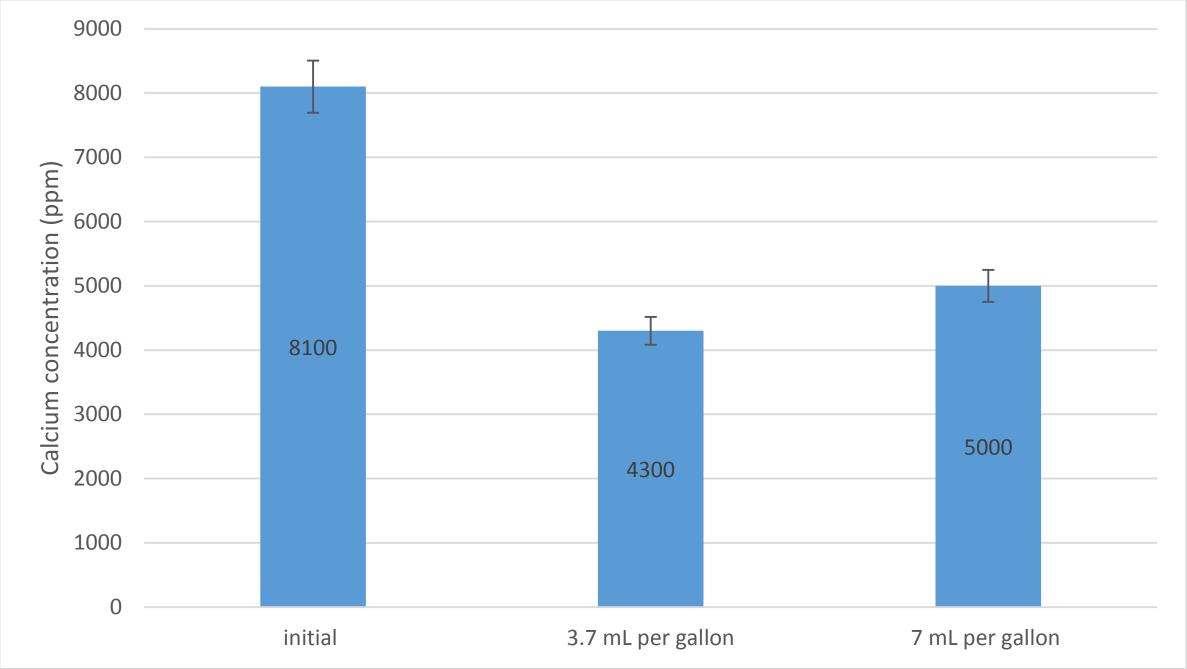

Figure 11: The Calcium Removal using Polymer

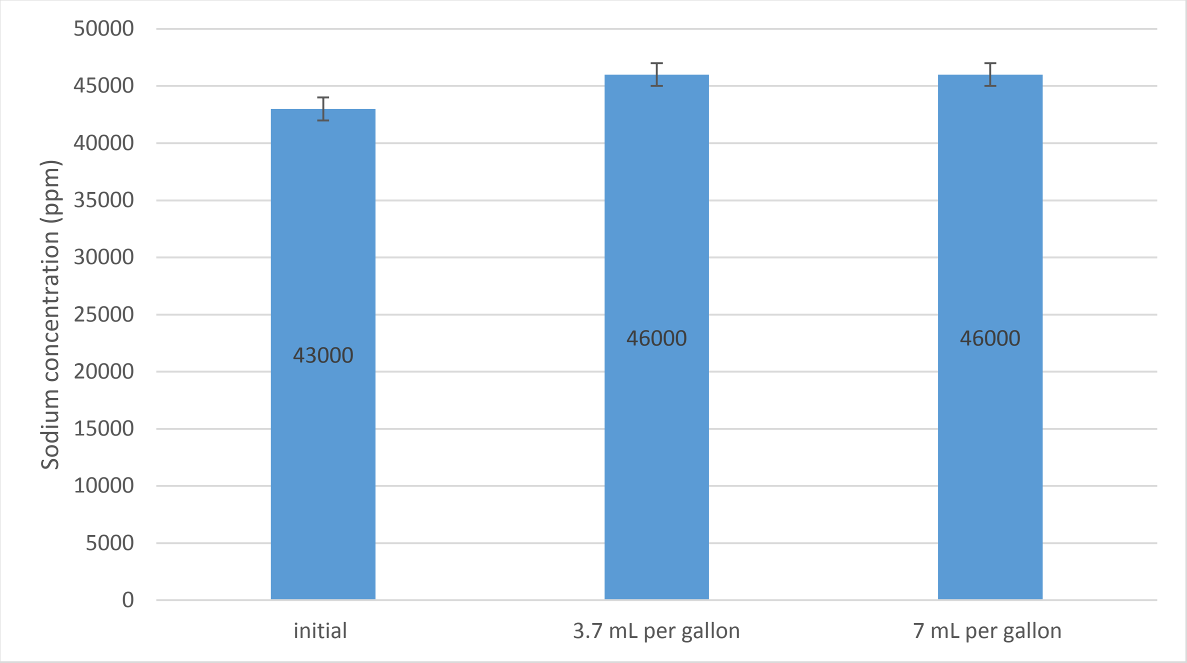

Figure 12: The Sodium Removal using Polymer

Lime, soda ash, and coagulated polymer were added to remove calcium from Oklahoma flowback water. Their effectiveness in calcium removal were graphed on Figure 2 (appendix). It revealed lime had 35% of calcium removal, soda ash had 15%, and the polymer had 47%. The figure proved that polymer gave the highest percent removal. In addition, the polymer created a small amount of sludge than lime and soda ash. Thus, coagulation polymer was the most suitable process out of three options to treat the flowback water.

4.2.3. Activated Carbon

This research investigated the effectiveness of activated carbon by using excess amount of PAC. Three PAC were provided by Norit and had the ability to remove organic components in flowback water. Treatment from PAC resulted in the average COD concentration of 25,000 ppm. The PAC had reduced over 50% of the COD level in Oklahoma water. Unfortunately, it was still higher than the limit for reuse water. The treatment can be used as pretreatment of flowback water for other methods. Also, the ratio of PAC versus flowback water is very important. Depend on the quality of water, the amount of PAC and mixing time are determined. Figure 13 displayed the COD concentration after each treatment process. Water samples treated with lime had 46,000 ppm COD, while samples treated with coagulant had 41,000 ppm. Figure 13 emphasized that activated carbon filtering was best in removing organic compounds in hydraulic fracturing water.

