Treatment of contaminated Flowback water in shale gas development

By

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FINAL PROJECT REPORT

Submitted to the Department of Chemical Engineering
In Partial Fulfillment of the Requirements
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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Department of Chemical Engineering
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Approved:

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Project Supervisor

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January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AHMED ZIDAN ABDELALIM

ABSTRACT

Flowback water from shale gas well drilling has a high TDS (total dissolved solids) content, ranging from 5000 ppm to 261,000 ppm, along with a TSS (total suspended solids) content of 300–3000 mg/L. Recently, the rapid expansion of shale gas production in Marcellus Formation has raised serious environmental concerns about the large amount of flowback water in this area. In this project a process based on ceramic membrane filtration and ion-exchange is optimised for the treatment of the flowback water from Marcellus Formation. Mixed bed ion-exchange will then be employed to reduce the high TDS concentration of flowback water. Finally, a preliminary cost estimation of the proposed treatment process will be conducted. The studied process contains a combination of two MF (microfiltration) membranes. After treatment, all TSS and >99% of TDS should be successfully removed from the flowback water to meet the criteria for surface discharge. The cost estimation of the treatment is expected to be around 18.4 $\$/m^3$.

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Finally, I would like to apologize if any party was inadvertently excluded from being mentioned above.

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CHAPTER 1

PROJECT BACKGROUND

1.1 Background Study

Shale gas is the natural gas entrapped in impervious clastic sedimentary rock. According to the Energy Information Administration (EIA), the estimated reserves of global shale gas are about 716 trillion cubic meters, and may secure the worldwide fuel supply for more than 100 years. Unfortunately, until the beginning of this millennium, the large-scale economical extraction of shale gas was thought to be impossible due to its low permeability and the lack of cost effective drilling methods. In recent decades, the utilization of hydraulic fracturing and horizontal drilling has brought the production of shale gas to center stage.

A typical drilling operation consists of three stages – drilling, hydraulic fracturing and flow back. During hydraulic fracturing, about 2–5 million gallons of hydrofracture water, a mixture of water and chemical additives, is pumped into the gas bearing formation. After hydraulic fracturing, about 10–40% of the hydrofracture water will return to the surface as “flowback water”, depending on the geology and geomechanics of the formation. The flowback water contains high total dissolved solids (5000–261,000 ppm TDS) and total suspended solids (300–3000 mg/L TSS), most likely from interaction with the underground rocks in the shale gas formation.

1.2 Problem Statement

With the rapid development of shale gas production in the Marcellus Formation, a large volume of flowback water is impounded at the surface of drilling sites for subsequent disposal, treatment or recycled however, the Environmental Protection Agency (EPA) recommends that the Secondary Maximum Contaminant Level for TDS in drinking water should be 500 mg/L. The Pennsylvania Environmental Quality Board (EQB) also published regulations to ensure that the TDS in Pennsylvania's streams does not exceed 500 mg/L. Under these restrictions, the discharge and dilution of flowback water into municipal wastewater treatment becomes an inadequate or unsustainable approach for managing flowback water. Compared to discharge, deep injection is considered to be a more responsible method. However, the availability of adequate deep-well disposal capacity is a critical constraining factor in the Marcellus Formation.

1.3 Objectives

The objectives of this project are:

- To treat the flowback water from Marcellus shale gas production using ceramic membrane and ion-exchange technologies.

- To comprehensively characterize the properities of flowback water from hydro-fracture shale gas.

- Study the effects of different types of membranes, including microfiltration and ultrafiltration, on the treatment of flowback water.

1.4 Scope of Study

The composition of flowback water is complicated, varying from well to well. It mainly consists of dissolved salts, chemical additives and solid particles. The flowback water sample to be used in this project will be prepared in the lab based on the characterization of Flowback water. The flowback water will be stored in a refrigerator prior to use. The TSS of the sample will be determined according to the Standard Methods for the Examination of Water and Wastewater.

