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INVESTIGATION INTO OILFIELD WASTE WATER DISPOSAL THROUGH EUTECTIC FREEZE  
CRYSTALLIZATION

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INVESTIGATION INTO OILFIELD WASTE WATER DISPOSAL THROUGH EUTECTIC FREEZE  
CRYSTALLIZATION

A THESIS APPROVED FOR THE  
SCHOOL OF AEROSPACE AND MECHANICAL ENGINEERING

BY

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## Dedication

*For Molly, and all the joy she brought into this world*

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## Abstract

The principal question for this thesis is as follows:

*“How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?”*

Current waste water disposal methods in the oil industry primarily include water injection into disposal wells, with limited utilization of electrocoagulation for in-field reuse and thermal distillation at refineries. Brine hypersalinity and residual hydrocarbon has limited the application of membrane technology and simple environmental expulsion is heavily regulated by the EPA [2]. The problems associated with injection disposal, coupled with a lack of nearby Class II injection wells has limited the development of the Pennsylvanian Marcellus Shale Gas due to economic constraints imposed largely by the cost of water disposal. The challenge gas producers must now face is how to preserve the economics of shale gas production while simultaneously upholding responsible stewardship of resources and protecting public health. With increased concerns regarding induced seismicity from injection wells and the safety of that type of disposal, the need for water recycling methods has grown.

Eutectic Freeze Crystallization (EFC) has the potential to treat complex, hypersaline co-produced brine and represents a sustainable water treatment technology towards achieving a near zero waste by producing potable water and pure salts [3]. Given that the hypersaline brines of the Marcellus Shale are sodium and chloride rich [4], EFC could be used to selectively recover the sodium as a pure sodium

chloride salt while simultaneously producing pure ice crystals. The pure ice would have innumerable uses; reuse for hydraulic fracturing, release into estuaries, and agriculture being only a few.

The sodium chloride salt represents a potential revenue stream for water treatment companies and its sale to industrial chemical synthesizers could offset the cost of water treatment. While the applicability of using EFC to remove multiple salts from complex multi-component, hypersaline brines has not yet been demonstrated [5], the thermodynamics of freeze crystallization are extensively known. Verbeek shows that the overall efficiency an EFC crystallizer is 59% and that the energy requirement per unit feed is comparable to that of typical commercial evaporative crystallizers [6]. The cost of a large-scale freeze crystallization facility is estimated to be equitable to that of evaporative crystallization [7], but to be competitive EFC needs to be comparable to the injection disposal cost of \$1.00 - \$6.50 per barrel to be of interest to Exploration and Production companies [8].

Original simulation research of eutectic freeze crystallization of produced water using OLI Stream Analyzer was performed on various brine compositions generated from water quality reports provided by Baker Hughes Inc. This analysis shows EFC is suited for desalination of co-produced waters. These results indicate that EFC has a high level of compatibility with the task of co-produced water desalination and can be applied under favorable economic situations. A statistical cost estimate for water treatment by EFC is performed and concludes that if not currently economically viable,

in the near future EFC will be financially feasible in the Middle-Atlantic Region for shale gas water treatment.

Additional research needs to be performed to complete the validation of EFC for the task of treating brines for release. Namely, it is unclear to date whether the presence of hydrocarbons, organic chemicals and biomass, fracturing fluid chemicals and other additives, or NORM material would interfere or contaminant the pure effluent streams of EFC. In Chapter 4 a research proposal to finish the validation of this method is included.

The major findings are:

- The co-formation of other salts near the eutectic point of hydrohalite can be limited through the mixing of waste water streams from multiple wells
- An average Marcellus/Utica brine exhibits first the formation of ice, followed by eutectic co-formation of hydrohalite and ice
- Marcellus produced water volumes in Pennsylvania are expected to raise to 71 MMbbl by 2022
- The nonrecoverable energy requirement for an average Marcellus Shale produced water stream is  $179\text{kWh/m}^3$
- The cost of EFC treatment in the Middle-Atlantic Region is estimated to be \$1.93/bbl
- When accounting for recovered costs from the potential sale of crystallized salt the treatment cost is reduced to \$0.82/bbl, similar to that of membrane distillation [9]

## Chapter 1 - Background and Motivation

### 1.1 BACKGROUND AND MOTIVATION FOR SELECTION OF RESEARCH FOCUS

#### *1.1.1 What is Eutectic Freeze Crystallization*

Eutectic Freeze Crystallization (EFC) is a low temperature desalination technique that can retrieve salt and water in pure form from a brine at a relatively low energy cost. The basis of EFC is the existence of eutectic point (EP) for every salt solution. The EP is a characteristic point in the phase diagram of a salt-water mixture where an equilibrium exists between ice, salt and solution with a specific concentration. This specific concentration is called eutectic concentration (EC) and the temperature at which the equilibrium is achieved is called the eutectic temperature (ET). EFC is less energy intensive compared to evaporative crystallization because the energy required to separate water as ice is significantly lower than that required for separating it as a vapor. Numerically this can be seen by the fact that the heat of fusion of ice (6.01 kJ/mol) is less than the heat of evaporation of water (40.65 kJ/mol). Additionally, EFC allows for the recovery of pure salts from the solution.

#### *1.1.2 Oil and Gas Industry Overview*

The oil and gas industry is encompassing and broad; employing or supporting nearly 10 million U.S. jobs, thereby accounting for a sizeable stimulus (9%) of the domestic economy [10]. Including jobs, the O&G industry includes an extensive network of pipes and refineries necessary to refine and produce useable forms of energy for crude oil and natural gases as well as chemical precursors used in nearly every industry on the planet



[11]-[12]. Internationally, the yearly consumption of hydrocarbons is around 35 billion barrels of oil and liquid equivalents (BOE) [13].

In general terms, the oil and gas industry is divided into three components: upstream, downstream and midstream [14]. Each provides different services and performs a distinguishing task in the job of producing hydrocarbon to the products consumers desire. Upstream production primarily includes those companies and industries involved with the exploration and production of the hydrocarbons to the surface, while downstream focuses on refining and distributing the products that are used by consumers, be it gasoline for automobiles, or industrial chemicals for the synthesis of plastics and polymers [11]. Naturally, the midstream division is responsible then for facilitating the transportation of the raw hydrocarbons from the upstream production sites to these downstream refineries and distribution centers. This is accomplished through a network of pipes, railcars, and oil tanker ships [15]. The service and supply structure of the actual hydrocarbon production process is also extensive. A network of service companies provides the technical expertise to these hydrocarbon producers as well as the products required, such as pipe, mud, sand, etc. it is this service and supply that help to drive innovation and growth in the oilfield by focusing on new methods of recovery, as well as innovative tools and equipment to produce at higher levels of recovery and lower the environmental impact of operations [16].

The “Shale Boom” or “Shale Revolution” that started in 2008 has been a game changer that has reshaped both the US energy industry, and the global energy landscape [17].

As crooks (2015) puts it: “The US oil boom has had profound implications for the rest of

the world, boosting economic growth and enhancing America’s global influence [18].”

Due to the recent massive exploitation of unconventional oil and gas reserves, the US has become the number one producer of the unconventional oil and gas in the world.

As shown in **Figure 1.1** and **Figure 1.2**, oil and gas production from unconventional reservoirs has grown significantly since the early days and has continuously increased until the downturn in 2014. Natural gas production is projected to increase by 49% of the total US gas production by 2035. Furthermore, as shown in **Figure 1.3**, the US net import of natural gas has drastically decreased, and the US has gained more energy security as it has grown ever closer to energy independence from domestic sources.

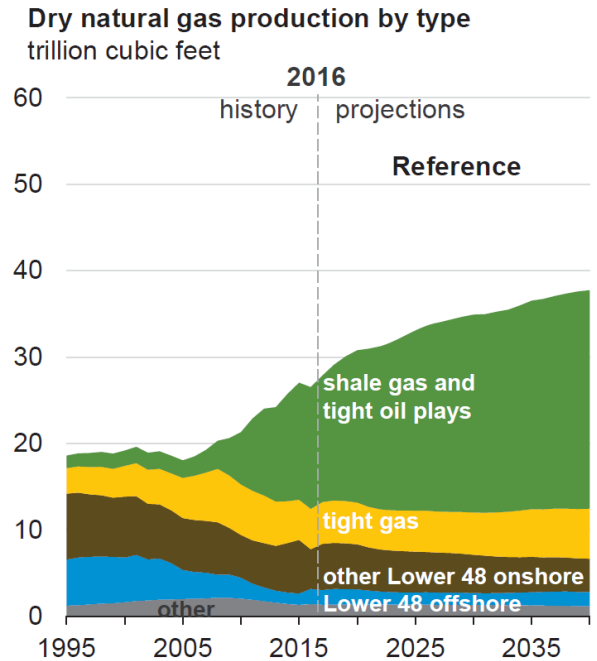


Figure 1.1 - US Oil and Gas Production Historic Data and Projection (1995-2040) [1].

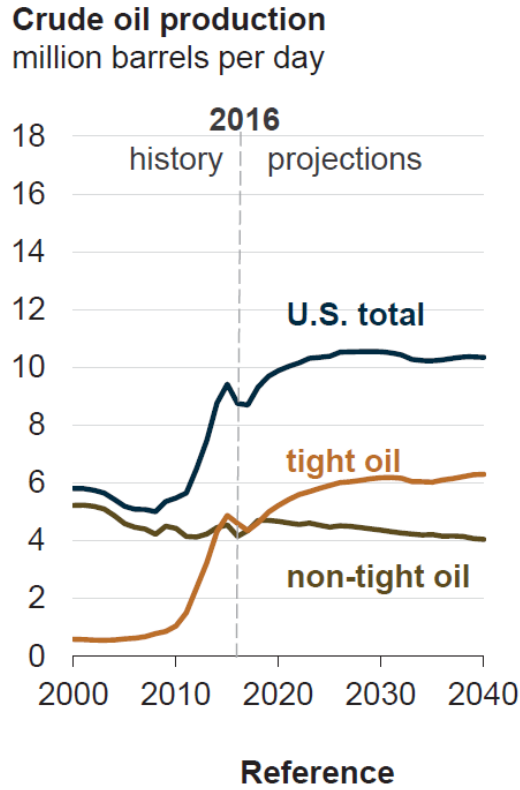


Figure 1.2 - US Tight Oil Production Historic Data and Projection (2000-2040) [1].

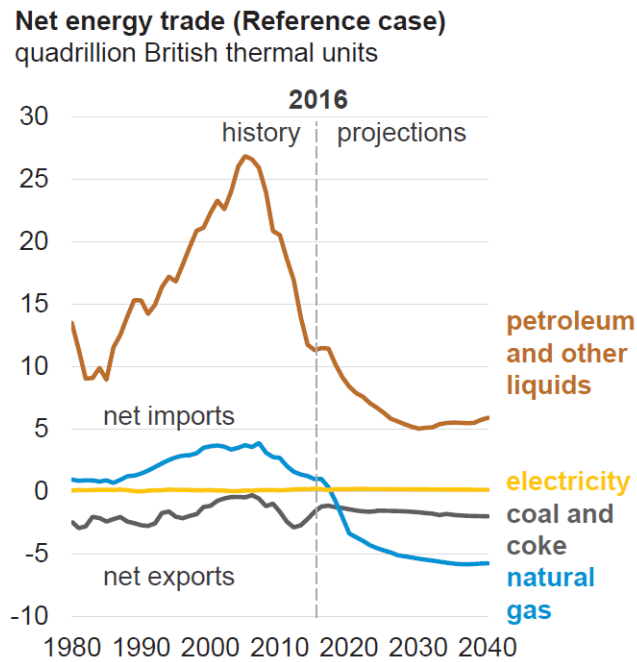


Figure 1.3 - Impact of Shale Boom on US Energy Independence [1].

In addition, the Shale Boom has greatly influenced the job market in the oil and gas industry, adding a significant number of jobs. According to Reuters (2015), “A U.S. oil and gas drilling boom fueled by hydraulic fracturing technology added about 725,000 jobs nationwide between 2005 and 2012 [19].” In addition to such huge economic impacts, this boom has had political, social, and environmental effects domestically and globally, but these are beyond the scope of this work and will not be discussed further.

The main causes of this boom are the recent technological advancements in horizontal drilling, and multistage hydraulic fracturing that enables drilling of extended reach wells that can contact a large section of the reservoir laterally. Hydraulically fracturing the formation to create fractures increases the formation permeability and allows for the petroleum to flow through into the wellbore.

Permeability of a reservoir rock describes how easily or fast the fluids can be moved into the wellbore and brought to the surface. Conventional reservoirs are characterized as high permeability reservoirs, while unconventional reservoirs have extremely low permeability. Due to high permeability of conventional reservoirs, when a vertical well is drilled into the reservoir rock, the fluids within the rock can easily travel through the rock and reach to the wellbore. However, in unconventional reservoirs, the fluids cannot travel and reach to the wellbore with native formation permeability. This is the main reason why the industry has been producing from conventional reservoirs for over one hundred years with vertical wells but has not been able to produce from unconventional reservoirs until just recently. The sources of unconventional reservoirs are shale oil,

shale gas, coalbed methane, tight sandstones, and methane hydrates. The US shale plays are shown in **Figure 1.4**.

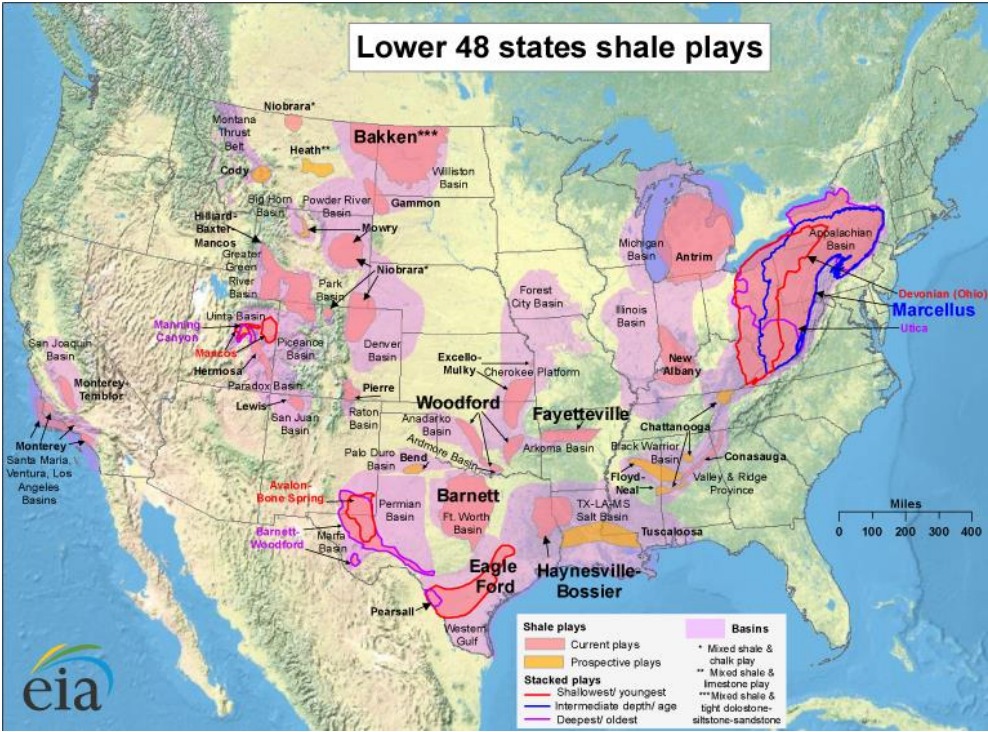


Figure 1.4 - Currently Producing Shale Plays in the Contiguous U.S [1].