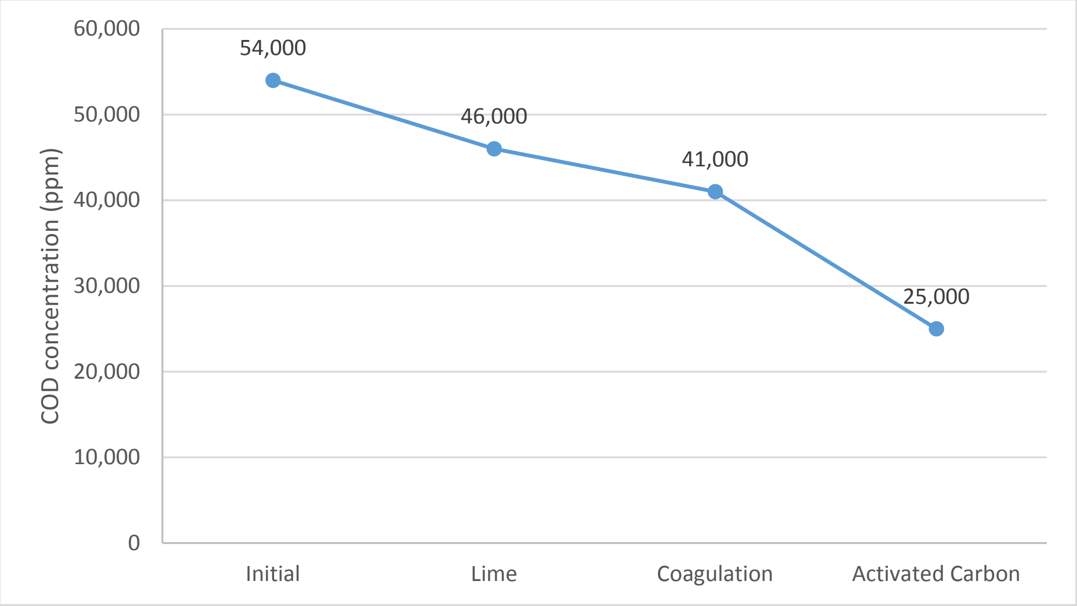

Figure 13: COD Concentration of Three Process Treatments

4.2.4. UF

The UF was supplied by KOCH and was a one square foot hollow fiber membrane. Texas flowback water was chosen for this experiment because of availability and its high contents of contaminant (Table 1 listed the Quality of Flowback Water from Four Locations). Water was pumped through UF for 30 minutes. Samples of permeate were collected for analysis at 10, 15, and 30 minutes.

As shown in Figure 14, the flux stayed steady around 1.3 gal/ hr*ft^2. Conductivity, turbidity, and COD levels were recorded on Table 6. Values on Table 6 revealed that UF was very effective in the removal of turbidity and COD, while it was not as effective when removing hardness. The majority of calcium and sodium was able to pass through the UF membrane because of its large porous size. Table 7 kept record of calcium and sodium concentrations of UF permeate throughout the 30 minutes run. From Table 7, on average only 30% calcium and 28% sodium were removed. The end concentrations of calcium and sodium were higher than specifications for reuse water. This experiment confirmed that UF was only capable of pretreating Texas hydraulic fracturing water.

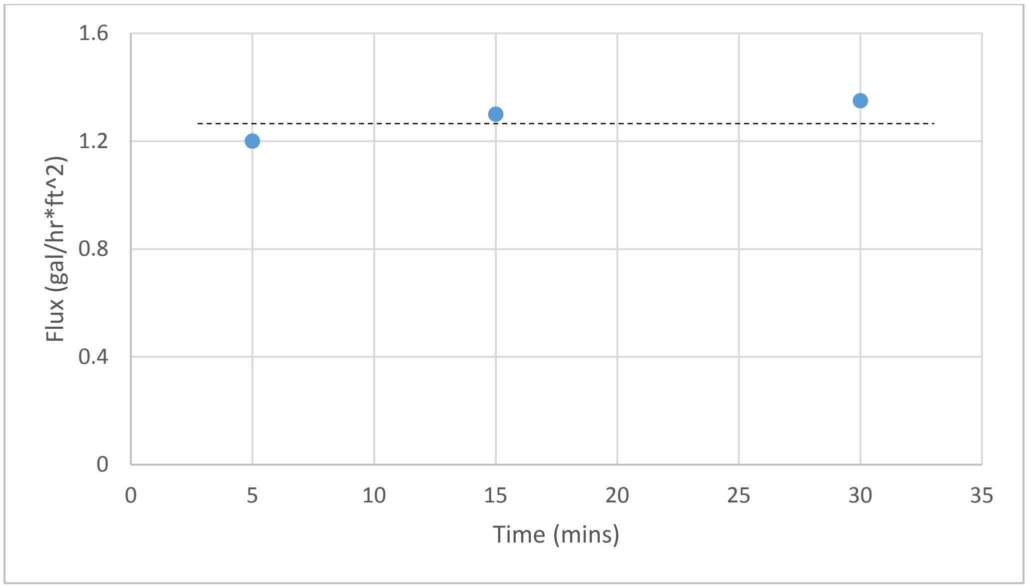

Figure 14: The UF Flux for Texas Flowback Water Pretreatment

Table 6: The Quality of Texas Flowback Water after UF Treatment

Time (minute)	Conductivity (mS)	Turbidity (NTU)	COD (ppm)
Feed	85	75	21,000
10	75	0.04	2,600
15	80	0.04	2,460
30	79	0.04	2,750

Table 7: The Calcium and Sodium Concentration in the UF Permeate

Time	Calcium		Sodium	
	Concentration (ppm)	Rejection (%)	Concentration (ppm)	Rejection (%)
Feed	16,000		50,000	
10	10,400	35	35,000	31.1
15	10,400	35	36,000	28.2
30	12,800	29	36,000	28.2

4.2.5. NF

Multiple types of NF were provided by Ultura to test in this experiment. They were NF3A, NF3.1A, NF2A, NF6, and XN45. The experiment started with two premade standards of calcium and sodium solutions. Their concentrations were 16,000 ppm calcium chloride and 50,000 ppm sodium chloride. Standard solutions were pumped at various pressures through individual NF membranes. Permeate samples were collected and analyzed for all membranes at 250, 400, 600, 700, and 800 psi.