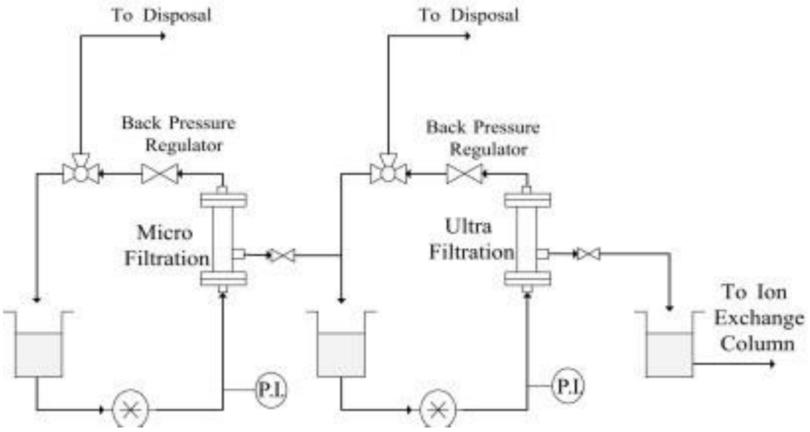
- A 10 g well-mixed sample will filtered through a standard filter by applying a vacuum and the residue retained on the filter will be dried to a constant weight at 105 °C in an isotemp oven (BEMCO Ultra). The increase in weight of the filter represents the TSS of the sample.
- The anionic analysis such as Cl^-, Br^- of flowback water samples will be obtained using ion chromatography.
- The pH of the samples will be measured using a pH meter (Omega PHB-212) with a combination pH electrode.
- The alkalinity of the samples will be measured by a titration method according to the Standard Methods for the Examination of Water and Wastewater (2320B).The sample will be titrated using the sulfuric acid solution The alkalinity of the sample to be determined by the amount of sulfuric acid required to adjust the pH of the sample to the desired value.

CHAPTER 2 LITERATURE REVIEW

2.1 Membrane Treatment System

Membrane based separation processes are attractive for a number of reasons: they are often less costly to operate, scale up is frequently easier and they are environmentally benign. Membrane based separations are often ideally suited for niche applications. However membrane fouling frequently compromises their economic viability especially in water treatment applications.

The membrane treatment apparatus in this project consists of a cross-flow microfiltration (MF) sub-system and a cross-flow ultrafiltration (UF) sub-system.



(Fig.1) Schematics of the cross-flow MF and UF membrane system

The sub-systems can be operated separately or operated serially according to the objectives of research. Backpressure regulators (GO 250, USA) were installed in each sub-system to control trans-membrane pressure (TMP). MF and UF filters used in this study were ceramic membranes sealed in stainless steel membrane vessels which can be made in our own lab (300 mL/min flowback water at ambient pressure will be pumped to the tube side of the membrane vessel, and the permeate can be collected from the shell side of the vessel. The choice for a certain kind of membrane system is determined by a great number of aspects, such as costs, risks of plugging of the membranes, packing density and cleaning opportunities. Membranes are never applied as one flat plate, because this large surface often results in high investing costs. That is why systems are built densely to enable a large membrane surface to be put in the smallest possible volume. Membranes are implemented in several types of modules. There are two main types, called the tubular membrane system and the plate & frame membrane system. Tubular membrane systems are divided up in tubular, capillary and hollow fiber membranes. Plate &

frame membranes are divided up in spiral membranes and pillow-shaped membranes.

Membrane fouling

During membrane filtration processes membrane fouling is inevitable, even with a sufficient pre-treatment. The types and amounts of fouling are dependent on many different factors, such as feed water quality, membrane type, membrane materials and process design and control.

Particles, biofouling and scaling are the three main types of fouling on a membrane. These contaminants cause that a higher workload is required, to be able to guarantee a continuous capacity of the membranes. At a certain point the pressure will rise so much that it is no longer economically and technically accountable.

2.2 Microfiltration

The permeate fluxes of the flowback water filtered through different membranes exhibit different behaviors. The different behaviors of flux decline reflect the different fouling mechanism of the membranes. There are four classical types of flux decline mechanisms describing characteristic change in flux over time: cake filtration, intermediate blocking, standard blocking, and complete pore blocking. Complete pore blocking describes the worst fouling, meaning the solids in the feed block the pores on the surface or in the depths of membrane filter. Cake filtration occurs when solids are deposited on a membrane filter as a homogeneous porous layer without pore blocking. This analysis demonstrated that applying the MF membrane with larger pore size to treat the flowback water can mitigate fouling of the membrane. Most TSS should be removed from the flowback water by the MF ceramic membrane.

MF is loosely defined as a membrane separation process using membranes with a pore size of approximately 0.03 to 10 microns, a MWCO of greater than 100,000 daltons, and a relatively low feedwater operating pressure of approximately 100 to 400 kPa (15 to 60 psi). MF is not an absolute barrier to viruses; however, when used in combination with disinfection, MF appears to control these microorganisms in water. The primary impetus for the more widespread use of MF has been the increasingly stringent requirements for removing particles and microorganisms from drinking water supplies. Additionally, there is a growing emphasis on limiting the concentrations and number of chemicals that are applied during water treatment. By physically removing the pathogens, membrane filtration can significantly reduce chemical addition, such as chlorination. Another application for the technology is for removal of natural or synthetic organic matter to reduce fouling potential. In its normal operation, MF removes little or no organic matter; however, when pretreatment is applied, increased removal of organic material, as well as a retardation of membrane fouling can be realized