**1.1.3 Water Production in Oil and Gas Industry**

This constant need for technological advances is ever growing as societies and governments become more conscious of the environmental impact of anthropological carbon emissions and pollution caused by industrial processes. Technological improvements will always be necessary for companies to remain competitive, whether it's designing new tools or developing unconventional energy resources [20].

While common knowledge to industry professionals, the subject of co-produced water (also sometimes referred to as associated water) with the production of hydrocarbons is often unknown to those professionals of other industries. To explain how and why

water is present with oil, first an overview of the hydrocarbon generation process is necessary.

Hydrocarbons originally form from bitumen, a thick tarry substance leftover from the decay of organisms that expire and are transported to anoxic conditions. Typically, this is either plankton sinking to the sea bed, or trees and plant material preserved in marshes and estuaries [21]. This organic material is chemically altered by the heat and pressure of successive sediment burial over time. Eventually the bitumen turns to kerogen and in turn to oil and/or gas, depending on the temperature and pressure to which it is subjected. Because this bituminous rock and subsequent sedimentary reservoir rocks were deposited in aquatic environments, they are naturally saturated with brine. The salinity and makeup of these brines can vary substantially based on the location and minerals present but consists largely of sodium chloride with some calcium carbonate. Shown in **Figure 1.5**, These newly formed hydrocarbons, being less dense than water, begin to migrate towards the Earth's surface through this brine reservoir under buoyancy drive.

It is because of this replacement of brine with oil that there remains brine in reservoirs that are produced for their oil and gas. In the United States, the average ratio of water-to-oil production in 2012 was 9.2 [22].

This produced water represents a significant challenge from a disposal perspective as it is too saline for release to the environment without detrimental ecological effects but

can't always be put back underground without ill effects to the reservoir. These dilemmas and their significance are further explored in Sections 2.3 and 2.4.

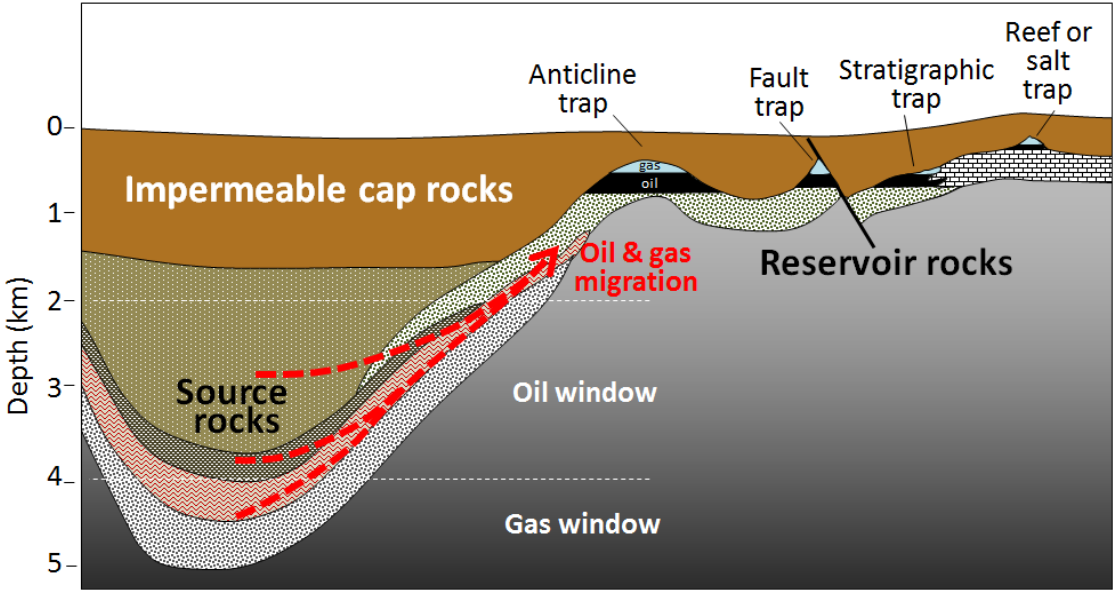


Figure 1.5 - Depiction of hydrocarbon migration [23]

**1.1.4 Baker Hughes Challenge Problem**

The Baker Hughes 21<sup>st</sup> Century Co-Op at the University of Oklahoma through the Gallogly School of Aerospace and Mechanical Engineering and the Mewbourne School of Petroleum and Geological Engineering is a five year BS/MS degree pilot program in mechanical and petroleum engineering aimed at developing technical competencies and meta-competencies needed by engineers to hit the road running and succeed in the oil and gas industry [24]. In addition to core courses in mechanical engineering, the curriculum includes customized courses jointly offered by company engineers and faculty during summer internships, a senior capstone experience and graduate theses that are of relevance to the sponsoring company, and graduate cross-disciplinary courses from the School of Industrial and Systems Engineering and the Mewbourne School of

Petroleum and Geological Engineering. This program is dual disciplinary, bringing together undergraduates of both petroleum and mechanical disciplines so that they might leverage from each other's foundational strengths to become successful future engineers. The Co-Op spanned multiple classes of students, each divided based on their year of program matriculation (i.e., BHI-13 consists of scholars who were undergraduate sophomores in the Spring of 2013).

Larry Watkins of Baker Hughes Inc. presented the BHI Scholars with the "challenge problem" in the beginning of the 2014 Fall Semester. Below was the problem presented to the team:

*"The BHI-13 team focused on establishing an overview of unconventional hydrocarbon resources, primarily shale plays. The challenge for BHI-14 is to extend the efforts from where BHI-13 ended. The challenge for BHI-14 is to review and identify the go forward challenges facing development of shale. For this challenge, consider the following dimensions (question areas) for developing shale:*

- *Technical Issues*
- *Political Issues*
- *Economics of Shale Development*
- *Recovery Factors in Shale*

*Political Issues: Identify and discuss factors in the political realm that currently influence development of shale resources. Provide thoughts on ways to mitigate these factors including but not limited to education or improved operating methods.*

*Economics of Shale Development: Identify key factors that currently limit the economics of shale development. These factors include but are not limited to knowledge required for planning well paths and*



*completion methods, approaches of different types of E&P companies to well placement and planning, costs/supply of components for well completions and fracture operations. Discuss how these factors influence the overall economics for E&P companies in shale operations.*

*Technical Issues: Identify and discuss the limitations of current technologies used in shale development. Discuss if the limitations are specific hardware, methods, materials, fundamental knowledge or combinations of these. Describe which technology areas influence the other elements of this challenge and then rank the technology issues in order of greatest positive impact on shale development going forward.*

*Recovery Factors in Shale: Identify the factors that currently determine initial recovery factors in shale development areas. Describe how uncertainty in the input parameters influences the recovery from shale reservoirs. Provide a prioritized list of which information would provide the greatest reduction in uncertainty when initially estimating recovery. Discuss what actions might be possible to improve recovery.”*

As a group, the BHI Scholars framed the shale development problem in the industry today looking at four different perspectives: technical, political, economics, and recovery factors. Identifying the drivers, focuses, issues, and major dilemmas within the perspective further expanded each perspective using research techniques to be expanded upon in Sections 1.2.2 and 1.2.3. The dilemmas allow the team to pose research questions that will provide knowledge to manage the dilemmas.

#### **1.1.5 Baker Hughes Challenge Problem: Research Approach**

The BHI scholars broke into two interdisciplinary teams in order to tackle the challenge problem. Mechanical and petroleum engineering backgrounds were represented in both groups. The perspectives were split on terms of apparent connectivity. Each perspective

was framed using the sustainability triangle.

A sustainability triangle, which is elaborated upon in Section 1.1.3, allows the team to organize complexity. The team assessed the perspectives from three different drivers including: social, environment, and economic. We further analyzed the drivers by determining the focus of the driver and the issues that are present in the industry from the corresponding perspective. The next step is to connect each issue from each driver to another issue of another driver. This connection needs to reveal tension present between the issues. These tensional connections propose dilemmas. The three types of dilemmas we analyzed are social/economic, social/environment, and economic/environment. This step is repeated for each of the issues in each of the drivers connected to each of the other issues in each of the other drivers. Once the team identified multiple dilemmas around each perspective, we were able to narrow down the choices to focus on the most relevant challenges that the industry is facing today. The end use for the Baker Hughes Challenge Problem paper was to identify these industry dilemmas, thereby allowing for research questions and, ultimately, master's thesis topics to be identified by the BHI scholars.

#### *1.1.6 Sustainability Triangle and Issue Refinement*

It should be noted that the triangle is focused around a particular perspective. The three drivers, social, environmental, and economic, are used to identify issues surrounding the core perspective. Once the issues are addressed, tensions can easily be identified between the issues. A tension is represented by two issues that seemingly pull against each other. Once the tensions are identified, the dilemmas, or tensions with 0-1 solutions

can be identified. These dilemmas are quite complex and cannot be easily solved with a simple solution. The 0-1 solution to the dilemma implies that if one issue is addressed, the other issue seemingly must be ignored; in other words, there can seemingly be only one winner. A visual representation of the sustainability triangle used to identify industry dilemmas can be seen below as **Figure 1.6**.

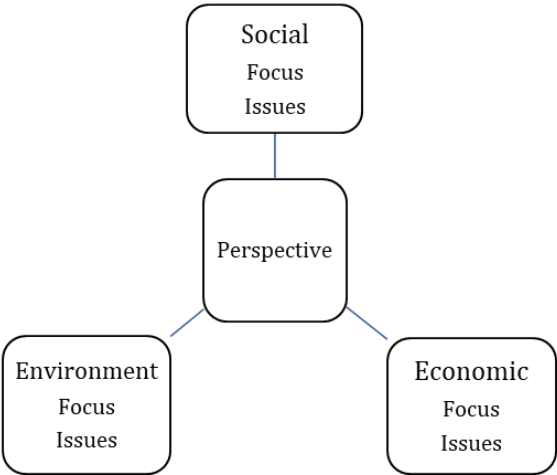


Figure 1.6 - Visual Representation of the Sustainability Triangle

The completed sustainability triangle for the political perspective can be seen below in **Figure 1.7**. Notice the difference between the tensions and the boxed dilemmas. This sustainability triangle yielded six dilemmas which were later refined to just three; one for each node on the triangle. After each perspective had a completed sustainability triangle, the BHI team created a mind map, shown in detail in Section 1.2.1, which reveals the connectivity between the issues in all perspectives. By looking at the connectivity, the team is able to reveal tension present between perspectives resulting in dilemmas. The team was then able to further prioritize the dilemmas and decide where the focus of the challenge has the most tension present and thus is in most need of an innovative positive sum solution.

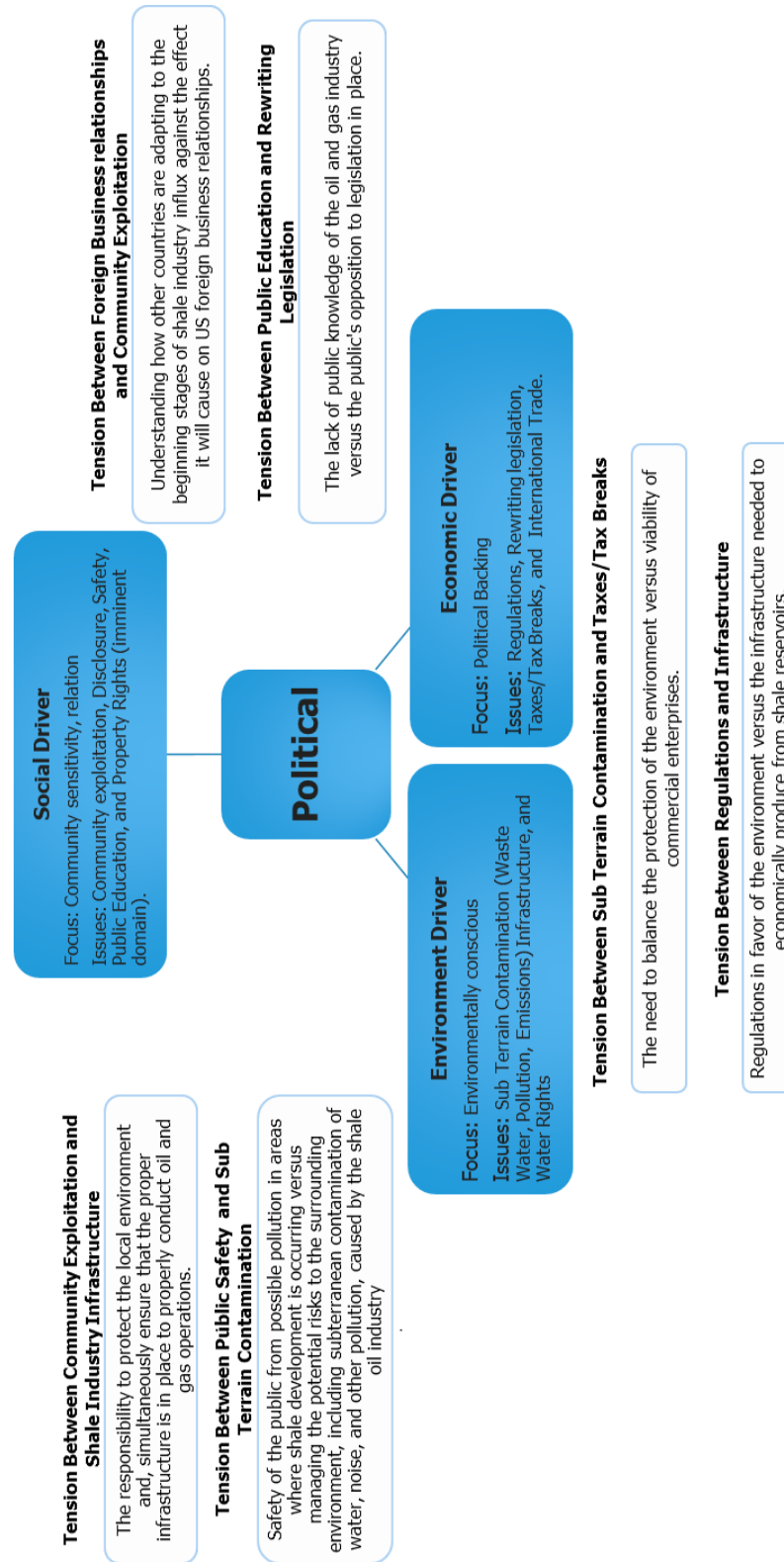


Figure 1.7 - Completed Sustainability Triangle for the Political Perspective

## 1.2 FORMULATON OF RESEARCH QUESTIONS

### 1.2.1 Process for Selection of Research Questions

Research Questions were formed from the tensions represented in each dilemma. The tensions lead to natural questions about the cause and effects of the dilemma. Why do these phenomena occur? What effects can come about because of the tension between issues? In what ways are the issues opposing one another? What variables are relevant to the tension? These high-level questions regarding the nature of the dilemma must lead to specific Research Questions that can be investigated through experimentation. The dilemma triangle that was used to construct these Research Questions is shown below in **Figure 1.8**. In the scope of this thesis, such question development follows:

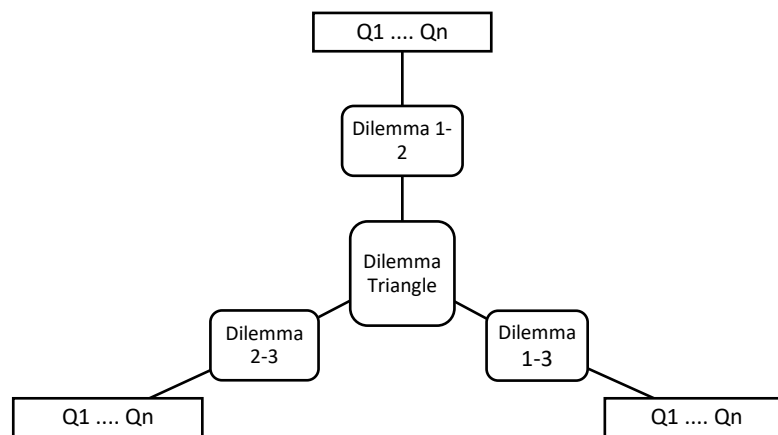


Figure 1.8 - Visual of the Dilemma Triangle used to select Research Questions

Since the beginning of the challenge problem research, my focus has been on the political perspective. The two primary dilemmas that were identified by my work on the challenge problem that I have chosen to investigate further both stem from environmental/social issues and are as follows:

- The dilemma between existing infrastructure and current regulations and legislation
- The dilemma between concerns for public safety and the effects of subterranean contamination, specifically induced seismicity

From these dilemmas and the connectivity “mind map” (**Figure 1.9**), I was able to develop four complex research questions based on the main research question:

- How can the subterranean effects of waste water injection be reduced?

The decision-making process to narrow down the potential research questions was complex. It was important that the questions were relevant to the main research question and also would provide valuable insight once addressed. Because the foundation of the issues with subterranean contamination surrounding waste water injection wells are largely economic and political, it made sense that those were the areas on the connectivity mind map that were utilized in the decision-making process. Also, the current social relevance of seismic activity resulting from injection wells around and in the state of Oklahoma heightened not just the importance and relevance of this thesis, but also the breadth and quality of available information. Because of the need for a new and more technological method for the disposal of waste water brines exists, the purpose of this thesis is to analyze in depth the applicability of an unconventional brine desalination method to the needs of oilfield waste water processing.

The four research questions to be explored throughout this paper are:

1. What changes need to be made to freeze crystallization desalination technology

with oilfield operations?

2. What environmental benefits will be realized by treating water for reuse/release over underground injection?
3. How can public safety be maintained or improved while decreasing the use of underground water injection?
4. How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?

The connectivity between the Baker Hughes 21<sup>st</sup> Century Co-op and the research focus of this thesis can be seen below in **Figure 1.9**. The primary research question in consideration for this thesis, as well as secondary research questions, are discussed in further detail in Section 1.3.1. In order to expand upon and improve current knowledge, a firm understanding must be established on both the current laws and regulations surrounding waste water in ejection, as well as the current alternative methods of wastewater disposal. This is expounded upon in Section 2.1.1.

### 1.2.2 Additional Information Needed to Proceed with Research

Considering my Research Questions:

1. How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?
2. What changes need to be made to freeze crystallization desalination technology for compatibility with oilfield operations?
3. What environmental benefits will be realized by treating water for reuse/release over underground water injection?

4. How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?

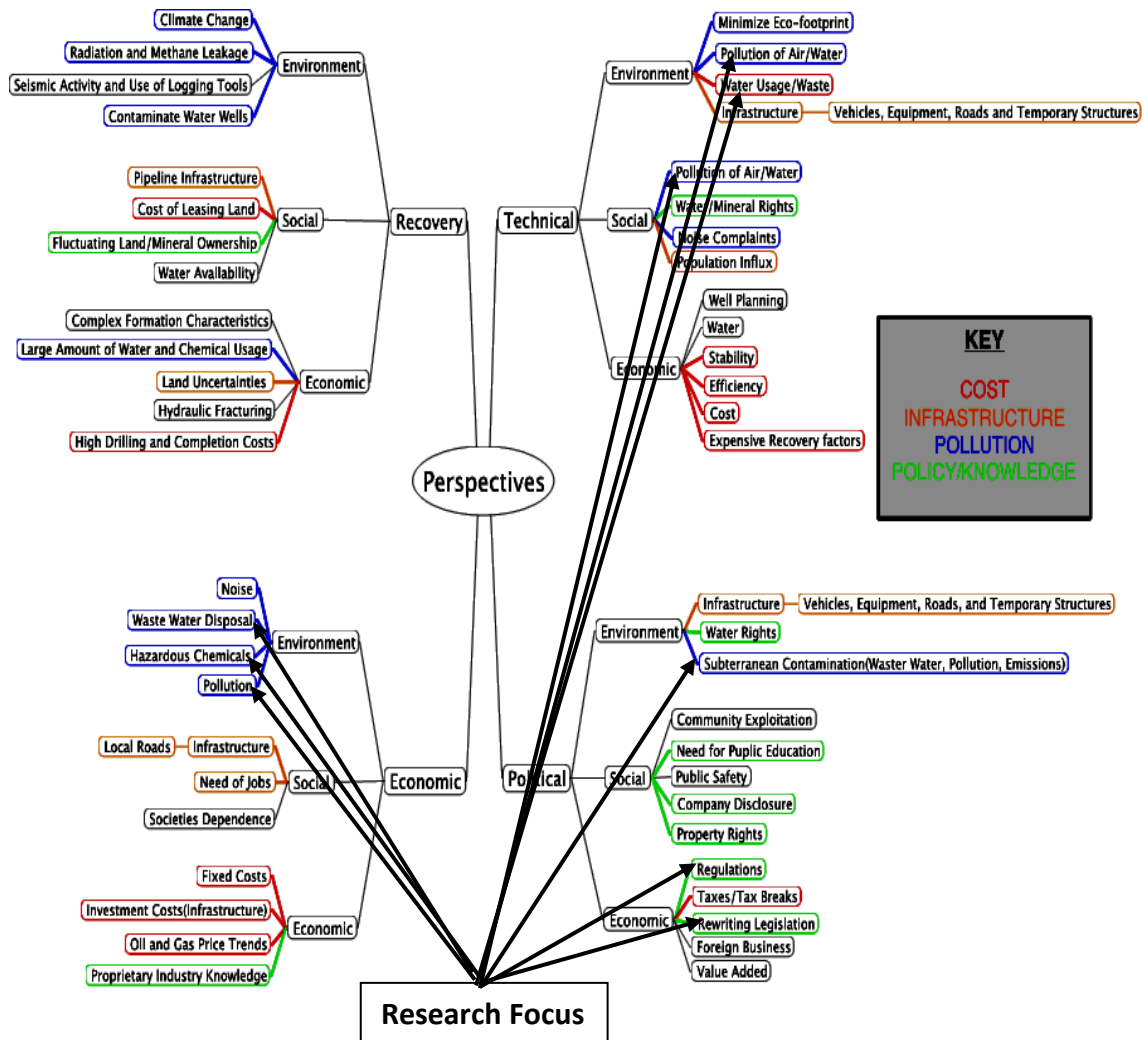


Figure 1.9 – “Mind Map” Showing the Connectivity of Research Questions

In order to continue my research, narrow in on potential methods, and to get started with more technical literary review, I requested the following information from Baker Hughes Inc.:

- Lists of all injection wells in Oklahoma or Texas, including their positions and average volume of water injected per year.



- Current research papers Baker Hughes has written/taken part in that discuss negating seismic effects.
- Current research papers Baker Hughes has written/taken part in that discuss alternative methods of wastewater disposal.
- Information regarding potential resources for conducting experiments surrounding waste water injection volumes (and/or flow rates).
- Water Quality Reports from wells under Baker Hughes authority, including common freshwater Water Quality Reports
- The names of a few Baker Hughes contacts who I could communicate with regarding research questions and technical issues.

The information requested, specifically the current research papers Baker Hughes has written/ taken part in that discuss negating seismic effects, will help substantially in narrowing my focus onto a feasible solution method that is not only logical, but of relevance to Baker Hughes. The information requested will assist me in addressing the Research Questions in the following ways:

Table 1.1 - Visualization of the Requested Information for Each Research Question

INFORMATION REQUESTED	RESEARCH QUESTION 1	RESEARCH QUESTION 2	RESEARCH QUESTION 3	RESEARCH QUESTION 4
Lists of injection wells in Oklahoma or Texas, including their positions and average volume of water injected per year.	X	X		

Current research papers Baker Hughes has written/ taken part in that discuss negating seismic effects.		X	X	
Current research papers Baker Hughes has written/taken part in that discuss alternative methods of wastewater disposal.		X	X	X
Information regarding potential resources for conducting experiments surrounding waste water injection volumes (and/or flow rates)	X			X
The names of a few Baker Hughes contacts who I could communicate with regarding research questions and technical issues.	X	X	X	X

### 1.3 GOALS AND FOCUS FOR THE WORK

#### 1.3.1 Intellectual Questions for Investigation

In this section, I will outline and explain the importance of the intellectual research questions in the grand scheme of the entire paper. The four Research Questions serve not only as supplemental information for satisfactorily addressing the main Research Question, but they will individually provide amazing insight and connectivity to the process as a whole; all of the questions have elements that tie them to the issues and solutions posed with the other questions.

- What changes need to be made to freeze crystallization desalination technology

with oilfield operations?

- What environmental benefits will be realized by treating water for reuse/release over underground injection?
- How can public safety be maintained or improved while decreasing the use of underground water injection?
- How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?

The first Research Question addressed the physical nature of what causes seismic activity in the first place. Answering this question is central to this thesis. Without understanding what about waste water injection causes a predisposition for seismic activity, the problem could not be sufficiently addressed. This question leads into the discussion of the actual act of wastewater injection, how it could potentially be updated or improved, and how it could be done in a way that would reduce seismic activity.

The second question is the most basic and fundamental. The legislation surrounding the oil and gas industry and hydraulic fracturing in particular, is a very interesting and complex topic in its own right. However, in order to appreciate the complexities of hydraulic fracturing and its byproducts in a political-economic mindset, one must first understand the legal boundaries and political opposition of the technology. In order to propose an alternative plan for waste water injection, understanding the intricacies of the laws is essential. This question is also particularly relevant currently, as litigation surrounding the amount of waste water injected in the state and the environmental and seismic concerns it is raising is coming to the forefront as oil and gas companies battle

with environmental and special interest groups. Another slightly subtler issue that answering this question will address is the education (or lack thereof) of the general public on the technology and methods involved in hydraulic fracturing and waste water disposal. The importance of this subtlety should not be overlooked, because public opinion is such an important influence over state legislators and their decision-making process.

The third question is crucially important not only to myself, but to every single employer in the world. Employee safety is and should be the highest priority when it comes to oil and gas operation. Because of this, while investigating ways to make fundamental changes to the way waste water is disposed it is essential that worksite safety is factored into decision making. There are always ways to cut corners and take unnecessary risks to increase profits, but those are not acceptable solutions to a complex problem like the one posed in this thesis.

The fourth Research Question addressed the utilization of existing infrastructure to address the waste water disposal issue. This is especially important when maintaining the economic feasibility of any proposed solution due to the massive savings associated with the utilization of existing infrastructure in lieu of building new facilities. Large scale waste water treatment plants have been utilized in North Dakota and Texas and are used to recycle massive amounts of flow back water and reuse it as fracking water, which greatly decreases associated costs of new water and water disposal. There are municipal wastewater plants all over North Dakota, but in the past, the flow back water has proven far too polluted with suspended particulates, radioactive earth, and other

fracturing chemicals to be treated in a municipal treatment center. Finding a way to utilize existing technology and water treatment facilities would be a step in the right direction to lower the dependence on waste water injection as the state's primary method of disposal.

### *1.3.2 Objective for the Thesis*

This thesis is to be one primarily of utility to Baker Hughes and the service industry as a whole, as well as lobbyists and policy makers in the state of Oklahoma and abroad by accomplishing the following objectives:

- Proposing a reduction of the seismic effects of waste water disposal in Oklahoma and other actively developed petroleum regions by suggesting specific alternative methods and/or procedures of waste water disposal that could be utilized by corporations. Alternative methods to be considered are the surveying of fault lines prior to drilling injection wells to decrease the probability of seismic reactions, utilizing waste water recycling and reuse technology, or otherwise disposing of the water in a cost effective, environmentally friendly way.
- Describing in detail the current available methods and technologies associated with waste water, as well as the current legislation and laws surrounding its disposal and reuse.
- Providing insight amidst pending litigation to ongoing environmental, social, and political conflicts between waste water injecting companies and environmental groups.

The following table outlines exactly where each intellectual research question is

addressed in the remaining chapters.