Experiment data was used to calculate the sodium and calcium rejection percent of all NF membranes. Figure 15 and Figure 16 compared the calcium rejection percent for all NF membranes at different pressures. As shown in Figure 15, NF3A and NF3.1A membranes had high removal rate for 16,000 ppm calcium chloride standard. Both NF3A and NF3.1A had greater than 80% rejection of calcium chloride. Both membranes performed most efficiently at 700 psi. Figure 17 revealed that NF3.1A and NF6 had over 20% sodium rejection rates for 50,000 ppm sodium chloride solution.

NF3A displayed most efficient overall in removal of salt ions in water even though it did not have the highest sodium chloride rejection compared to the other four membranes. NF3A was believed to be the best candidate in treating hydraulic fracturing water.

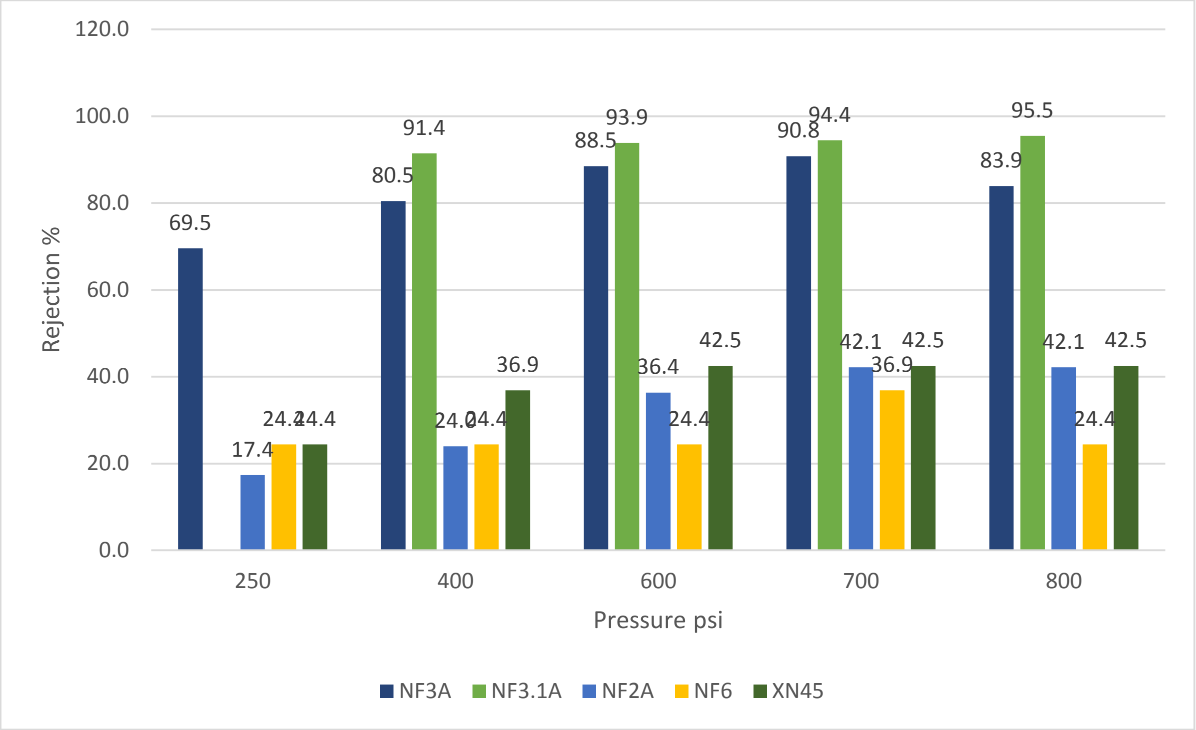

Figure 15: Rejection of Calcium Ion (Ideal Solution 16,000 ppm)

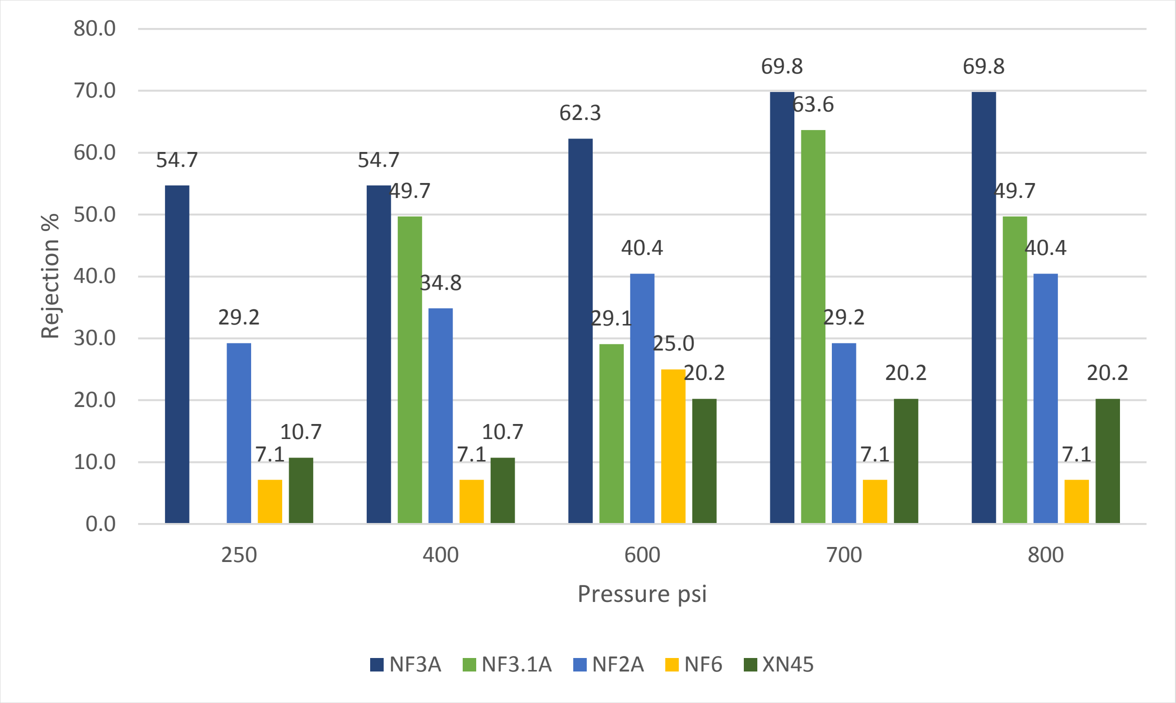

Figure 16: Rejection of Calcium Ion (Real Texas Flowback Water)