MF membranes provide absolute removal of particulate contaminants from a feed stream by separation based on retention of contaminants on a membrane surface. It is the “loosest” of the membrane processes, and as a consequence of its large pore size, it is used primarily for removing particles and microbes and can be operated under ultralow pressure conditions. In the simplest designs, the MF process involves prescreening raw water and pumping it under pressure onto a membrane. In comparison to conventional water clarification processes, where coagulants and other chemicals are added to the water before filtration, there are few pretreatment requirements for hollow-fiber systems when particles and microorganisms are the target contaminants. Prefilters are necessary to remove large particles that may plug the inlet to the fibers within the membrane module. More complex pretreatment strategies are sometimes employed either to reduce fouling or enhance the removal of viruses and dissolved organic matter. In such cases, pretreatment by adding coagulants or powdered activated carbon (PAC), has been employed. In some cases, the cake layer built up on the membrane during the water production cycle can remove some organic materials. It may be necessary to adjust the flowback water pH by chemical dosing prior to membrane filtration in order to maintain the pH within the recommended operating range for the membrane material employed. It should be noted that pH adjustment is not required for scaling control, since MF membranes do not remove uncomplexed dissolved ions.

2.3 Ultrafiltration

UF involves the pressure-driven separation of materials from water using a membrane pore size of approximately 0.002 to 0.1 microns, an MWCO of approximately 10,000 to 100,000 daltons, and an operating pressure of approximately 200 to 700 kPa (30 to 100 psi). UF will remove all particles removed by MF (partial removal of bacteria), as well as some solids (but not an absolute barrier to solids). It can provide a second barrier to contamination and is therefore recommended. The primary advantages of low-pressure UF membrane processes compared with conventional filtration and treatment processes are:

- No need for chemicals (coagulants, flocculants, disinfectants, pH adjustment).
- Size-exclusion filtration as opposed to media depth filtration.
- Good and constant quality of the treated water in terms of particle and TOC removal.
- Process and plant compactness

- Simple automation, Fouling is the limiting phenomenon responsible for most difficulties encountered in membrane technology for water treatment. UF is certainly not exempt from this fouling control problem. Therefore, membrane productivity is still an important subject, which should be thoroughly researched in order to have a better understanding of this phenomenon and its mechanisms.

UF is a pressure-driven process by which colloids, particulates, and high molecular mass soluble species are retained by a process of size exclusion, and, as such, provides means for concentrating, separating into parts, or filtering dissolved or suspended species. UF allows most ionic inorganic species to pass through the membrane and retains discrete particulate matter and nonionic and ionic organic species. UF is a single process that removes many water-soluble organic materials, as well as microbiological contaminants. Since all UF membranes are capable of effectively straining solids, carbon, and most contaminants from water, the process offers a filtered product with little load on any post-treatment sterilization method, such as UV radiation, ozone treatment, or even chlorination. Unlike RO, the pretreatment requirement for UF is normally quite low. Fortunately, due to the chemical and hydrolytic stability of UF membrane materials, some of the pretreatments essential for RO membranes, such as adjustment of pH or chlorine concentration levels, do not apply. However, it may be necessary to adjust the pH to decrease the solubility of a solute in the feed so that it may be filtered out. UF is designed to remove suspended and dissolved macromolecular solids from fluids. The commercially available modules are therefore designed to accept flowback water that carry high loads of solids. Because of the many uses for UF membranes, pilot studies are normally conducted to test how suitable a given stream is for direct UF. Approximately 0.001 microns and an MWCO of 1,000 to 100,000 daltons. Pushing water through these smaller membrane pores requires a higher operating pressure than either MF or UF. Operating pressures are usually near 600 kPa (90 psi) and can be as high as 1,000 kPa (150 psi). These systems can remove virtually 99% of TOC and TDS.

2.4 Ion Exchange Treatment

Ion exchange is the process through which ions in solution are transferred to a solid matrix which, in turn releases ions of a different type but of the same polarity. In other words the ions in solutions are replaced by different ions originally present in the solid.

Since ion exchange occurs between a solution and the internal surface of a solid it can be viewed as a special type of sorption process. There are many similarities between adsorption and ion exchange. The two processes are often analyzed using similar models. Unlike adsorption ion exchange requires an interchange of materials, i.e., the ions (as opposed to a unidirectional transfer) since the electroneutrality of the solution must be maintained, during ion exchange the ions being exchanged are reversibly removed from the wastewater and transferred to the ion exchanger, This means that ion exchange is a physical separation process in which the ions exchanged are not chemically altered. Since the chemical characteristics of the ions exchanged are not modified the use of ion exchange in wastewater treatment is associated with the removal of hazardous ionic material(s) from the wastewater and its transfer to the ion exchanger. Since the ion exchanger only collects the hazardous material the spent exchanger must be treated at the end of a cycle. Typically this involves the regeneration of the ion exchanger by contacting the spent exchanger with a concentrated solution of an ion (such as H+ or OH-) which can replace the ions adsorbed on the exchanger during the treatment process. This results in the generation of a spent regenerating solution containing the waste ions in a concentrated form.