Table 1.2 - Research Questions and Chapter Layout

Relevant Sections: Intellectual Questions	Chapter 2				Chapter 3					Chapter 4			
	2.1	2.2	2.3	2.4	3.1	3.2	3.3	3.4	3.5	4.1	4.2	4.3	4.4
What are the main factors that facilitate seismic activity near the well site and how	X	X	X	X	X				X				X
What legislation and regulations are currently in place that interferes with the	X	X		X	X	X	X	X	X		X		
How can wellsite safety be maintained or improved all while decreasing the seismic effects associated	X	X		X					X				
How can alternative methods of waste water disposal be utilized with	X	X		X	X	X	X	X	X	X	X		

It is hoped that in the completion of this thesis, it will act as a comprehensive report on waste water disposal that can be used and referenced as a means of educating citizens about the oil and gas industry, their methods and technology, as well as the necessity of the safe and efficient disposal of waste water in the state.

In Chapter 2 is a detailed literature review and research gap analysis, as well as framing the thought process for Chapters 3 and 4 while continuing to remain connected to the Challenge Problem outlined in Chapter 1, Sections 1.1.1 and 1.1.2.

A very utility-heavy chapter, Chapter 3 includes simulation and commentary on a state of the art water recycling method used intermittently in the mining industry; Eutectic Freeze Crystallization. This chapter is of crucial importance to developing a deep

understanding of the benefits and drawbacks of alternative disposal methods, as well as the feasibility compared to underground injection in regards to the geographical and geological conditions and laws and regulations of oil producing states.

Chapter 4 includes descriptions of further Research Gaps that must be explored to validate EFC for compatibility with oilfield operations and a system design for freeze crystallization is proposed, along with corresponding cost and feasibility analysis.

Chapter 5 includes a statistical economic assessment of EFC thermodynamics and compares this to other methods that are employed to date for commercial water desalination and treatment in the petroleum industry.

### *1.3.3 Connection of Thesis to Baker Hughes Challenge Problem*

The main, driving force behind the Baker Hughes 21<sup>st</sup> Century Co-Op program was to create a group of inter-disciplined, motivated and hardworking engineering students who would be able to hit the road running in the oil and gas industry after graduation thanks to the experiences gained in three summer internships, inter-disciplinary course work, and the team dynamic. The blending of mechanical engineering and petroleum engineering curriculum would make students a very unique and qualified candidate for employment.

Because of this, it was very important that from the beginning, the master's theses produced by the group be related and relevant to Baker Hughes, further strengthening

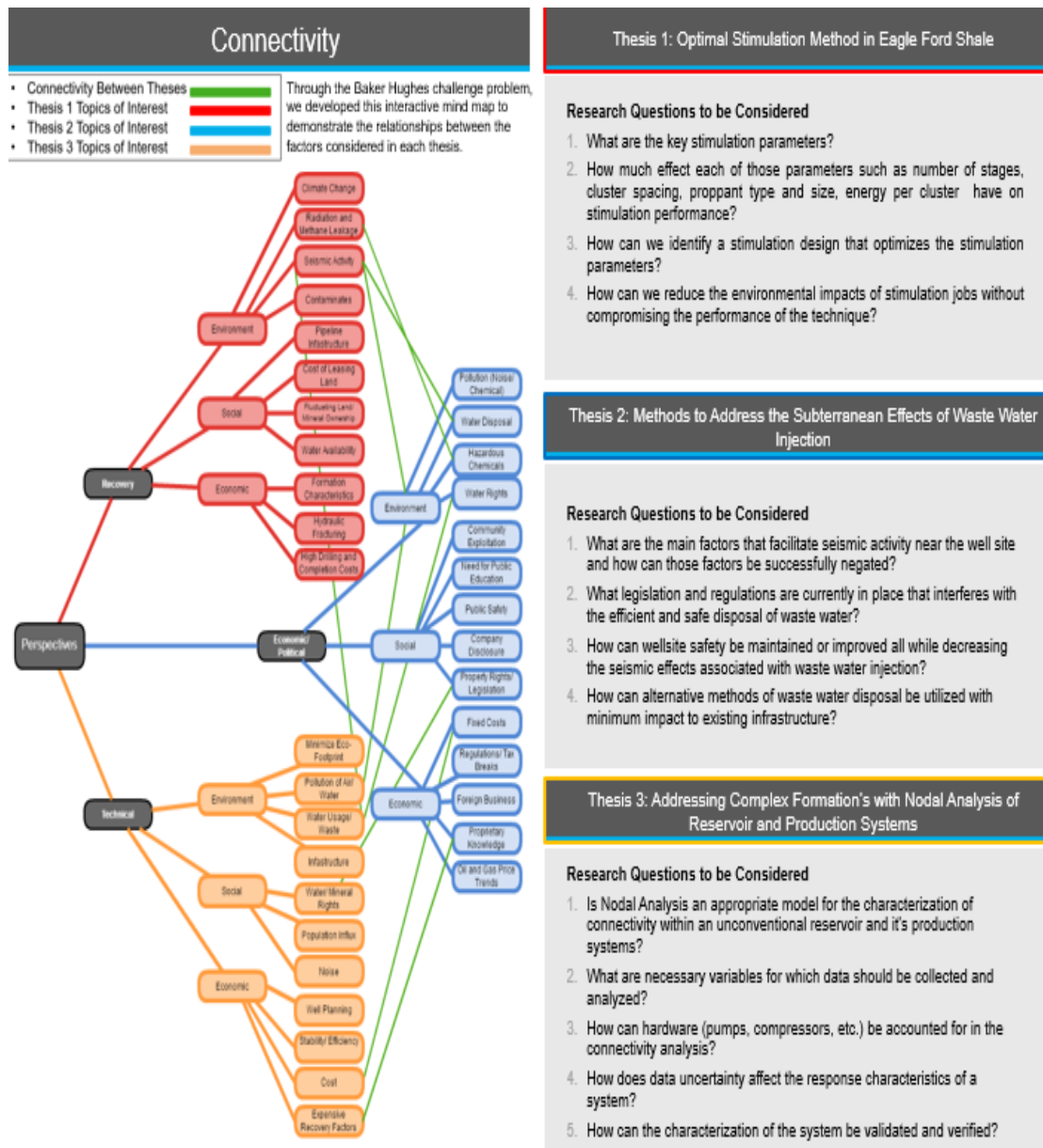


Figure 1.10 - Graphic Showing the Connectivity of Master's Theses

the utility to them and the industry. Similar to the mind map, the **Figure 1.10** is designed to demonstrate the connectivity between the research done in the Baker Hughes 21st Century Co-op and the thesis. However, this refined graphic shows not only the connectivity to this thesis, but also the connectivity to the other BHI15 member's thesis.



Shown in Figure 1.10 are the dilemmas that were created through the use of the Baker Hughes challenge problem research using the dilemma triangle method. They are color coded to demonstrate their association with one of the three thesis topics seen to the right of the image. The green lines seen between the dilemmas cross into multiple theses, showing the connectivity between the two theses.

#### 1.3.4 Engineering and Scientific Relevance of the Work

The engineering and scientific relevance to this thesis lies in the utility it provides to oil and gas corporations, Baker Hughes, and the general public. Regardless of one's stance in the debate over what is causing the influx of earthquakes, it is fact that seismic activity is damaging, expensive, and increasingly prevalent in Oklahoma.

Through a thorough analysis of the main existing methods of wastewater disposal (recycling for reuse, recycling, cleaning, and release into the environment, transportation away from well site and left in evaporation pools, and deep waste water injection) the potential for identifying research gaps in industry methods and research increases dramatically. Currently, waste water disposal methods vary based on region due to factors like legislation, cost, water availability, and executive decisions. By learning about the reasons behind the methods used across the country, the ability to propose a realistic, feasible solution in Oklahoma becomes possible. Ideally, after the method is proposed, seismic simulations can be used to verify the method's "success." The ability to propose a solution that would decrease the seismic effects associated with waste water injection would be a large leap in the correct direction for the state of Oklahoma, as well as for any corporation that actively altered their procedures and

policies to adhere to a stricter, more seismic-friendly method of waste water disposal. Especially for a company like Baker Hughes, an industry leader in environmental protection, public and employee safety, and innovation, it would be groundbreaking for them to consider a method to reduce waste water injection volumes. Hopefully, other companies would follow suit, creating a wave of change throughout the world as more companies look to decrease their negative environmental impacts.

## 1.4 ORGANIZATION OF THE WORK

### 1.4.1 Overview of Implementation Strategy

Firstly, literature will be evaluated and compiled into a detailed review in order to sculpt the final structure of the research questions, while also leading towards the use of industry standard modelling software for the use in simulation. At this point, many chapters will be completed concurrently which will benefit each by making them more interconnected and easily updateable for a PhD dissertation at a later time.

Verification and Validation of the work outlined above will be performed using the method described in Section 1.4.2. Applicability of the research questions will continue to be tested through the use of the Sustainability Triangle (Section 1.1.3).

### 1.4.2 Overview of Verification and Validation Strategy

In this report, the terms validation and verification refer to the justification of knowledge claims and the internal consistency of the context, respectively. We will be paying close attention to the validation square which is also going to be the bases of the logical flow of the content of the thesis. As shown in **Figure 1.11**, the validation square

is composed of four categories which are theoretical structural validity, empirical structural validity, empirical performance validity, and theoretical performance validity.

Theoretical structural validity deals with the internal consistency of the design method or the approach which basically means considering the logical soundness of the individual parts and integrated parts of the design or approach. Chapters 2 and 3 in the thesis will be focused on this aspect of the validation square and will indicate if the design method is internally consistent. In Chapters 2 and 3, we will do a literature review of the topics and subjects related to the investigated problem, and we will identify the current common methods used to deal with and study the investigated problem. Once a common method has been determined or developed, the important parameters of the design method will be identified and discussed. To ensure the internal consistency of the design method, the limitations and the uncertainty of the developed method will be clearly demonstrated at the end of chapter 3.

The second aspect of the validation square is empirical structural validity which refers to the appropriateness of the chosen example problems intended to test the design method. Chapters 4, and 5 are used to test the empirical structural validity of the design method. In Chapter 4, some examples will be used to develop a decision model and the relationship of those examples to the actual problem will be closely checked to ensure they reflect the important parameters associated with the investigated problem. We will also include a discussion about the uncertainty associated with the chosen examples and how that uncertainty can affect the results. In Chapter 5, we will show some examples that can measure or show the performance of the design method or model

developed. Those examples will test only the performance of the model and at this stage some changes may be made to the model or method if required to ensure that the desired performance is achieved. In Chapter 6, we will develop a comprehensive method or model and make all the changes needed based on the results of the examples used in Chapters 4 and 5. Once a comprehensive model is developed, examples will be used to test the efficiency and effectiveness of the model and how reasonable are the results, this will lead us to the quadrant three of the validation square which is empirical performance validity. This quadrant deals with the ability to produce useful results for the chosen examples. The outputs of the approach or model will be checked for their feasibility against all the constraints of the chosen examples. We also perform a sensitivity analysis of the model to check the rationality of the model's outputs and to see how realistic the results are.

The last part of the validation square is theoretical performance validity which deals with the ability of the model to produce useful results beyond the chosen example problems which requires testing the model with other problems and analyzing the results to see if they are reasonable and realistic [25].

Chapter 5 is focused on this aspect of the validation square, and in this chapter, we also conclude the thesis with a discussion of the limitations of the model and the uncertainty associated with the results gained from the model. Some recommendations for future studies in the related area will be introduced.

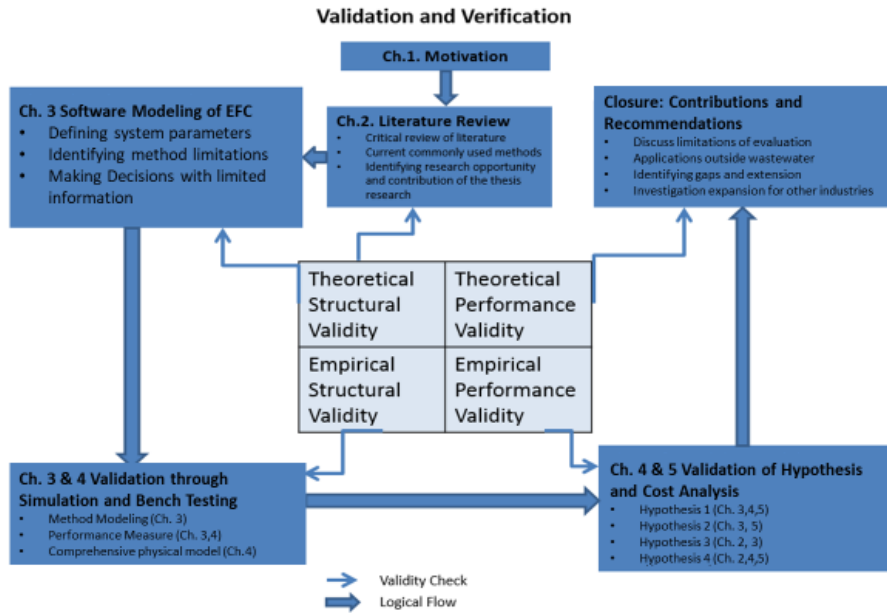


Figure 1.11 - Verification and Validation Square and Strategy

## 1.5 SYNOPSIS OF CHAPTER ONE

In this chapter, the foundation for the thesis is laid. We begin with an introduction to the oil and gas industry and a review on the process of oil generation and cohabitation of brine in oil systems. A review into the necessitation of technological advance in the industry is followed by a background and a motivation section that describes the 18-month long process of working with the Baker Hughes Challenge Problem, and the process of identifying and refining my research areas. From this process, four research questions are defined and the connectivity to the overall theme of the thesis is identified, only to be further elaborated upon throughout the rest of the thesis. Once the questions are posed and a strategy for their solution is created, significant engineering and scientific contributions of the work are discussed in Section 1.3.3. The connectivity between the research questions and the challenge problem will be further substantiated in Chapter 2 through the critical literature review.

## Chapter 2 - Critical Literature Review

In this Chapter, literature about the social and political implications of waste water disposal is critically evaluated. Further, literature surrounding the physical components of the wellsite that contribute to the issue, as well as previous industry attempts to negate the effects of this problem will be considered and analyzed. From the information gathered, Research Gaps that exist in the current procedure are explored in the context of the Sustainability Triangle introduced in Section 1.2 and value of the thesis topic in relation to the needs of the industry as a whole and Baker Hughes is evaluated in Section 2.4. Our aim with this Chapter is to introduce the complexity of water disposal in the oilfield to those who might be unfamiliar, and to highlight shortcomings of current methodology which leads to the justification and potential benefit of using EFC as a new technology for waste water treatment. Once we have provided an overview of waste water disposal techniques currently in use and justified the Research Questions, we start answering the Research Questions in Chapter 3.