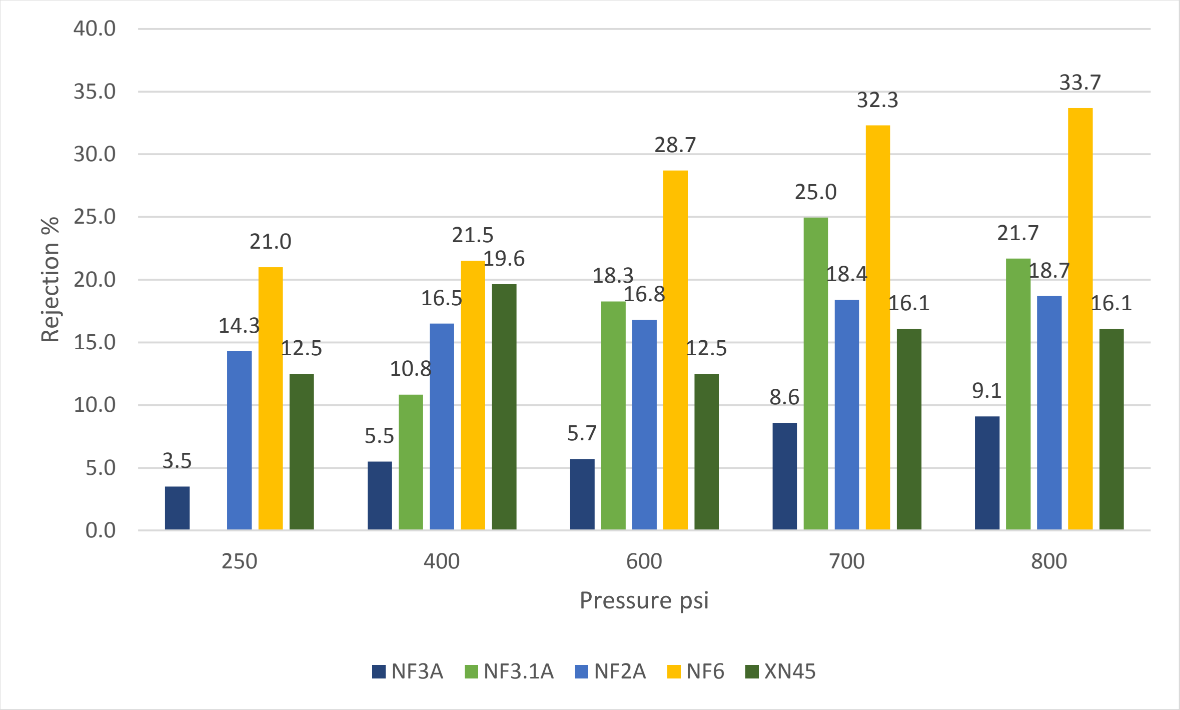

Figure 17: Rejection of Sodium Ion (Ideal Solution 50,000 ppm)

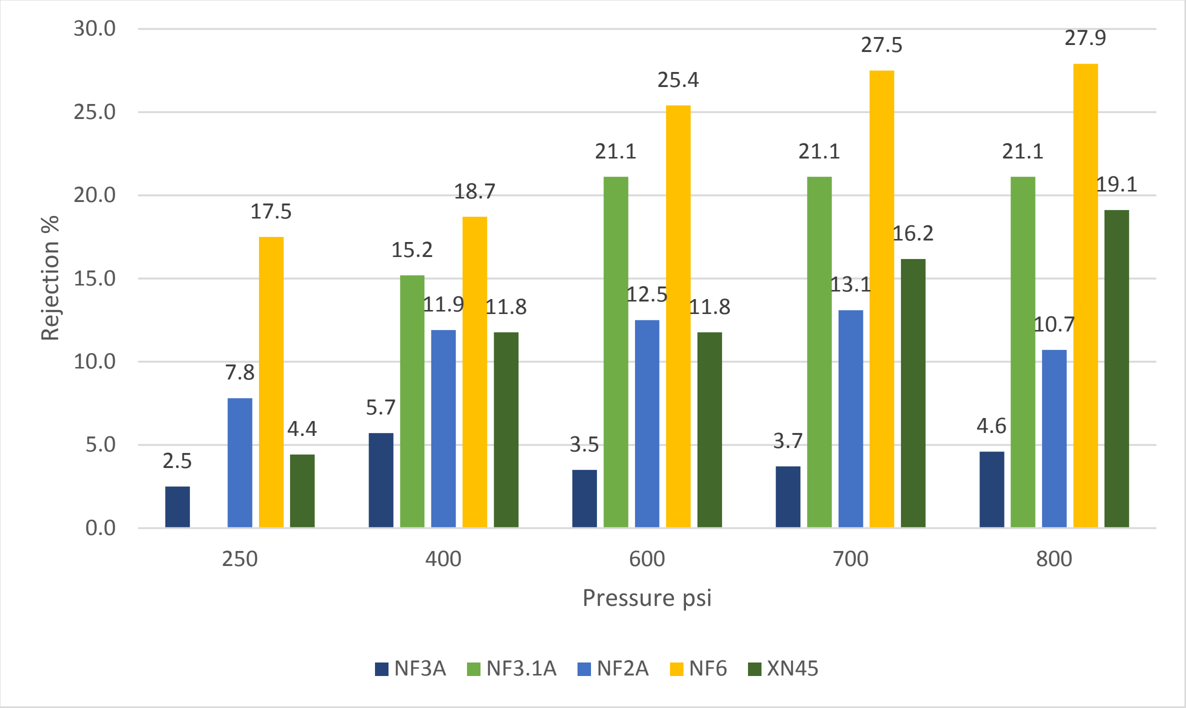

Figure 18: Rejection of Sodium Ion (Real Texas Flowback Water)