In the vast majority of cases ion exchanger are used to treat wastewaters containing inorganic wastes (i.e., inorganic ions). The kinetics of sorption of organic species from non-polar solvents by ion exchangers is typically unfavorable. In addition, ion exchangers are generally not very effective against large organic molecules, mainly because the size of the molecules which dramatically reduces the exchange rate However, ion exchangers are effectively used in the treatment of specific organic compounds (such as phenol sorption or decolorization of kraft paper mill effluents). In this case the ion exchanger does not act as such but more as an conventional adsorbent.

There are plenty of advantages of using Ion Exchange Technology; Capability of handling and separating components from dilute waster, Possibility of concentrating pollutants, Capability of handling hazardous wastes, Possibility of recovery expensive materials from waste (e.g., precious metals), Possibility of regenerating ion exchanger and Possibility of recycling components present in the waste and/or regenerating chemicals.

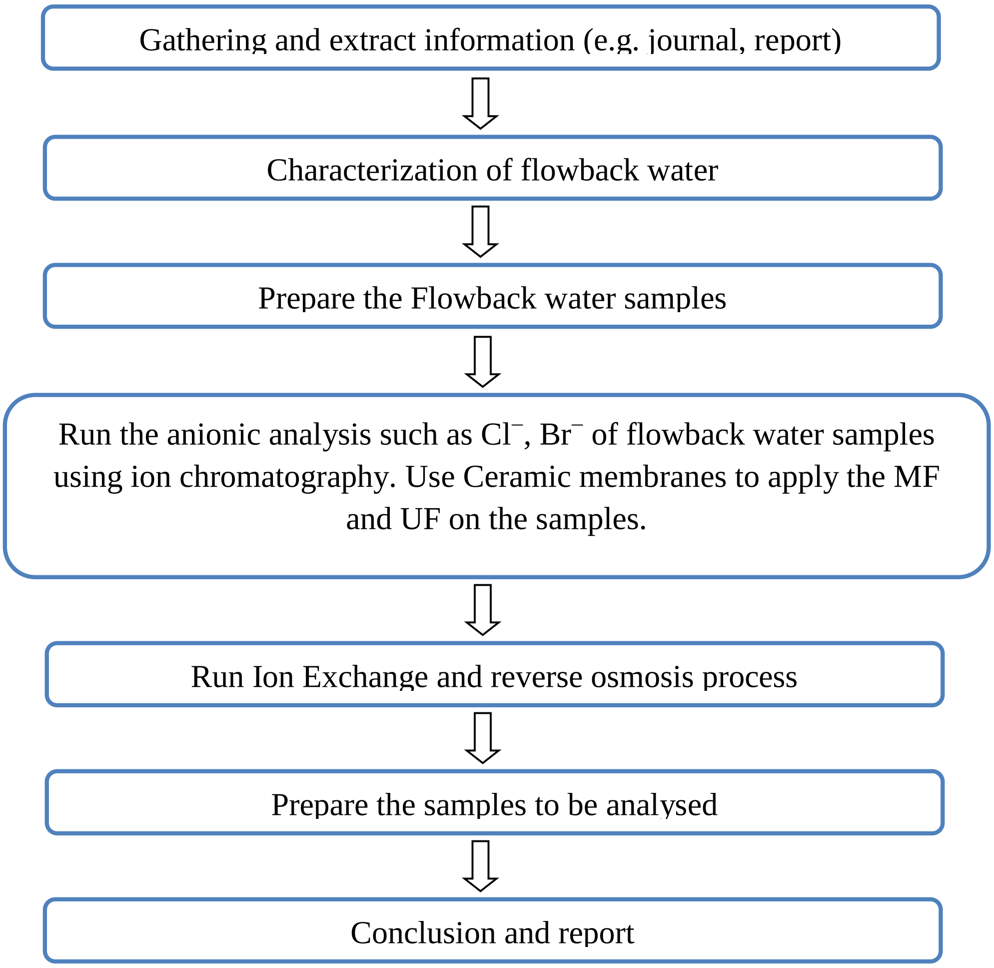
Ion exchange materials are made of organic or inorganic matrices containing ionic functional groups, both natural ion exchange materials (zeolites) and synthetic ion exchange materials exist. The vast majority of the ion exchangers used in industrial wastewater treatment is of synthetic origin. The most common type of synthetic ion exchange materials are organic resins. Ion exchange resins are organic compounds polymerized to form a porous tridimensional matrix. A crosslinking agent (e.g., divinylbenzene) is added during the polymerization reaction to generate the tridimensional structure. The resins, in the form of spherical particles, are chemically activated by reacting the polymer matrix with a compound capable of introducing the desired ion exchange functional group (e.g., with sulfuric acid to introduce sulfonic groups)

The resins of different diameters can be employed as cationic and anionic resins respectively. Prior to use, the resins will be soaked in the deionized water with gentle stirring for 10 minutes to obtain complete wetting. The well-mixed cationic and anionic resins will be packed into anion-exchange column of 2 cm diameter and 30 cm length (Kontes Chromaflex, Fisher). The ion exchange between the resins and water occurred as flowback water would be pumped through the resin column.