### 2.1 CRITICAL LITERATURE REVIEW SUMMARY

Provided in this Section is a condensed version of the overall literature review provided in the succeeding Sections (2.3 – 2.5) and that provides a contextual commentary to frame the Research Gap identification and Research Question generation of Section 1.2 as they relate to Eutectic Freeze Crystallization. Following the connection of the Research Gaps to the relevant Research Questions, we show the connection of the literature review as a whole back to the Research Questions tabularly to show the connection of each succeeding section to this one. This connection of each individual

Research Question to the relevant following Chapters is outlined in Section 2.1.2 at the end of each paragraph.

### 2.1.1 Connectivity of Literature Review to Research Questions

In this Section, the connection between the critical evaluation of the literature and the elucidated Research Gaps is discussed. In **Table 2.2** below, connection between key papers and the characteristics of a sustainable water treatment method (discussed in Section 1.2.1) are shown. Additionally, the objectives, constraints and uncertainties discussed within the papers are abbreviated and included to show connection to the Research Questions and their formulation (discussed in Section 1.2.2). The color scheme ties the sources to the specific Research Questions that are included in **Table 2.1**.

*Table 2.1 - Connection of Literature Review to Research Questions*

Chapters	Research Questions	1	2	3	4	5
	RQ1: How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?	F	J	Q1	Q2,3	Q4
	RQ2: What changes need to be made to desalination technology for compatibility with oilfield operations?	F	J	Q1,2		Q3,4
	RQ3: What environmental benefits will be realized by treating water for reuse/release over underground water injection?		F, J	Q1,2	Q3	Q4
	RQ4: How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?	F	J	Q1,2	Q3,4	

Following the table in Section 2.1.2 is a dialogue in which the key points from each paper are synthesized and identifies the Research Gaps that exist and what needs to be done to resolve them. Specific continuation of the Research Gap identification through literature review is performed in Section 2.3. The 'Objective' identified in Table 2.2 is the objective of the author in the paper as it pertains to the Research Questions for this thesis, primarily the cause and effect of waste water disposal and recycling and the use of Eutectic Freeze Crystallization for desalination of produced water. 'Constraints' refers to the constraints I have identified that prohibit the use of the method the author has either introduced or defended, and in the case of papers regarding social implications, the effect of location and social attitude to the perception of the implemented technology. Finally, 'Uncertainty' refers to the factors to which the proposed method or information is sensitive and what changes in the system could make it become unstable in the future. While this might seem unclear, with the use of an example it should become clear. Pierce and Bertrand [26] mention that water recycling helps with sustainability in their paper. Their analysis acknowledges that in shale plays "the access to injection wells for disposal of produced water is very limited" and that a partial solution to costly disposal that necessitates transportation would be "to recycle the [water] for use as Frac Fluid or as drilling fluid." Their reasoning for the need to recycle water is not because of environmental damage caused by release or injection (such as induced seismicity), but rather cost; it is simply sometimes more economical to try and use the produced water for frac fluid (recycling) rather than paying for transportation to a disposal site. Therefore, in the 'Objective' category there is a label of "Max profit" as



the authors motivation for the paper and the technology is to maximize the margin for producers. Similarly, for 'Constraints', they understand and pose the question to the reader of "What techniques are used to clean this water and what regulations [pertain] to the various techniques." Therefore, the constraint as identified is what laws and regulations must be followed in order to comply and simultaneously lower water management costs. Finally, the 'Uncertainty' in their analysis requires more evaluation than analysis. Pierce and Bertrand mention and pose the question of what techniques or methods should be used but they do not acknowledge that the method might not be uniform for all fields and could vary depending on the degree of separation desired, as well as the properties of the water itself. Additionally, their analysis focuses on the cost of disposal for West Texas which is enormously lower than that of the Northeast, therefore they have not considered the effects of regionality on proposing a solution. Because of the aforementioned, the 'Uncertainty' is identified as what method or methods to use. Similarly, the other papers were categorized, and the 'Objective', 'Constraint', and 'Uncertainties' are listed, if they are pertinent or identifiable to the task at hand. The connection between the papers and the characteristics of the solution to the Research Gaps is performed in Section 2.3.

Table 2.2 - Connectivity of Literature Review to Research Gaps

Paper	Waste Water Management																Objective	Constraints	Uncertainty	
	Reduce			Reuse			Recycle			Revenue			Other							
	Access to Underground Injection	Reduces Revenue Stream	Reduces Seismic Activity	Provides use for Limited Treated Water	Fresh Water Availability	Reuse for Hydraulic Fracturing	Insensitive to Water Quality	Zero Liquid Discharge (ZLD)	Safety of Released Water	Provides Revenue Stream	Reduced Energy Cost	Low Facility/ Equipment Costs	Market for Treated Water	Reduces Impact to other Industries	Uses Existing Technology	Removes or Insensitive to TSS				Removes or Insensitive to O&G
[26]	*				*			*										Max Profit	EPA Regulations for Release	What method or methods to use
[27]									*			*				*	*	Reduce Environmental Footprint	Regulations, Local concerns	Long term effects
[28]	*		*	*										*				Improve Reserves w/ Econ. Disposal	-	Scale of increase
[29]					*	*	*								*	*		Reuse Prod. Water for Fracking	Water Quality	Scalability
[30]					*		*	*					*					Increase Regulation	Anticipated Technology	Regionality
[31]		*		*						*	*							-	Cost of Disposal	Regulatory Changes
[32]					*								*					-	-	Model Adequacy
[33]					*			*		*			*					New Source of Potable Water	Water Availability	Climatic Changes
[34]						*		*	*		*	*					*	-	-	-
[35]				*						*	*	*		*				-	-	-

Waste Water Management																					
Paper	Reduce			Reuse			Recycle			Revenue				Other					Objective	Constraints	Uncertainty
	Access to Underground Injection	Reduces Revenue Stream	Reduces Seismic Activity	Provides use for Limited Treated Water	Fresh Water Availability	Reuse for Hydraulic Fracturing	Insensitive to Water Quality	Zero Liquid Discharge (ZLD)	Safety of Released Water	Provides Revenue Stream	Reduced Energy Cost	Low Facility/ Equipment Costs	Market for Treated Water	Reduces Impact to other Industries	Uses Existing Technology	Removes or Insensitive to TSS	Removes or Insensitive to O&G	Scalability			
[36]	*		*	*	*	*			*				*						Reduce Water Intensive Development	Alternatives to Injection Disposal	Local Needs and Impact
[8]		*			*				*	*	*								Disposal Cost	Regionality	Reuse
[2]		*	*		*				*	*			*						Reuse Water	Non-potable Use	Demand
[37]	*				*				*	*		*						*	Improve Reserves w/ Econ. Disposal	-	Scale of increase
[4]	*					*	*		*	*	*	*						*	Increase Shale Development	Water Disposal	Natural Gas Demand
[38]								*	*		*				*				Social Water Management	Social Education	Degree of Water Recycling
[39]	*										*		*					*	Increase Shale Development	Water Disposal	Natural Gas Demand
[40]	*	*													*	*			Inject High Salinity Brines	Suspended Solids	Formation Compatibility
[41]		*	*		*		*	*	*					*				*	Desalination with EFC	Salinity and Refrigeration	Effect of Contaminants
[42]	*				*	*								*					-	-	Water Availability
[6]		*							*	*					*			*	Validate EFC	System Adequacy	Heat Transfer, Measurement

Waste Water Management																					
Paper	Reduce			Reuse			Recycle			Revenue				Other					Objective	Constraints	Uncertainty
	Access to Underground Injection	Reduces Revenue Stream	Reduces Seismic Activity	Provides use for Limited Treated Water	Fresh Water Availability	Reuse for Hydraulic Fracturing	Insensitive to Water Quality	Zero Liquid Discharge (ZLD)	Safety of Released Water	Provides Revenue Stream	Reduced Energy Cost	Low Facility/ Equipment Costs	Market for Treated Water	Reduces Impact to other Industries	Uses Existing Technology	Removes or Insensitive to TSS	Removes or Insensitive to O&G	Scalability			
[43]	*		*		*	*				*	*						*	Validate EFC	Regionality of Water	Sensitivity of EFC	
[3]		*							*			*					*	EFC for multicomponent Brine	System size	pH, common ion effect, etc.	
[44]		*			*		*	*					*				*	Lifecycle Assessment	Desired Degree of separation	Water Quality Throughput	
[5]		*		*	*		*	*			*	*		*			*	Achieve ZLD	Value of crystallized components	Water Quality, interactive effects	
[45]	*		*	*	*		*								*		*	Recover produced water	Reduce energy consumption	Climate and water availability	
[46]		*									*			*	*		*	Utilize RO for water treatment	No O&G	Degree of separation	
[47]											*		*	*				Reduce environmental impact	Delivery method of water	Impact of traffic on road quality	
[48]					*			*				*		*				Increase water availability	Cost	Lifecycle of method	
[49]	*	*						*		*					*		*	Desalination of produced water	Salinity	Effects of O&G	

### 2.1.2 Identification of Research Gaps

In Section 2.3, we see that there are few sustainable options that exist in the current technology of waste water disposal/treatment that are being applied to the task of produced water treatment in the oil industry. Little water treatment is performed on waste water due to the high perceived cost of treatment and the low cost of disposal through injection wells [50]. Aqwaterc [35] mentions that the relevant constituents for removal in produced water are: “Salt content, Oil and Grease (O&G), organic compounds, and Naturally Occurring Radioactive Material (NORM).” Given the current research status of EFC is very young, there has been no investigation into the sensitivity of the crystallization nucleation process to the presence of contaminants such as suspended solids, O&G, or NORM. therefore, first an investigation of what effects, if any, the presence of these components would have on the EFC process needs to be performed to validate the method for the task of waste water treatment at an industrial capacity. The work presented in this thesis focuses primarily on the effects of NORM components on the nucleation of both salt and ice crystals, as it is assumed that a high level of preliminary treatment can be performed to remove most of the O&G and suspended solids. There are many well-known solutions to these problems, such as the use of an API separator for solids and gross Oil and Grease removal, while electrocoagulation can be used to flocculate remaining O&G [51, 52]. Further experimentation should be performed to determine the effect of suspended solids and O&G to determine whether their removal by pretreatment is warranted, or whether this step can be removed as well. This gap in knowledge between the ability of EFC to

desalinate brine streams and the effects of common coproduced water stream contaminants is a gap that leads to the formulation of **Research Question 1: *How can freeze crystallization be utilized to treat flowback and coproduced water from oilfield operations?*** The ability of EFC to desalinate complex brines is explored through Chapter 3 via simulation to determine if the technology is capable of separating multi-species brines that are common of produced water. Sections 4.1 and 4.2 include discussion on future bench scale work that should be performed to validate EFC through physical processes. Finally, economic considerations are included in Section 5.2 to evaluate if the method of EFC desalination could be implemented commercially.

The current EFC freeze chamber design that F. vd Ham [41] presents is of utility only for bench scale experimentation due to size (10 L). He outlines the design of a scraped cooled wall crystallizer (SCWC) capable of separating ice and salt crystals gravimetrically and the recycling of the mother liquor for further processing. Verbeek [6] builds on this original SCWC design and investigates the EFC process on a skid mounted EFC design that is capable of treating 200 L at a time. While this is a substantially larger volume, it is still not adequate in addressing whether EFC can accommodate the substantial ( $\geq 1,500,000$  L) stream that can be associated with a moderate (5 wells) sized advanced age oilfield. However, their work into the scalability of the EFC process can be expanded to address the gap of whether freeze crystallization desalination technology can be upscaled enough to handle the waste water streams. The compatibility of EFC to oilfield operation is primarily investigated to address any deficiencies or roadblocks that would delay implementation of this technology into the current infrastructure of treatment

facilities in the industry, such as refineries or injection wellhead locations where significant infrastructure already exists. Lu [43] addresses the use of EFC for treating coproduced water from Kuwait and the treatment of low salinity flowback water from Shale gas fracturing in the Marcellus. Unfortunately, Lu does not address what effect, if any, the presence of minute contaminants such as NORM, or solid contaminants such as residual hydrocarbon and suspend solids would have on the EFC process. He acknowledges that, “In order to be able to make better cost calculations and compare them with evaporative crystallization, a more thorough study of all parameters involved in the EFC and recrystallization process is necessary. Some examples of important aspects to investigate are continuous operation (a commercial process will be continuous) and scaling up to larger scale. Also, EFC of produced waters from different origin and composition have to be studied.” He hints on an important issue. The driving factor for adoption of this technology by the oil industry is precisely the cost of a commercial operation and the robustness of the method to be applied to waters of varying qualities and origin. The latter is addressed through Research Question 1, while the former relates to the changes that need to be made to the technology for commercial upscaling. This gap is foundational to **Research Question 2: *What changes need to be made to freeze crystallization desalination technology for compatibility with oilfield operations?*** This gap is further explored in Section 3.5 by investigating the effect of common waste water stream contaminants on the EFC temperature for streams from the Marcellus and Utica shales. Additionally, Section 5.2 contains a

discussion into the economics of EFC and preliminary work into cost estimation for treatment via EFC (in \$/bbl) is presented.

Many areas with developed oilfields in the U.S. are in areas deemed as vulnerable to drought [33] and there is an alarming history of mega-droughts lasting 300 years or longer in many western U.S. states such as Nevada, California, Arizona, and Utah [32]. This disturbing potential future of little potable water is underscored dramatically by the use and disposal of > 20,000 gallons per well of fresh water for hydraulic fracturing of new wells in these states. In many cases, the solution means recycling flowback or produced water to limit the need for fresh water in the production of hydrocarbons [31]. However, the recycling or release of produced water is often met with unintentional ecological consequences. Current regulation in Eastern Shale gas states (Pennsylvania and West Virginia) is heavy on regulating underground injection as a legacy of existing legislation passed in historic oil producing states such as Oklahoma and Texas, but have failed in implementing meaningful legislation regulating the release of tainted waters to the environment [30]. Given that there are little Class II brine disposal wells associated with the Marcellus Shale Gas production states, it is likely that recycling will be the way forward for development, but that underground injection is currently the only long term viable option for a future of gas production in the area. Arthur, Dutnell, and Cornue [28] acknowledge that there is an associated infrastructural cost to the disposal through injection in the form of road damage, minor releases, and traffic related casualties that should be considered in an injection schema. Because of the potential detriments associated with injection are so many, Gupta and Hlidek [29] speculate that there is



potential for an optimized recycling operation for the recycling of frac fluid as the cost of sourcing fresh water and disposal of waste water increases with water scarcity that will reduce the dependence on injection for disposal and water management. Recently in Oklahoma a connection between Class II injection wells and earthquakes (hereto referred to as induced seismicity) has been noted [53]. A gap exists regarding whether there is a current recycling method that can help hydrologically impacted areas while simultaneously reducing anthropogenic seismic activity and associated environmental destruction such as roads and bridges by overuse of heavy disposal trucks and machinery and whether these recycling methods can reduce unforeseen environmental damage in the form of detrimental releases of toxic salts into estuaries and streams. This gap is analyzed through **Research Question 3: *What environmental benefits will be realized by treating water for reuse/release over underground water injection?*** This Research Question is evaluated through Section 3.5 in a discussion regarding the reduced water volumes associated with freeze crystallization and the potential energy savings realized through the use of the crystallization method over others. Additionally, in Section 4.2 commentary on the economic value of pure crystallized salt is presented and what impact this could have on national anhydrous NaCl production and associated environmental impact. Finally, in Section 5.2 a holistic economic analysis of freeze crystallization is performed that highlights the usefulness of the technology in reducing water injection disposal and the potential release of fresh water to the environment.