Texas flowback water was selected to treat with NF membranes. Figure 16 and Figure 18 compared rejection percent of salt ions for five NF membranes at 250, 400, 600, 700, and 800 psi. In Figure 16, NF3A displayed the best calcium rejection rate of 70% at both 700 and 800 psi. NF3.1A followed second at 63.6% at 700 psi. Figure 18 showed that NF6 had the highest sodium rejection rate at 27.5% and NF3A at 700 psi. Even though NF3A did not lead in rejection percent of sodium, this experiment concluded that NF3A had the overall highest removal capability of divalent ions in hydraulic fracturing water.

Fluxes of five NF membranes were documented at different operating pressures. Figure 19 charted the progression of flux over various pressures. It showed that NF3A and NF3.1A had the lowest flux rate at any giving pressure when compared to the other NF membranes.

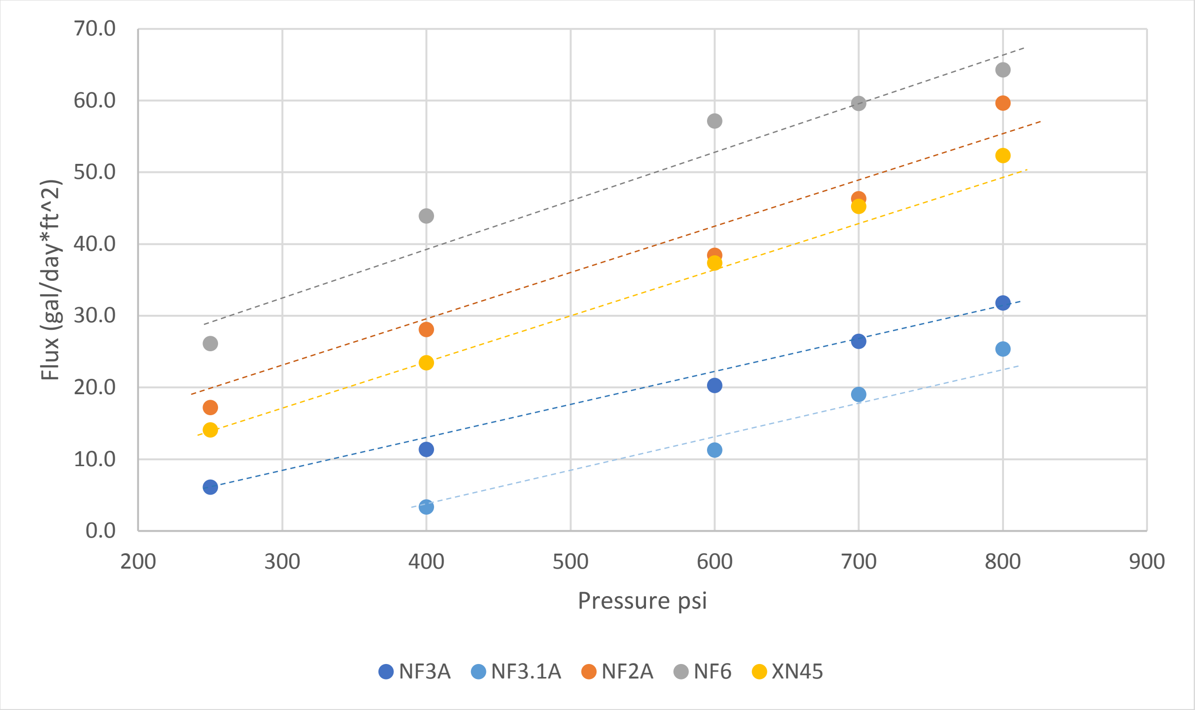

Figure 19: The Flux of Five Membranes in Treating Texas Flowback Water

NF3A was examined further to determine the likelihood of membrane fouling. Texas flowback water was pumped through NF3A at 700 psi. Both retentate and permeate were set to flow back into feed tank. NF3A treated Texas flowback water for six hours. Figure 20 traced the flux of NF3A over that time. NF3A's flux remained constant at 32 gal/ day*ft^2. NF3A's percent of salt ions rejection was also traced during this experiment and plotted on Figure 21. Figure 21 showed that NF3A had sustained 70% removal of calcium for six hours. For sodium removal, the rejection was slightly fluctuated over the six hour period. Still, the experiment indicated the less likelihood of NF3A fouling.

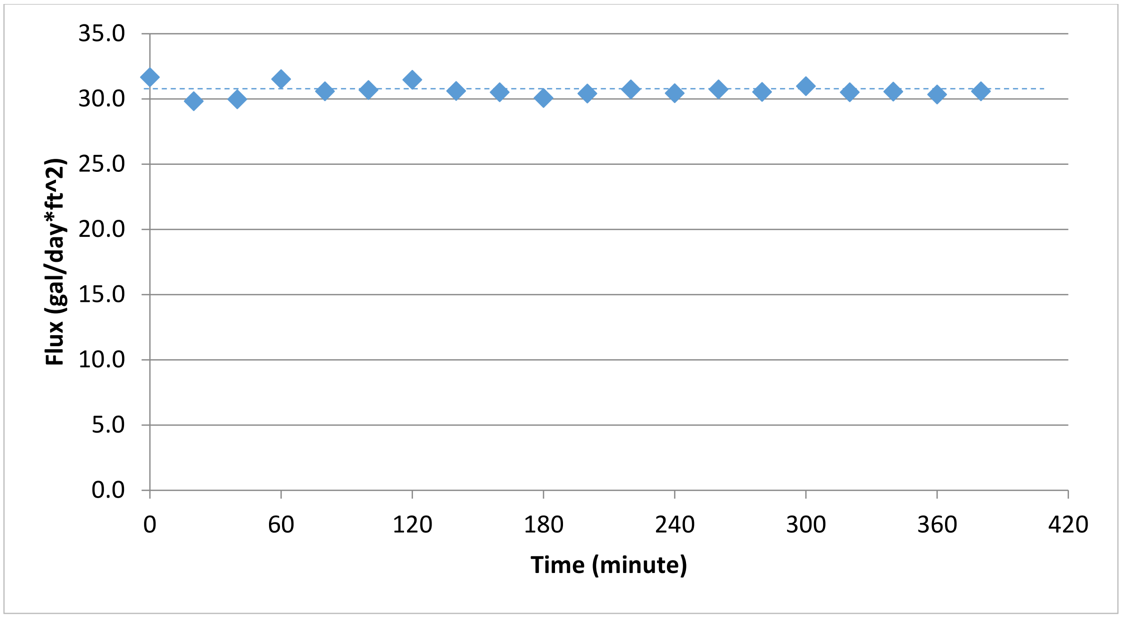

Figure 20: NF 3.A Flux without Concentrated the Feed (700 psig, 25^0C)