CHAPTER 3 METHODOLOGY

3.1 Project Activities

3.1.1 Project Flow



Gathering and extract information (e.g. journal, report)

Characterization of flowback water

Prepare the Flowback water samples

Run the anionic analysis such as Cl^-, Br^- of flowback water samples using ion chromatography. Use Ceramic membranes to apply the MF and UF on the samples.

Run Ion Exchange and reverse osmosis process

Prepare the samples to be analysed

Conclusion and report

In this project, the research methodologies are divided into seven different stages as stated in Figure 2.

(Fig.2) Project Activities

3.1.1 Preliminary Research Work

This stage focuses on data collection related to the project. All information existed from journals, articles, technical papers and books that are related to the project are gathered and compiled to have a better understanding to the project.

Meeting with the previous students are also done to have a better overview regarding the overall projects that will be done including any problems faced and recommendations suggested by the previous students.

3.2 Lab Experiment

After all the related information has been gathered, experiments can be carried out to investigate the relationship of third harmonic with the cable capacitance.

In a given well, one fracturing job can involve the injection of as much as 100,000 barrels of water and may require additional fracturing to maximize yield. In the first three weeks of the hydraulic fracturing process, approximately 20 - 30% of the water used to fracture the well comes back to the surface and is called flowback water. It is generally contaminated with spent fracturing fluid chemicals and substances present in the shale itself. Until recently, and depending on location of the fracturing job, sourcing has been from surface waters and municipal water treatment facilities and discharging of the flowback water into disposal wells. However, reconstitution and reuse of flowback water for future fracturing operations presents advantages in the form of reduced fresh water quantities for fracturing operations and for the need of disposal options, with the concomitant reduction in operational cost and issues related to environmental and regulatory concerns. The flowback water is contaminated with suspended and dissolved solids, with the concentrations varying depending on location.

Constituent	SGFW	Irrigation [15]	Surface Water Discharge[16]
TOC (Total Organic Carbon) (mg/L)	720		
TSS (Total Suspended Solids) (mg/L)	881		
TDS (Total Dissolved Solids) (mg/L)	48<comma>000	2000	500[12]
pH	6.85		
Alkalinity (mg/L)	205	510	200
Conductivity (μs/cm)	67<comma>000	3000	
Turbidity (NTU)	770		
Na (mg/L)	12<comma>200	920	
K (mg/L)	363	2	
Mg (mg/L)	104	122	
Ca (mg/L)	2935	800	
Ba (mg/L)	697		10[12]
Sr (mg/L)	591		10[12]
Al (mg/L)	105		
Fe (mg/L)	<1		1
Mn (mg/L)	<2	0.2	1.5
Cl (mg/L)	28<comma>500	1064	230
Br (mg/L)	19		
F (mg/L)	<1		
Sulfate (mg/L)	12.9	1920	250

(Table.1) Characterization of flowback water

Typical concentration ranges for such contaminants are captured in Table 1. Additional contaminants include traces of oil, bacteria, polymers and fractioning fluid chemicals. The goal of the flowback water treatment is to produce clear and largely desalinated water with minimum tendency to interfere with fractioning fluid components or with the shale formation. The degree of necessary desalination depends of the chemistry of the fracturing fluid and can range typically from 1,000 to 10,000 ppm total dissolved solids (TDS), although research has been cited in the literature regarding the development of fracturing fluid chemistries compatible with unaltered flowback water containing TDS levels up to 150,000 ppm. In the field, flowback is treated in stages involving pretreatment and desalination steps. Desalination treatment approaches include membrane and thermal technologies and the necessary level of pretreatment depends on the selected desalination method. Membrane technologies require the removal of oil, hardness, bacteria, and total suspended solids (TSS) due to scaling and potential fouling of the membrane surfaces. Thermal technologies are less susceptible to some of the contaminants, yet are sensitive to hardness and TSS because of scaling issues. In addition, the concentration of divalent ions in the water such as barium, calcium and magnesium may cause scaling and plugging of the formation and therefore need to be removed from the flowback water. Understanding the composition of the flowback water is essential in determining the extent of required treatment. While all water analyses required to characterize the flowback water before, during and after treatment can be performed at off-site laboratories, it is clear that the greatest challenge is to analyze the flowback water in the field in order to enable rapid and reliable monitoring for efficient decision making regarding required treatment, treatment performance or reuse, and safe disposal. Laboratory methods for analysis of flowback water range from titration to spectroscopic determinations such as atomic absorption (AA) and inductively coupled plasma (ICP), X-Ray Fluorescence (XRF); in some cases, these methods are cited as standard ASTM methods or practices. However, field operations for flowback water treatment frequently require evaluation techniques that are less delicate and easier to mobilize and use, yet are adequately accurate and reliable to permit operators and service providers to monitor key operational variables for timely process adjustment to ensure that target objectives are achieved.