Refineries on average use 2.5 gallons of water for every gallon of crude processed. This combined with the introduction on entrained water from crude delivery means that the

typically refinery deals with upwards of 10 million gallons of 'dirty' water daily. Typical dirty water processing at the refinery level includes membrane technologies (RO) and thermal distillation for water reuse [54]. Thermal distillation is the most common water treatment technique as it is economical and technically simple, the plants already have the necessary permits to use this technology. New refineries are stressed to reduce costs and consumption by adopting new lower energy desalination and treatment methods while minimizing discharges. Haddaway [55] mentions that the key is [to], "use existing waste or low-value streams from oil and gas exploration (and other industrial processes) to reduce the amount of effluent generated." By recycling water again and again for use in the refinery, the newer plants are able to reduce their environmental footprint, reduce costly permitting and consumption costs, while simultaneously reducing energy consumption with energy efficient new equipment. What hasn't changed however, is the technology that is in use. Thermal distillation, while appropriate for refinery use, is at the edge of what is theoretically possible through energy efficiency, and there are little gains to be had from further optimization at this point. EFC has the potential to use less energy than a thermal process while simultaneously allowing for the continued recycling of water within the refinery and being at an early technological stage, has numerous opportunities for energy optimization. While it is clear that there is need for efficient water treatment at the refinery level, and indeed waste water treatment from crude production as well, it isn't certain what changes would need to be implemented at the refinery level to have compatibility with freeze crystallization, given refineries have been utilizing thermal distillation for so many years. This gap is addressed by the

**Research Question 4: *How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?*** This Research Question is developed in Section 4.4 with discussion on the sensitivity analysis of EFC temperature and this implication on the design of a EFC treatment facility. Through Section 5.5, future research needs for EFC and discussion about other problems for which EFC can be applied are covered to strengthen the relationship between EFC as a water treatment method and refinery operations.

## 2.2 CONCEPT AND RESEARCH GAP EXPLORATION

In this Section, the connection of the Challenge Problem introduced in Chapter 1 to the Research Gaps identified in Section 2.1 is presented. The key background subjects and their connection to the Research Gaps are explored in Sections 2.2.2 and 2.2.3. Finally, having established the principal background subjects and the connection of the Research Gaps to the motivation for this work, the needs of desalination specifically in waste water recycling is explored. This Section is instrumental in understanding the disposal method critical literature evaluation performed in Section 2.3 and justifies the need subject of desalination in a sustainable oilfield environment for those unfamiliar with produced water and its properties.

### 2.2.1 Connection of Challenge Problem to Research Gaps

The main, driving force behind the Baker Hughes 21<sup>st</sup> Century Co-op program was to create a group of inter-disciplined, motivated and hardworking engineering students who would be able to hit the road running in the oil and gas industry after graduation thanks to the experiences gained in three summer internships, inter-disciplinary course

work, and the team dynamic. The blending of mechanical engineering and petroleum engineering curriculum would make students a very unique and qualified candidate for employment.

Because of this, it was very important that from the beginning, the master's theses produced by the group be related and relevant to Baker Hughes, further strengthening the utility to them and the industry as a whole. Similar to the mind map, **Figure 2.1** below is designed to demonstrate the connectivity between the research done in the Baker Hughes 21st Century Co-op and the thesis. However, this refined graphic shows not only the connectivity to this thesis, but also the connectivity to the other BHI15 members' theses. This is a visual demonstration of exactly how we can work as a team and support each other and our research endeavors throughout the thesis writing and research process.

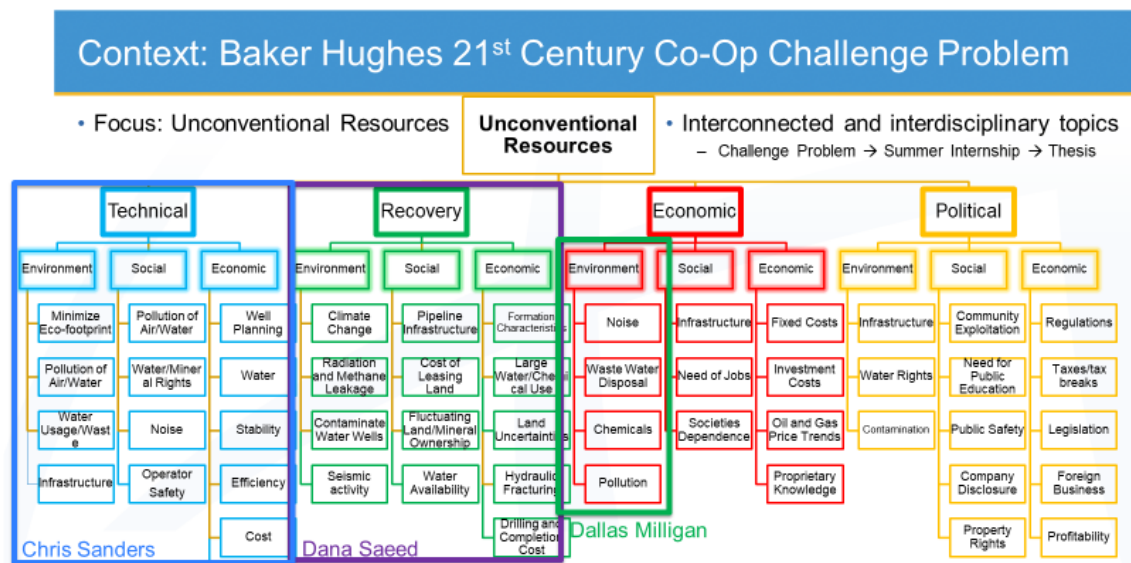


Figure 2.1 - Connectivity of Research Gaps to Challenge Problem

Having identified the relevant drivers through the process described in Section 1.1.3, the Research Gaps that are identified in Section 2.1 are anchored in the context of the Challenge Problem, specifically in the perspective of environmental effects in the focus of economic exploitation of unconventional resources.

### *2.2.2 Introduction to Desalination*

Desalination is defined as any process that removes salts from water, or another solvent phase. Desalination processes are used in municipal, industrial, and commercial applications. With improvements in technology, desalination processes are becoming cost-competitive with other methods of producing usable water for our growing needs, but many new methods are being developed. The primary methods in use today are thermal or membrane technologies.

During World War II, with limited fresh water availability in certain localities, it was felt that desalination should be developed to convert saline water to useful fresh potable water for use. Subsequently, “The Saline Water Act” was passed by Congress in 1952 to provide federal support for desalination technology for use both domestically and internationally. The U.S. Department of the Interior provided funding during the 1950s and 60s for initial development of desalination technology, and for construction of small scale desalination plants [56].

Desalination is a relatively new science and continues to undergo technological improvements. While it is a new science, it has resounding social implications for maintaining quality of life and reducing political rancor the world over. President

Kennedy has said, “No water resources program is of greater long-range importance than our efforts to convert water from the world’s greatest and cheapest natural resources – our oceans – into water fit for our homes and industry. Such a break-through would end bitter struggles between neighbors, states and nations”. Those statement are truer today more than ever.

### 2.2.3 Introduction to Produced Water

According to OSPAR [57] (OSLO-PARIS) “Recommendation 2001/1” Produced Water means water which is produced in oil and/or gas production operations and includes formation water, condensation water and re-produced injection water; it also includes water used for desalting oil. Produced water is a complex mixture. It also has wide variations in composition within and between reservoirs as well as with the age of fields. The following materials are generally associated with produced water:

- Dispersed hydrocarbons – oil droplets mainly aliphatic hydrocarbons
- Dissolved hydrocarbons – aromatic and polycyclic aromatic hydrocarbons (PAHs)
- Soluble organics: phenols, fatty acids
- Salt content
- Production chemicals
- Heavy metals
- Radioactive materials

Hydrocarbons originally form from bitumen, a thick tarry substance leftover from the decay of organisms that expire and are transported to anoxic conditions. Typically, this is either plankton sinking to the sea bed, or trees and plant material preserved in marshes and estuaries [21]. This organic material is chemically altered by the heat and pressure of successive sediment burial over time. Eventually the bitumen turns to kerogen and in turn to oil and/or gas, depending on the temperature and pressure to which it is subjected. Because this bituminous rock and subsequent sedimentary reservoir rocks were deposited in aquatic environments, they are naturally saturated with brine. The salinity and makeup of these brines can vary substantially based on the location and minerals present but consists largely of sodium chloride and calcium carbonate. Shown in Figure 1.5, These newly formed hydrocarbons, being less dense than water, begin to migrate towards the Earth's surface through this brine reservoir under buoyancy drive.

Because of this replacement of brine with oil that there remains brine in reservoirs that are produced for their oil and gas. In the United States, the average ratio of water-to-oil production in 2012 was 9.2 [22].

This produced water represents a significant challenge from a disposal perspective as it is too saline for release to the environment without detrimental ecological effects but can't always be put back underground without ill effects to reservoir performance. These dilemmas and their significance are further identified in Sections 2.3 and 2.4.

#### 2.2.4 Needs of Desalination in Waste Water Recycling

If there is any hope to recycle produced water for uses other than hydraulic fracturing or subsurface reuse in the oilfield, extensive treating need occur. Specifically, the majority of treating that needs to occur is in the desalinating of the produced water. As stated before in Section 1.1.2 and 2.2.3, produced water is a hypersaline brine that consists primarily of sodium, calcium, carbonate and chloride ions. The high salinity of this brine makes it unsuitable for release into estuaries and for agricultural given the stress sensitivity of flora and fauna [58]. As well, some dissolved minerals and trace elements that are harmful to life are present in produced water. This ranges from carcinogenic trace aromatic and aliphatic hydrocarbons to boron and NORM. While most hydrocarbons can be separated gravimetrically using an API separator [51], micro emulsions and polar hydrocarbons often remain in solution after separation and pose a threat to life if released to the environment immediately. Given that the largest proportion of contaminants, and the most difficult to remove, in produced water are the dissolved solids, it is therefore important that desalination occur prior to release in ensure that treated water meets the EPA standards for released waters [2]. The moral and legal obligations of corporations who wish to participate in water recycling over water disposal will be discussed in further detail in Section 5.3.

### 2.3 WASTE WATER DISPOSAL ANALYSIS

In this Section, expanding on Table 2.2 we provide a critical literature evaluation of the currently employed methods of waste water management and disposal in Section 2.3.1. Next in Section 2.3.2, the limitations of the disposal methods introduced in Section 2.3.1



are evaluated. In Section 2.3.3 the connection between injection disposal wells and seismic activity are explored briefly as a context setter for potential ramifications of the current methods discussed in Section 2.3.1. Because of many perceived notions of the higher cost of recycling compared to injection, this topic receives its own Section in 2.3.4. The recycling cost is directly related to one of the characteristics of a sustainable water management system of Table 2.2 presented in Section 2.1. Given the validity of Section 2.3.4 on the economic considerations of recycling waste water, the potential of release of the treated water versus reuse is discussed in Section 2.3.5. Specifically, what potential reuse parameters and uses are also discussed. Finally, in Section 2.3.6, the current status of water recycling in the oilfield industry is discussed to set the scene for the potential implementation of recycling in the industry given the causes of induced seismicity presented in Section 2.3.3 and the potential for reuse in Section 2.3.5. Limitations and potential road blocks to the implementation of water recycling in the oilfield is introduced in Section 2.3.7 with specific emphasis on the impact of trace organics on different water processing methods and to what degree this issue must be solved for water recycling to move forward as a viable solution in the industry. This entire Section is foundational to the justification of Research Question 2 and the thesis as a whole by introducing the current status of the water management in the industry and evaluating to what degree current recycling methods are successful or unsuccessful.

### *2.3.1 Study of Available Disposal Methods*

Historically, the treatment of produced water has been limited to the removal of free oil and suspended solids using physical separation, followed by overboard disposal for

offshore platforms or injection either for pressure maintenance or disposal inland [48]. Development of unconventional resources in deep shale reservoirs has emerged as a hotly debated issue in the domestic energy production market. The use of hydraulic fracturing to liberate the gases and oil is associated with the flow back of high TDS water to surface. These waters are costly and challenging to treat. Current economic constraints have promoted the use of Class II disposal wells as the primary management method of the water resources. Unfortunately, in many areas where shale gas production will be abundant, injection sites are not available and other management strategies will need be implemented to make economical exploitation of natural gas a viable fuel for the future of the United States [4]. Injection of water for disposal purposes is a relatively simple and low-cost management solution. Limitations and ramifications of its continued use in some shale play areas, such as Northeast Oklahoma, will be discussed in the succeeding Sections 2.3.2 and 2.3.3.

A more technologically advanced method of disposal with limited application to the treatment of produced water is membrane distillation [46]. The use of this technology is limited to moderately high salinity water (70,000 mg/L) that is free of contaminants that could cause membrane fouling, such as suspended oil, aromatics, organics, solids, and microorganisms. Because of these constraints, the use of membrane distillation technology is limited to those uses where pretreatment has occurred. In some low contaminant, clean water areas membrane technology has been successfully implemented to reduce injection volumes of deep-well injection, thereby diminishing the environmental impacts associated with underground injection. The limitations of

current membrane technology to the task of treating specifically produced water are discussed in Section 2.3.2.

In addition to deep-well injection, current refinery entrained water disposal methods include the use of thermal evaporators. These allow for the total evaporation of produced water which dramatically reduces the fresh water volume required to makeup fracturing water and other refinery water needs. The evaporation systems do require significant pretreatment to remove the oleic residuals and other suspended solids. Interestingly enough, the use of thermal evaporation has grown in niche markets where there is significant gas to power the thermal evaporators, but no nearby market connections for gas transportation. Specifically, its growth has been successful in SAGD areas such as the oil sands of Canada where the heated steam has local uses as well.