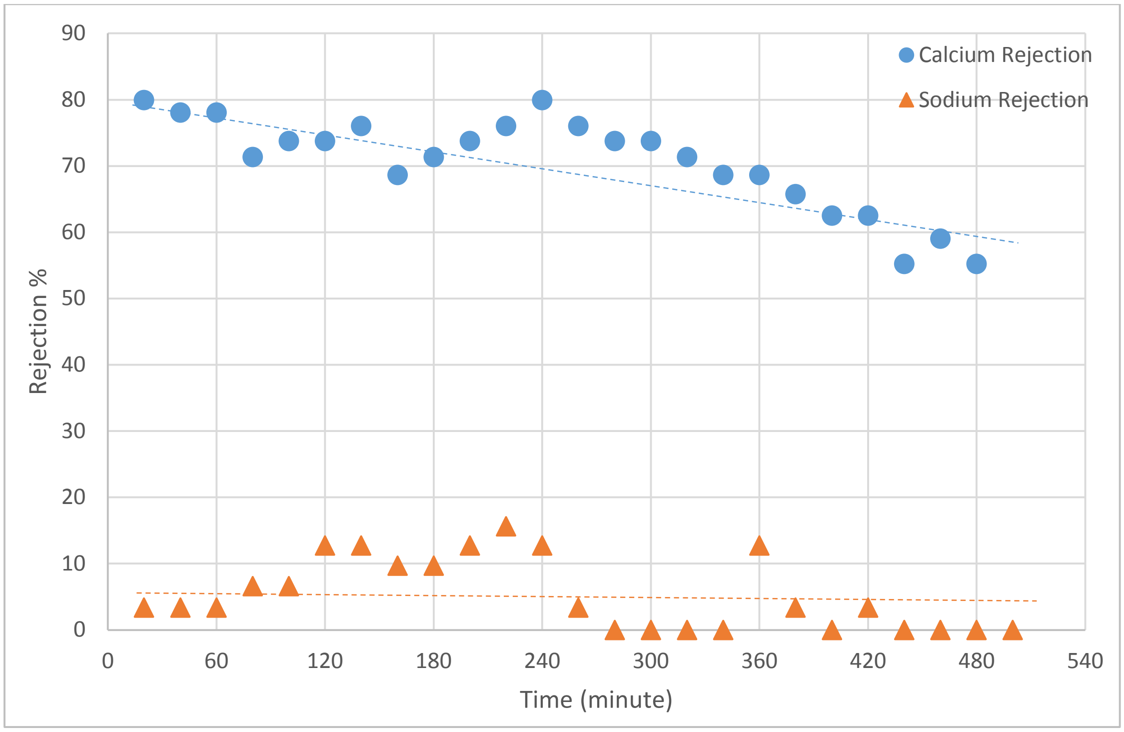

Figure 21: Rejection of Calcium and Sodium of NF 3.A as Permeate Collected Separated (700 psig, 25^0C)