3.3 Testing Methods

Testing Methods Field analytical methods and laboratory analysis were employed in this study. The analytical determinations were done for benchmarking purposes. For the laboratory characterization AA and in some instances ICP was used for aluminum, barium, calcium, magnesium, manganese and silica, whereas ion chromatography (IC) was used for determining anionic species such as sulfate and chloride. Additionally, the laboratory used titration for chloride and alkalinity, and gravimetric methods for TSS and TDS. For the field analysis, colorimetric methods were used for the analysis of aluminum, barium, calcium, chloride, iron, magnesium, manganese, sulfate and silica. Titration methods were used for alkalinity, chloride, calcium and magnesium. Conductivity was used to evaluate TDS. Turbidity measurements were used in lieu of TSS measurement.

The principle of colorimetric analysis involves the introduction of a reagent that produces a color when reacting with the element to be analyzed. The intensity of the color is proportional to the amount of that element in the specimen. The concentration of the element can be quantified in accordance with the Lambert-Beer Law by passing a light beam through the specimen. The concentration is automatically computed by the colorimetric spectrometer using the Lambert-Beer equation shown below:

$$A = -\log(I1/\ Io) = Єlc$$

Where:

A: Absorbance

Io: Initial intensity

I1: Transmitted intensity

Є: Extinction coefficient

Any preexisting color in the sample to be analyzed would interfere and will adversely affect the result of the colorimetric test. Flowback water is not always colorless and also typically turbid, which can cause interferences when using colorimetric techniques. In order to eliminate interference due to the color or turbidity of the analyzed samples, dilution techniques and filtration using a 0.45 µm filter were implemented. In addition to optical interferences, chemical interferences can also occur due to the presence of one or more elements that can react with the reagent added to produce the color or with the target analyte obscuring the true intensity of the color attributed to the concentration of C, α Io I1 l ϵ the analyte of interest. Chemical interferences associated with the analytes investigated in this study are summarized as follows:

Analyte	Interferences
Aluminum	alkalinity
Barium	calcium, magnesium, silica, sodium chloride and strontium.
Chloride	pH below 3 or above 10.
Iron	calcium, chloride, magnesium, pH below 3 or above 10.
Magnesium	chromium, copper, iron, manganese and zinc.
Manganese	calcium, chloride, magnesium, iron, and pH below 3 or above 10.
Silica	phosphate and sulfide
Sulfate	calcium, magnesium, chloride and silica.

(Table.2) Chemical Interferences Factors for Colorimetric Analysis of Flowback Waters

The principle of turbidimetric analysis involves the introduction of a reagent that produces a precipitate when reacted with the element to be analyzed, such as for the determination of barium and sulfate. The turbidity relies on detecting the transmittance of the light through the suspension and any inherent precipitate in the sample. Interferences are similar to those observed in the colorimetric methods.

3.3 Key Milestone

Table 1: Key Milestone for Final Year Project 1

No.	Item/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Submission of final year project title selection form		■												
2	Submission of extended proposal						■								
3	Proposal defense									■					
4	Submission of interim draft report													■	
5	Submission of interim final report														■

Table 2: Key Milestone for Final Year Project 2

No.	Item/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Submission of progress report								■						
2	Pre-Sedex											■			
3	Submission of Draft Report												■		
4	Final Report													■	
5	Viva														■

3.4 Gantt Chart

Table 3: Gantt Chart of Final Year Project 1

No.	Item/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Select & confirmation of project title	■	■												
2	Early research on the proposed topic			■	■	■	■	■							
3	Lab experiment								■	■	■	■	■	■	■
4	Proposal defense									■					
5	Preparing interim draft report											■	■	■	
6	Preparing interim final report														■

Table 4: Gantt Chart of Final Year Project 2

No.	Item/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Lab Experiment	■	■	■	■	■	■	■	■	■	■				
2	Flowback water Characterization						■	■							
3	Samples Preparation			■	■	■	■	■	■	■	■	■	■	■	
4	Ionic analysis of the samples								■	■	■	■	■	■	
5	Filtration&Treatment									■	■	■	■	■	

3.5 Tool & Software Required

Tools & software that will be used throughout the project are:

- Laptop
- Ultrafiltration machine
- Titration tools
- Microsoft Office (Excel & Word)
- Microfiltration
- Turbidity measurements
- Ion Exchange Resins
- Ion Chromatography
- Calculator
- X-Ray Fluorescence
- Atomic Absorption (AA)

CHAPTER 4

RESULTS & Discussion

Four sampling process were carried on within 5 days each and has been examined for 3 times using three different membranes. The table below shows the analysis of the four samples; Sample B didn't make the cut because the TDS value is a bit non-realistic. TDS of real flowback water is always above 100.