While not entirely a disposal method per se, the use of electroagulation has remained popular since the 1980s as the preferred method to remove suspended solids and residual O&G from produced water. This treatment method is currently paired with API water separators for field water management and in refineries for specific flocculation use. Enumerated in **Figure 2.2** is the process of electrocoagulation and how it allows for the flocculation of small suspended solids.

The last common disposal method currently employed for produced water is the simple recycling for onsite reuse for hydraulic fracturing [2]. Fracture fluid is generally significantly viscosified for enhanced fracture generation and to carry proppant to effective areas of the fractures. The chemistry of surfactant-gel fluid is insensitive to

water quality which makes the recycling concept successful [29]. The reuse for fracturing or mud mixing is as old as the use of mud in drilling itself. The new technology that is greatly increasing the acceptance and use of reuse for the particular task of fracturing is the use of evermore sophisticated gelling agents that foam and gel successfully at high TDS. Combined with the expense for injection disposal and the fact that many areas of drilling have been experiencing draught condition on and off for the last few years, the average 50% reduction in fresh water consumption through reuse has become an attractive water management process.

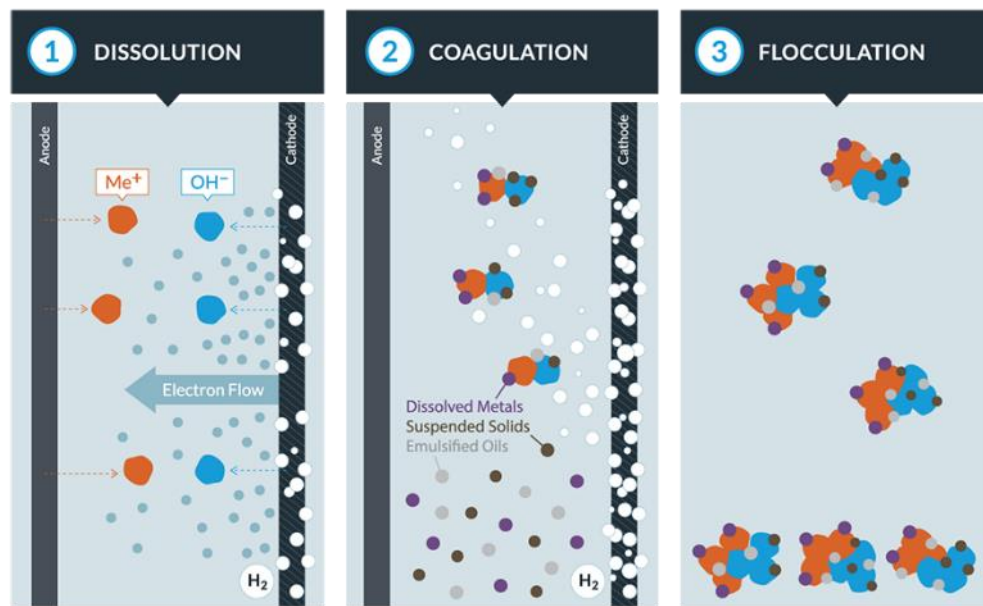


Figure 2.2 - Flocculation of suspended solids with Electrocoagulation [59]

In the proceeding Section the limitations and ramifications of the above commonly used water disposal methods will be analyzed as they pertain to a sustainable and environmentally friendly water management system.

### *2.3.2 Limitation of Available Disposal*

One of the major limitations of deep-well injection is the impacts and implications associated with seismic activity. For more detail on the connection to seismic activity of deep-injection wells, see Section 2.3.3. As mentioned in Section 2.3.1, the historical and main water management tool currently remains injection wells. Increasingly high salinity brines are reducing the injectivity of some wells, which in turn is causing some water management firms to reject large volumes of high salinity brine in favor of more injectable fluids [40]. The injection well offers a low-cost solution to water management needs and creates value from older nonproducing wells. Coupled with the fact that there are many nearby legacy wells that can be retrofitted to injection, it superficially appears to be a viable disposal solution for years to come. Only recently has there been a connection between injection rate and volumes with anthropogenic seismic activity. As perception of the negatives of injection disposal grows and the water cut of aging wells increases, the viability of injection disposal will diminish as costs inevitably rise [8]. As operators and the public become more aware of the ramifications of injection disposal and the possible environmental detriment caused therein, there will become a shift in mentality away from injection disposal to a water recycling method. This change will be fueled by cost effective and efficient solutions that need to be developed and designed for tomorrow.

Thermal evaporation is used successfully in many arid regions for freshwater generation and disposal of produced waters [60]. The product of thermal evaporation is water vapor and a conglomerated salt inclusive of all the species present in solution. This type

of disposal of produced water is similar in cost to membrane treatment but is also met with increased facilities and equipment costs due to the corrosion rate of saturated, hot brines. Additionally, the produced salt represents a solid waste with little economic value that must now be disposed of as well. The disposal of the solid waste is generally by transportation to salt flats or other environments where disposal of a solid salt would be minimally disruptive. There is some use of the crystallized salt in the stabilization of muds for mining near salt domes, but this demand does little to offset the great supply. By switching from liquid to solid waste, there is little positive to come from this disposal management solution, other than the fact that there is increased fresh water availability in the form of the water vapor [36].

Finally, reuse is the most recent waste water disposal development. By reusing water, the injection volumes diminish somewhat and allow of an economical reduction in fresh water use, simultaneously reducing the effect on municipal freshwater supply. The issues associated with reuse are mainly that of sustainability and cost. Currently the cost of reuse is still higher than the cost of purchasing fresh water. Additionally, the water cannot be reused indefinitely and needs to be disposed of eventually. This disposal then returns to one of the methods outlined above and the challenges associated with the available disposal methods. By reusing water, the operator can extend development into some areas where sourcing fresh water for fracturing and mud makeup can be difficult [39]. By targeting these areas that might be more difficult to reach but still economical with the reuse of flowback and produced water for fracturing, the domestic reserve capacity of the United States is increased [37]. The biggest concern when using

this water for reuse is the residual waste that comes out of the treatment processes that could be toxic and are not currently governed under waste rules [8]. Given the short transportation distance of the Appalachia shale plays and the profitable eastern U.S. gas fuels market, these shale plays represent a significant future market segment for exploitation and empowerment for the U.S. for years to come.

The limitations associated with EFC as a water treatment method mainly stem from issues of cost per unit water being unknown and the scalability of the method [44]. In Section 2.3.5, the specifics of proposed and common water recycling techniques are discussed in the context of their use to treating produced water.

In the next Section the causes and impacts of seismic activity on the viability of injection disposal are discussed. The implications associated with the impacts of seismic activity on the economics of water disposal are then discussed further in Section 2.3.4.

### *2.3.3 Causes and Impacts of Seismic Activity*

The jury is still out on the causes and ramifications of seismic activity in Northeast Oklahoma and its connection with the exploitation of unconventional resources. The USGS and OGS is investigating claims that wastewater injection wells are associated with the uptick in seismic activity in the area. There certainly appears to be a strong correlation as outlined below in **Figure 2.3**.

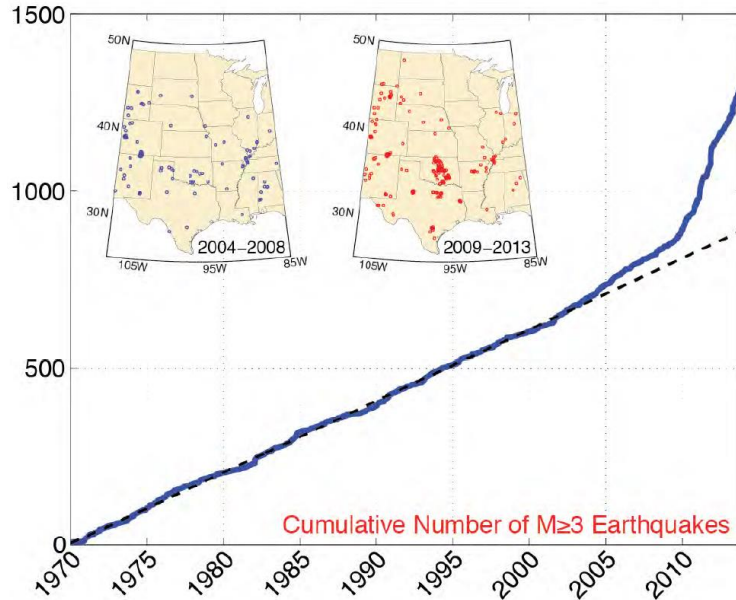


Figure 2.3 - Earthquakes in US Midcontinent 1967-2012 [61]

*“Between the years 1973–2008, there was an average of 21 earthquakes of magnitude three and larger in the central and eastern United States. This rate has ballooned to over 600 M3+ earthquakes in 2014 and over 1000 in 2015. Through August 2016, over 500 M3+ earthquakes have occurred in 2016.” [61]*

In the simplest sense, the physics behind the theory of induced seismicity is easy enough to understand. Just as the sweeper in curling uses a broom to reduce the friction between the ice and the stone, so too does injection water lubricate existing faults allowing them to slide with less force, thereby allowing earthquakes to occur with more frequency. **Figure 2.4** includes more detailed geophysics on the causes of seismicity that can be attributed to the production and alteration of in situ fluids.

Because of the connection between unconvensionals and waste water injection wells, the focus needs to shift to away from aiming to point blame at specific operators, but rather to governing remedial actions that can be taken to curb the seismic rates and determining if the causes of seismicity would appear in others plays, or to determining



if the conditions in Northeast Oklahoma are geologically more susceptible than others. If the latter is true, then this reiterates the imperative to finding an alternative water management system that does not include deep-well injection as a viable solution.

In Pennsylvania, there is one seismically active region as identified by the USGS. It is the Triassic Rift in the Northwestern part of the state. Even given this area of higher density seismic activity, to date, there has only been one identified instance of seismic activity being correlated to oil and gas operations [62]. Since there is little perceived impact of drilling or injection on seismic activity in the Marcellus and Utica shale formations, the DEP is recommending that volumes and rates not be regulated unless specific seismic events occur within 6 and 3-mile radii of any active wellpath.

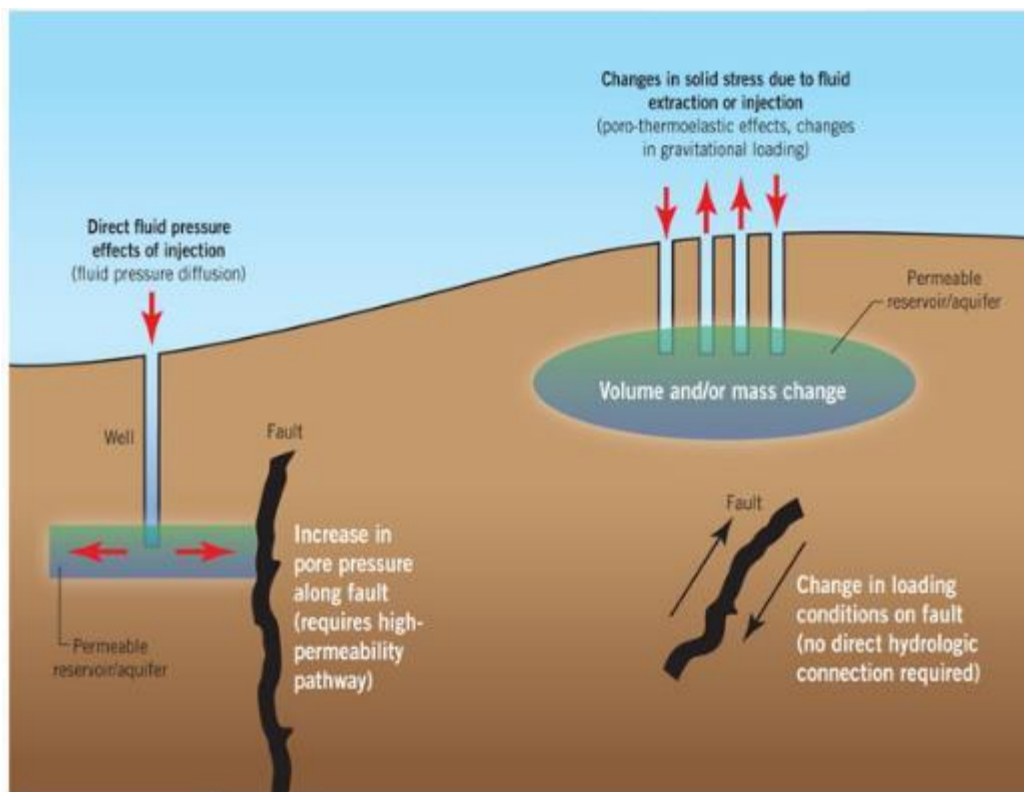


Figure 2.4 - Mechanism for Inducing Earthquakes [55]

Because of the potential for an increase in seismic activity and the associated ramification imposed by the DEP on drilling and injection as seismicity increases, it is recommended that an alternative water management method be used. By not relying directly on injection disposal, operators can plan for the long-term viability of their developments and not be as susceptible to changes in environmental policy regarding seismicity. Having an environmentally neutral or friendly water management solution would reduce long term costs of oil and gas development and aid in the perception of the industry [38].

#### *2.3.4 Economic Consideration of Recycling and Injection*

In the oilfield, economy is king. That operator who can produce oil and gas for the cheapest cost per barrel will always be viable, while the recent downturn has shown that many are susceptible to even the slightest amount of change in the commodity price. For recycling or reuse of water to be adopted by the industry, it must be competitive to disposal by deep-well injection, else there is no incentive for change. Even a comparison to injection disposal costs is difficult. Some operators own their own disposal pads, while others have leasing agreements with water management service companies. Additionally, there is a large discrepancy in cost for disposal between different oil and gas regions. Energy and disposal costs vary across the U.S. with injection into disposal wells averaging \$0.75-\$1/bbl in West Texas to \$6.50/bbl in the Northeast [8] due to regional differences in injection water volumes, disposal well availability, and transportation costs.

Recent chemical treatment advancements have made flocculation of suspended solids and O&G more economical. Current chemical treated water for reuse purposes is \$0.50-1.20/bbl. As the costs of chemical synthesis decreases and the cost of disposal increases, reuse for hydraulic fracturing and makeup is becoming more attractive and competitive. Compared to electrocoagulation at \$1.50-\$2.00/bbl, we see that the costs for reuse can be anywhere from 50% - 200% the cost of injection disposal.