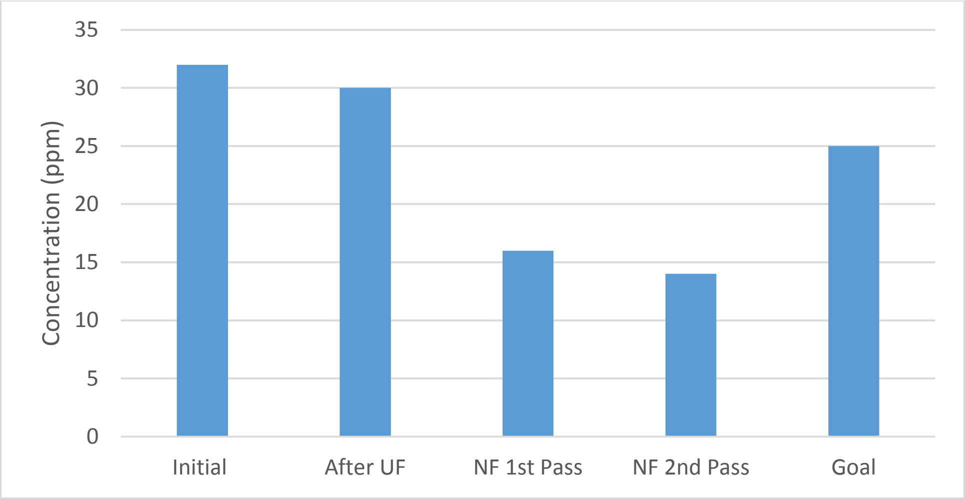

Figure 22: Strontium Concentration Following Each Stage

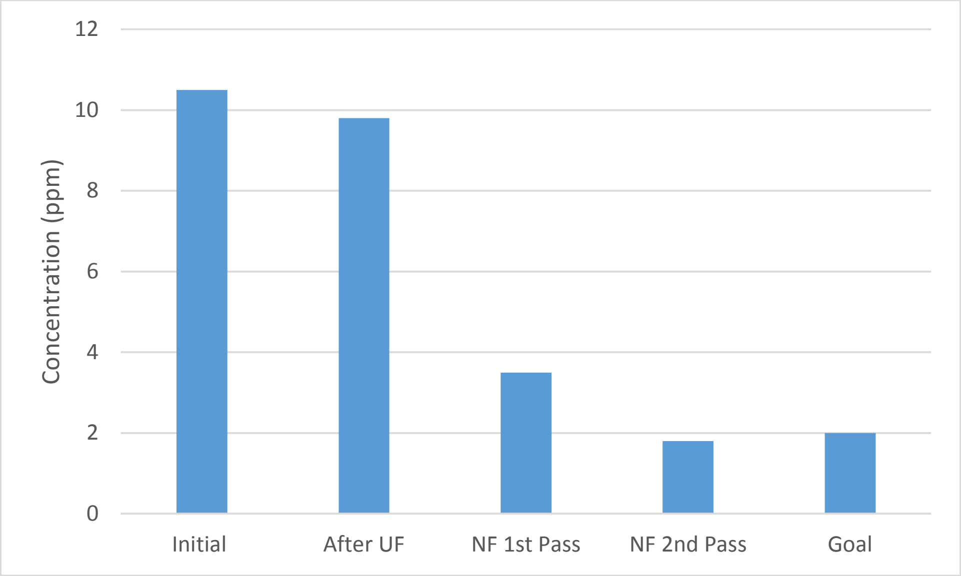

Figure 23: Barium Concentration Following Each Stage

Radioactive metals such as strontium and barium were tested in Texas flowback water. Levels of these metals were evaluated as water passed through the UF and NF treatment systems. Figure 22 compared strontium concentrations after each pass to the limit for reuse water. NF was necessary to remove strontium to the limit of reuse water. Two passes of NF were needed to drop the level of barium below reuse water specification. Figure 23 documented the barium concentrations after each pass through the membrane system.

4.3. Cost Calculation

The cost of membrane unit system was based on the report of Larry Kazemerski (Nation Renewable Energy Laboratory, 46). In this calculation, the NF and RO were built to handle 10,000 barrels per day. Design system was expected to last for 10 years with 10% annual interest rate with the replacement of the membrane every two years.

Energy costs were calculated with the assumption that the unit consumed 2.1kWh per cubic meter of water and price was $0.10 per kWh. Since the high pressure RO system was designed at 3000 psi, the capital, operating, maintenance, and energy costs were slightly higher than NF and the low pressure RO. Table 8 estimated the cost of using different membranes to treat hydraulic fracturing water. However, further research and calculation are required in order to achieve more accurate prices.

Table 8: Estimate the Cost to Treat Flowback Water Using NF and RO membranes
*Basis: 10,000 barrels/day, 365 day, 24/7

	NF	RO (Low Pressure)	RO (High Pressure)
Capital Costs	$511,647	$474,508	$711,762
Operating Costs	$396,631 /yr	$354,868 /yr	$427,622 /yr
Labor	$135,000 /yr	$135,000 /yr	$135,000 /yr
Chemical Cleaning	$37,139 /yr	$37,139 /yr	$37,139 /yr
Maintenance	$28,349 /yr	$23,725 /yr	$35,588 /yr
Energy	$121,864 /yr	$121,864 /yr	$182,796 /yr
Membrane Replacement	$74,279 /yr	$37,139 /yr	$37,139 /yr
Unit Product Cost	$0.13 /bbl.	$0.11 /bbl.	$0.14 /bbl.

5. Conclusions and Recommendation for Future Work

Flowback water generated by hydraulic fracturing during shale gas drilling can be reused for the fracturing process by using membrane technology. The system which combines UF and NF could treat flowback water from different shale gas formations. The design specific membrane can remove 70 percent of all divalent and have 80 percent or higher water recovery. Furthermore, the estimated cost is significant cheaper than the current price of treating flowback water.

Also, this research has proved that the commonly conventional methods such as coagulation, water softening, and activated carbon filter are inconsistent and inefficient.

However, due to limitations in flowback water samples, optimizing the condition of operation such as the temperature and the pressure could be further investigated. Also, a pretreatment process UF needs additional evaluating. Finally, this research has opened a new opportunity to explore the electrodeionization option. The permeate coming out of the membrane system is suitable to feed the electrodeionization process to generate power for the onsite drilling.

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7. Appendix

Table 1: Rejection of Sodium Ion (Ideal Solution 50,000 ppm)

	NF3.1A		NF2A		NF6		XN45		NF3A	
Pressure (psi)	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %
250			42850	14.3	39500	21.0	49000	12.5	50500	3.5
400	60000	10.8	41750	16.5	39250	21.5	45000	19.6	49500	5.5
600	55000	18.3	41600	16.8	35650	28.7	49000	12.5	49400	5.7
700	50500	25.0	40800	18.4	33850	32.3	47000	16.1	47900	8.6
800	52700	21.7	40650	18.7	33150	33.7	47000	16.1	47600	9.1
Initial	67300		50000		50000		56000		52400	

Table 2: Rejection of Sodium Ion (Real Texas Flowback Water)

	NF3.1A		NF2A		NF6		XN45		NF3A	
Pressure (psi)	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %
250			49400	7.8	40000	17.5	65000	4.4	46300	2.5
400	43000	15.2	47200	11.9	39400	18.7	60000	11.8	44800	5.7
600	40000	21.1	46900	12.5	36200	25.4	60000	11.8	45800	3.5
700	40000	21.1	46600	13.1	35200	27.5	57000	16.2	45700	3.7
800	40000	21.1	47900	10.7	35000	27.9	55000	19.1	45300	4.6
Initial	50700		53600		48500		68000		47500	

Table 3: Rejection of Calcium Ion (Ideal Solution 16,000 ppm)

	NF3.1A		NF2A		NF6		XN45		NF3A	
Pressure (psi)	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %
250			10000	17.4	12100	24.4	12100	24.4	5300	69.5
400	1200	91.4	9200	24.0	12100	24.4	10100	36.9	3400	80.5
600	860	93.9	7700	36.4	12100	24.4	9200	42.5	2000	88.5
700	780	94.4	7000	42.1	10100	36.9	9200	42.5	1600	90.8
800	630	95.5	7000	42.1	12100	24.4	9200	42.5	2800	83.9
Initial	14000		12100		16000		16000		17400	

Table 4: Rejection of Calcium Ion (Real Texas Flowback Water)