Measurement	Sample A	Sample B	Sample C	Sample D
pH	5.93	5.83	5.95	5.89
Sodium	548.43	629.1	477.34	54
Calcium	3,600	15,680	6,800	15,200
Magnesium	6,062	1,770	899	4,730
Barium	547	112	127	98
Iron	1,274	60	105	92
Manganese	100	1.4	1.7	1.8
Bicarbonate	415	183	348	195
Sulfate	10	10	20	60
Chloride	93,000	35,000	68,000	125,000
TDS	148,016	54,230	110,847	200,000

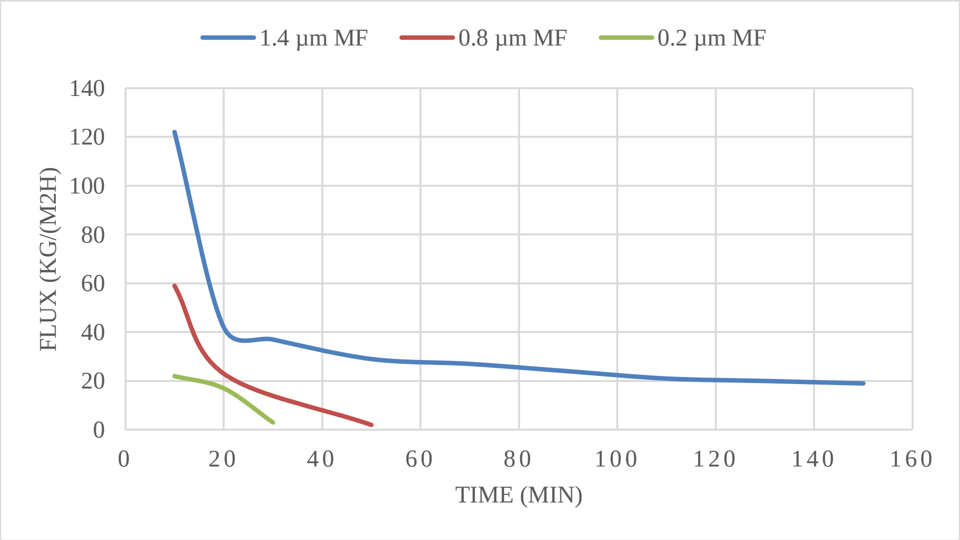
(Table.7) Analysis of the samples

UF ceramic membranes cannot be directly used to treat the flowback water because of their smaller pore size compared to MF membranes. However, a combined operation using MF and UF membranes in series may be a feasible process for the treatment of flowback water. Two MF–UF serial operations, MU-1 (1.4 µm MF + 0.02 µm UF) and MU-2 (1.4 µm MF + 5 nm UF) were investigated. Additionally, one MF serial operation, MM (1.4 µm MF+0.2 µm MF) yet to be evaluated for comparison.

Membrane	TSS Removal (%)	Turbidity Decrease (%)	Conductivity (	TOC Removal (%)
1.4 µm MF	71	68	65,900	3
0.8 µm MF	84	90	65,700	5
0.2 µm MF	100	97	64,100	11

(Table.8) Characteristics of the permeate from MF ceramic membranes

. Serious fouling led to the quick termination of permeation when using the 0.2 µm MF membrane alone to treat the flowback water (Fig. 3). However, the permeate flux of the 0.2 µm MF membrane in the second stage of the MM serial operation showed a more stable value without the termination of permeation (Fig. 4). Moreover, no termination of permeation was observed during the operation for other serial operation (MU-1 and MU-2), in which the UF membranes with small pore size were employed. This phenomenon confirmed that the serial membrane operation was more feasible for the treatment of flowback water since most solid particles were rejected by the 1.4 µm MF membrane and the permeation performances of the subsequent membranes in the serial treatment were improved. It was also observed that the final permeate fluxes of serial filtration varied according to the different types of the membranes used.



(Fig.3) Average permeate flux for the treatment of the flowback water using different MF ceramic membranes

Specifically, after flux decline within the first 30–40 min, the final permeate flux of the MM

Operation showed a stable permeate flux of 60kg/m2h, which is double the final permeate flux of the MU-1 operation and 3.5 times higher than the final permeate flux of the MU-2 operation.