	NF3.1A		NF2A		NF6		XN45		NF3A	
Pressure (psi)	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %	ppm	Rejection %
250			12000	29.2	14900	7.1	14600	10.7	7400	54.7
400	8300	49.7	11000	34.8	14900	7.1	14600	10.7	7400	54.7
600	11700	29.1	10100	40.4	12000	25.0	13100	20.2	6150	62.3
700	6000	63.6	12000	29.2	14900	7.1	13100	20.2	4900	69.8
800	8300	49.7	10100	40.4	14900	7.1	13100	20.2	4900	69.8
Initial	16500		16900		16000		16400		16300	

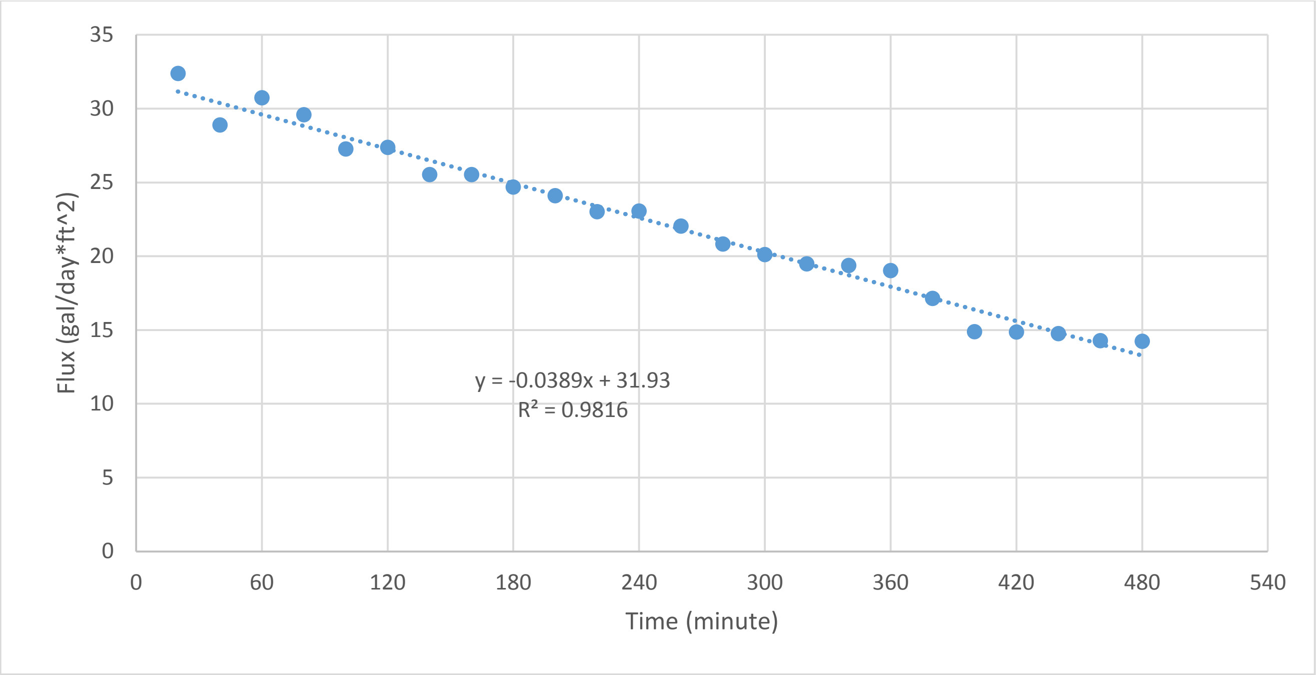

Figure 1: NF3A Flux with Time (Collecting the Permeate Separately 700 psig, 25^0C)

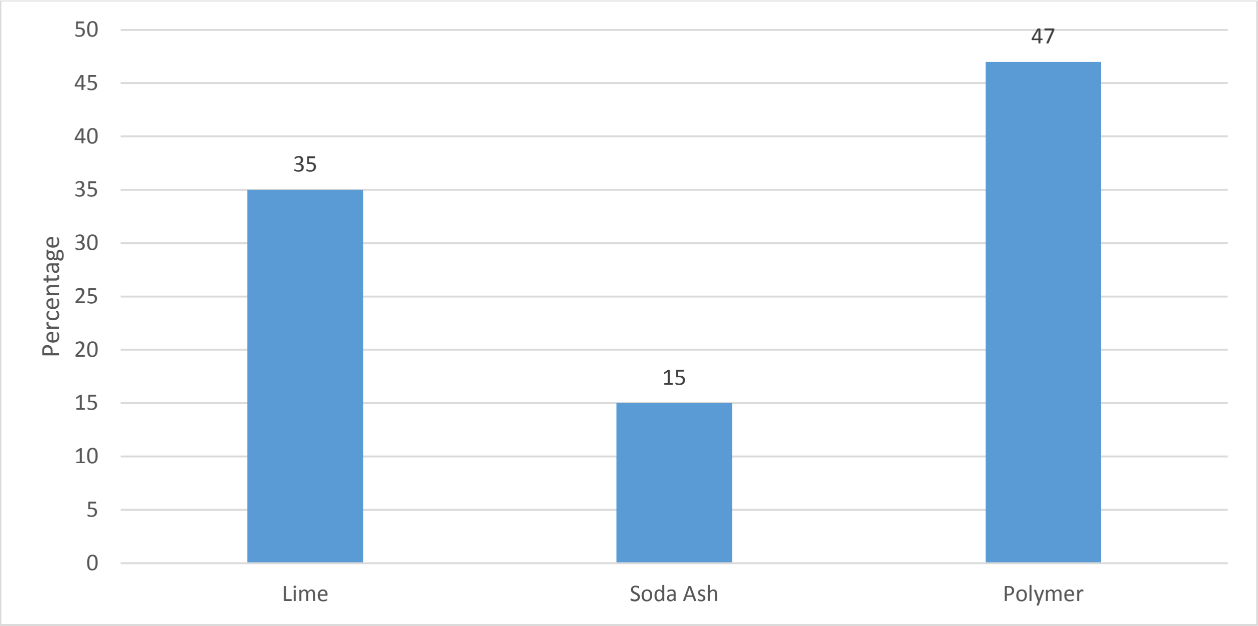

Figure 2: Comparing the Efficiency of Calcium Removal of Oklahoma Flowback Water