According to the results shown in Table 5, all serial membrane treatments showed the ability to remove TSS and reduce turbidity of flowback water. However, the conductivity and the TOC did not present a substantial decrease after serial filtration. For instance, the conductivity of the final permeate of the MU-2 operation was 12% lower than the conductivity of the raw flowback water. The TOC of the final permeate of the MU-2 operation was 17% lower than the TOC of the raw flowback water. At the same time, the comparison between the MM operation and the MU-1/MU-2 operation demonstrated that the application of the UF membrane does not lead to a substantial decrease of TOC and conductivity. The TOC and the conductivity of the final permeate of the MM operation was 640mg/L and 63,900 µS/cm, respectively. The TOC and the conductivity of permeate through the MU-2 operation was 600mg/L and 59,000 µS/cm, respectively.

Combined Operation	TSS Removal (%)	Turbidity decrease (%)	Conductivity (µS/cm)	TOC removal (%)
MM	98	95	62920	10
MU-1	99	99	60420	14
MU-2	98	100	59342	15

(Table.9) Characteristics of the final permeate from the filtration of the combined operation

As described above , the final permeate flux of the MF serial operation (the MM operation) was much higher than the final flux of the MF–UF serial operation (the MU-1/MU-2 operation), indicating that more membrane surface areas will be needed to treat the same amount of the flowback water for the MF–UF serial operation. According to commercial quotations, the cost of UF membranes is much higher than MF membranes. For example, the cost of a 5 nm UF membrane is almost twice as much as that of a 0.2 mm MF membrane. In this scenario, the capital cost for the MF–UF serial operation will predictably be higher than the MF serial operation.

Ion Exchange Phase

After the treatment through the serial membrane filters, the TSS and turbidity of the flowback water were significantly reduced while the TDS and conductivity remained high. Therefore, ion-exchange resins were examined for TDS and conductivity reduction. The water treated by the serial MF ceramic membrane (1.4 mmþ0.2 mm) was pumped through the mixed ion-exchange resin bed at a flow rate of 20 mL/min. The water treated by the ion-exchange resin was collected and characterized to determine the performance of the ion-exchange treatment.

Constituent	Raw flowback water	After ion-exchange treatment
TOC (mg/L)	720	80
TSS (mg/L)	880	0
pH	6.82	6.94
Conductivity (µs/cm)	65,000	46

(Table.10). Ion-*Exchange treatment of the water treated by MF*

The characterization of the raw flowback water isTOC (mg/L) TOC (mg/L) presented in Table 10 for comparison. After the ion-exchange treatment, the conductivity of the water is 54 mm/cm, less than 1% of the raw flowback water. The Na+ and Cl- contents were reduced to 3.7 mg/L and 7.5 mg/L, respectively.

Additionally, the ion-exchange resin also exhibits a high capability of removing TOC. The treated water shows a low TOC of 82 mg/L, indicating that about 90% TOC was removed by the ion-exchange treatment. The above results demonstrates that the quality of the flowback water could be sufficiently improved to meet the criteria for irrigation water and for surface water discharge. Therefore, the studied combined process of the serial MF membranes and ion- exchange can be used to treat flowback water with high TDS, TSS and TOC from a technical perspective. Further studies investigating the effectiveness of the process on flowback water from different wells are ongoing.

CHAPTER 5 CONCLUSION & RECOMMENDATION

5.1 Conclusion

This project seeks an efficient and cost effective on-site treatment of flowback water, it is believed that this cannot be accomplished using only one technology but a combination of water treatment technologies may prove feasible. Ceramic membranes have a number of unique advantages, such as high thermal and chemical resistances, superior mechanical strength and longer lifetime. Ion-exchange can effectively reduce the concentration of TDS. Both membrane and ion-exchange treatments are suitable for on-site treatment due to their small footprint. In this study, the combination of ceramic membrane and ion-exchange treatment was applied to flowback water.

5.2 Recommendation

The combined process of ceramic membranes and ion-exchange was used to treat the flowback water produced during shale gas production. The study demonstrated that filtration through the MF membranes with small pore size terminates rapidly due to serious fouling. Moreover, the UF membranes were not suitable for the treatment of the flowback water based on the consideration of cost-performance. A MF serial operation (1.4 mm and 0.2 mm membranes) was proven very effective for removing the TSS and improving the appearance of the flowback water. After treatment with the MF serial operation, the suspended solids were removed completely and the treated flowback water is colorless and transparent. However, the combination of the MF membranes cannot effectively reduce the TDS and TOC of the flowback water. Only less than 5% TDS was removed after treatment with the membranes. The combined process of MF membranes and ion-exchange showed a desirable performance for the treatment of the flowback water.

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