Estimates for the cost of produced water treatment using membrane technologies (RO or MD) is not widely available and varies significantly [46]. This is in part due to the costs of pretreating for the removal of hydrocarbons that could foul the membranes, the need for low salinity brine for treatment (30,000 – 100,000 mg/L TDS), and the type of membrane selected for treatment. Beni, Henni, and Duraisamy (2013) speculate that the cost for water treatment from coal bed methane is \$0.30/bbl, however the quality of the water is not mentioned. They do recommend that pretreatment of the water prior to membrane separation be performed to remove hydrocarbons from fouling. The recoverable water from their experimentation was 60-70% implying that there was a significant volume of highly saline brine to be disposed of.

Other considerations not included in many of the published literature include the need to account for the cost of environmental damage associated with disposal or reuse, and the byproducts of these processes. In the Bakken, disposal of solid waste from water treatment in a Class II Solid Waste Management System is compliant with the rule and regulations of the Montana's Department of Environmental Quality. However, residents of Lindsay, Montana maintain that NORM material has seeped from the landfill and

contaminated the town [27]. With aging pipeline infrastructure, injection wells being shut in at increasing rates, and crumbling roads caused by truck rumbling down dilapidated streets [47] the time will come, and may already have arrived, that the cost of disposal may be as much as the cost of treatment.

The recoverable water portion from EFC is discussed in Section 3.5. In Section 5.2 is a discussion about cost analysis for EFC and how it compares to the figures presented in this Section.

#### 2.3.5 Status of Water Recycling in the Petroleum Industry

Every year, the industry generates over 800 billion gallons of wastewater [63]. The massive volume of water created over the life of the well, coupled with the millions of gallons of water used annually to hydraulically fracture wells makes it clear that the production of hydrocarbons is as much a water issue as it is an energy issue. However, water is not extensively recycled in the petroleum industry currently. Most water is either disposed through injection wells, reused for refracturing, or recycled on a small scale as novel research. To some extent, water recycling is growing in the industry. Operators are acknowledging there is an environmental benefit of reusing water in that it eliminates the water-drought dependency of localities. Some groups are even pushing for mandatory recycling policies. To some extent the increase in water recycling is great. Especially for the drought-stricken localities where oil and gas production is a big business, the impact of recycling money and water can help mitigate the impact on local water sources. But water recycling also creates some environmental challenges as well

when not managed correctly. If the issues aren't addressed prior to implementation, there is the risk that there is only a tradeoff for one problem to another.

As mentioned previously, most reuse in the oilfield is done on treating produced and flowback water for refracturing. This makes sense as 41% of wells in the U.S. are in regions of extreme water stress or drought and in some counties in Texas, more than 80% of municipal water goes to industrial and agricultural use [31]. Some municipalities do take cleaner flowback fluid as a waste stream for sewage plant treatment. This policy is largely being reverted in much of the country as the plants struggle to sufficiently treat the water for release. In 2011, water at the Greene County municipal plant tested barium levels were 5.99 mg/L while treating flowback water, while just 0.14 mg/L before. This pushed the treated water outside the EPA drinking water standards of a maximum of 2 mg/L, putting the public's health at risk for the time the flowback water was treated [64].

Given the large use of freshwater in hydraulic fracturing new wells (2-6 million gallons per well) and the high cost of water handling in the Marcellus shale (\$3+/bbl for disposal or \$7-10/bbl for transport), there is a new way for companies to profit from water management in this area. With thousands of wells projected to be drilled through Pennsylvania, West Virginia, and Ohio in the next decade with targets in the Marcellus Shale [65], it will be a major revenue source for someone. Experts also agree that public pressure and regulation to pressure producers for more recycling are coming. Because of this need for future greenfield recycling, the analysis of centralized treatment of

wastewater using EFC for long-term efficiency as a water management source in the Marcellus Shale is the subject of this thesis.

## 2.4 JUSTIFICATION OF RESEARCH QUESTIONS

In this Chapter, a literature review of the status and limitations of the waste water management schema for the oilfield industry is presented. In Section 2.3.1, the available disposal methods commonly used for water management are discussed and analyzed. The impacts and causes of seismic activity are discussed and the expectations with regard to the industries' role in managing expectations of induced seismicity are introduced in Section 2.3.3. In Section 2.3.7 a brief introduction to the requirements for drinking water set forth by the EPA is given as motivation for the highest level of release Eutectic freeze crystallization could hope to achieve; release of fresh water into the U.S. water table as potable water. In this Section, the research opportunities identified through critical literature review are presented and the connection between the identifies research opportunities and Research Questions proposed in Chapter 1 is established.

***RQ 1. How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?*** In the study and limitations of available disposal methods Sections 2.3.1 and 2.3.2, almost all the methods currently in use in oilfield operations are shown to be in some way lacking, whether by causing detriment to the environment through unsatisfactory environmental release of tainted waters and induced seismicity, or by using unacceptable levels of energy without any realizable revenue generating stream. It is clear that there is no consensus or established method that is utilized

throughout the industry as all companies have a favorite method that has preference for internal reasons. It can then be concluded that there is a need to introduce a good reuse and release method that simultaneously generates revenue through low energy cost and isn't met with environmental disaster.

***RQ2. What changes need to be made to freeze crystallization desalination technology for compatibility with oilfield operations?*** In Section 2.3.4, I mention the economic consideration of recycling and how its higher economic cost has limited implementation to now versus the ease of use and low cost of underground injection and in Section 2.3.6 the current extent of water recycling and reuse in the oilfield is evaluated. This analysis leads us to the determination that while current recycling methods are more capital and energy intensive and therefore there is limited recycling being performed, there is opportunity for a cost and energy efficient recycling method in the industry. The furthering research that needs to be conducted is in regards to what changes, if any, need to be made to introduce and make compatible EFC for oilfield use. Typically, E&P companies prefer equipment to be skid mounted and portable, but in Section 5.2.1, discussion is presented that shows the extent to which this technology can conform to this desire.

***RQ3. What environmental benefits will be realized by treating water for reuse and release over underground water injection?*** In Section 2.3.5, the potential release of water extracted from effluent brine back into the environment is discussed. Many areas with developed oilfields in the U.S. are in areas deemed as vulnerable to drought and there is an alarming history of mega-droughts lasting 300 years or longer in many

western U.S. states. This disturbing potential future of little potable water is underscored dramatically by the use and disposal of > 20,000 gallons per well of fresh water for hydraulic fracturing of new wells in these states. In many cases, the solution means recycling flowback or produced water to limit the need for fresh water in the production of hydrocarbons. However, the recycling or release of produced water is often met with unintentional ecological consequences. In Section 1.3.4 it is shown that the main work that needs to be done to prove there is an environmental benefit to the release of this water is largely outside the scope of this thesis. However, what is discussed in Section 2.3.7 and Section 5. 2.4 regarding the release of water and the sale of crystallized salt provides motivation that there is clear environmental significance of the work by reducing the ecological footprint of other industries. The efficacy of an optimistic plan to release the extracted waters from EFC to streams and estuaries is underscored through the discussion on U.S. regulations for the release of produced waters and the requirements for drinking water (potable) discussed in Section 2.3.7.

***RQ4. How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?*** The most commonly used water treatment infrastructure in the industry is thermal distillation treatment at refineries for entrained waters with crude deliver, and water used during crude processing. Additional water treatment infrastructure exists in the form of transportation pipeline networks to and from production and disposal wellheads. In Section 2.3.6 discussion is presented on the citing and permitting of water recycling and disposal in the oil industry. The introduction of a new (to the industry) recycling method will necessitate the re-permitting and update of



current methods to allow for continued water processing. This Research Question is developed in Section 4.4 with discussion on the sensitivity analysis of EFC temperature and this implication on the design of a EFC treatment facility. Through Section 5.5, future research needs for EFC and discussion about other problems for which EFC can be applied are covered to strengthen the relationship between EFC as a water treatment method and refinery operations.

The utility of this thesis is to Baker Hughes and the Oil and Gas water management industry by:

- Proposing an alternative waste water recycling scheme in Oklahoma and other producing states by suggesting freeze crystallization for desalination of produced water
- Describing in detail the current available methods and technologies associated with waste water disposal, as well as the current legislation and laws surrounding disposal and reuse
- Providing insight for implementation of a Eutectic freeze crystallization desalination for Baker Hughes' H2PrO™ water reuse product line

## 2.5 SYNOPSIS OF CHAPTER TWO

In this Chapter, a critical evaluation of current waste water disposal methods, desalination, and water recycling literature are presented. In Section 2.1 this review of the literature is summarized and connectivity between the Research Questions and review established. In Section 2.2 principal concepts are introduced and the Research

Gaps connection to the motivation presented in Chapter 1 are discussed. Section 2.3 contains an analysis of the waste water disposal methods currently in use and their limitations, as well as the requirements for released water that will be expanded in Section 5.3. In Section 2.4, the utility of Eutectic Freeze Crystallization to the industry and specifically Baker Hughes is established and is foundational to addressing Research Question 4 in Chapters 4 and 5.

## Chapter 3 – Modeling of Eutectic Freeze Crystallization

In this Chapter, building on the critical evaluation of the literature presented in Chapter 2, the efficacy of Freeze Crystallization is tested using an established industry software. The use of software will allow for forward remarks to be drawn without the need for expensive bench scale research while also conforming to electrolytic chemical models, discussed further in Section 3.1.1. The simulation of EFC is performed in support of Research Questions 1, 2, and 3. Research Question 1 is addressed through the analysis of a singular species brine and complex brine system to address the question of how Freeze Crystallization can be utilized to treat produced water in Sections 3.3 and 3.5. Research Question 2 regarding the changes necessary to Freeze Crystallization for oilfield compatibility are discussed in Section 3.4 with commentary on the effects of contaminants and impurities on the sensitivity of the eutectic temperature. Finally, Research Question 3 regarding environmental benefits realized from implementation of EFC are discussed in Section 3.5 with commentary on the implications of water removal and salinity reduction on produced waters.

### 3.1 SOFTWARE INTRODUCTION

#### 3.1.1 Summary of utility of the software

In this thesis, The OLI Systems OLI Studio 9.5 Stream Analyzer [66] is utilized to model brine eutectic freeze crystallization. The use of this software allows for the direct production of results based upon water quality reports generated in the field for produced water streams, provided courtesy of Baker Hughes Incorporated. These water quality reports are generated by petroleum operators and service companies prior to

delivery of brines to commercial injection wells through pipeline or by truck. The report of water quality at minimum specifies TDS, pH, density, and major present ions so that companies and operators can assess whether there is likely to be corrosive damages, scaling or interaction with other disposal fluids. OLI Stream Analyzer is a commercially available software that is primarily used for electrolytic calculations and manipulations, thus allowing for easy industrial use with an active available help desk and an intuitive user interface. This widespread availability is beneficial should acceptance or use of eutectic freeze crystallization be realized as a feasible waste water processing method by allowing for researchers and technologists across the world to use one uniform platform for collaboration. The phenomena of eutectic freeze crystallization are introduced in greater detail in Chapter 3, Section 3.2.

The crystallization model developed by OLI utilizes the revised Helgeson-Kirkham-Flowers (HKF) model for calculation of thermodynamic properties of aqueous solutions and modifies the framework of the Debye-Huckel model for other excessive terms [3, 67]. OLI Stream Analyzer uses the HRK method to carry out crystallization calculations to temperatures of  $-50^{\circ}\text{C}$ , which is the lower limit of that model. Below this temperature, the OLI Stream Analyzer uses the Debye-Huckel model which causes a discontinuity of results between the two models; thus, all simulations in Chapter 3, Sections 3.3-3.5 are executed at temperatures greater than  $-50^{\circ}\text{C}$ . Additional rationale for only modelling crystallization to this temperature is the difficulty in finding any chiller currently that would be able to cool sufficient volumes of water to below  $-50^{\circ}\text{C}$  on a commercial level. The specifics of the freeze crystallization process are discussed in Chapter 3, Section 3.2.

Composition of brines can be altered by balancing to charge-neutral using the dominant ion method. In the case of these produced water streams, that would mean the addition of either  $\text{Na}^+$  or  $\text{Cl}^-$  in the form of HCl or NaOH. The addition of these industrial chemicals is evaluated in the economics discussion of brine freeze crystallization in Chapter 5, Section 5.2. The addition of small amounts of these acids/bases respond as slight pH changes in the brine as calculated thermodynamically in the software when compared to the physical pH measurement of the brine in the field prior to reagent addition. Therefore, the charge-neutral brine stream is accepted as a starting point for analysis with the OLI Stream Analyzer [3]. It is shown subsequently in Chapter 3, Section 3.5 that the use of charge-neutral balancing is not required in physical freeze crystallization. Limitations for the use of software to evaluate the efficacy of eutectic freeze crystallization on waste water streams is discussed further in Section 3.4.3 and Section 4.4.2.

### *3.1.2 Validation of its results through peer review*

As discussed in Chapter 3, Section 3.1.1, the OLI Systems is used to model theoretically the fractional crystallization due to temperature drops that are expected in a freeze crystallization system. Lewis et al. (2010) [3] first discussed The use of the OLI software for brine crystallization of multicomponent waste water streams. In their study, bench scale laboratory freeze crystallization of a 5 wt%  $\text{Na}_2\text{SO}_4$  brine is compared to that generated by the OLI Stream Analyzer. Using the validation square discussed in Chapter 1, Section 1.4.2., this agreement indicates a high level of confidence in the generated results of the OLI Systems software for multi component brines. However, their analysis

does not accurately capture the high complexity and variability of waste water streams that are present in the oil and gas field, nor is there sufficient evaluation of freeze crystallization economics to justify further study of the matter at an industrial level. As mentioned in Chapter 1, Section 1.1.3, the hope is that the analysis presented in this thesis can fill these gaps and present clear validation for further examination as well as provide a potential avenue away from the use of waste water injection as a disposal method discussed in Chapter 2, Section 2.3.3.

### 3.2 BENEFITS OF FREEZE CRYSTALLIZATION

In Chapter 2, Section 2.3.6 we mention that thermal (evaporative) distillation is the main recycling method of produced water in the oil and gas industry and that the clear majority of produced water is simply injected underground, whether for reservoir pressure maintenance or disposal. The main use of evaporative distillation is in the recycling of water at hydrocarbon refineries for the entrained water that comes with delivered crude; usually 3-5% by volume. A logical presentation of the benefits that freeze crystallization provides over traditional underground injection is presented in this Section and relates back to the Requirements List first presented in Sections 1.3 and 1.4. This section, in conjunction with Section 2.3.1, presents the foundational basis for the motivation for freeze crystallizations application in waste water streams, while Sections 3.3-3.5 focus primarily on the theoretical workings of freeze crystallization. This section is included to show the connection between the posed research questions from Section 1.3.1 and how they connect to the main needs of desalination in the oilfield, as shown

in **Figure 3.1**. I outline these needs of desalination in greater detail in Section 2.3 and in more general terms in Section 5.1.

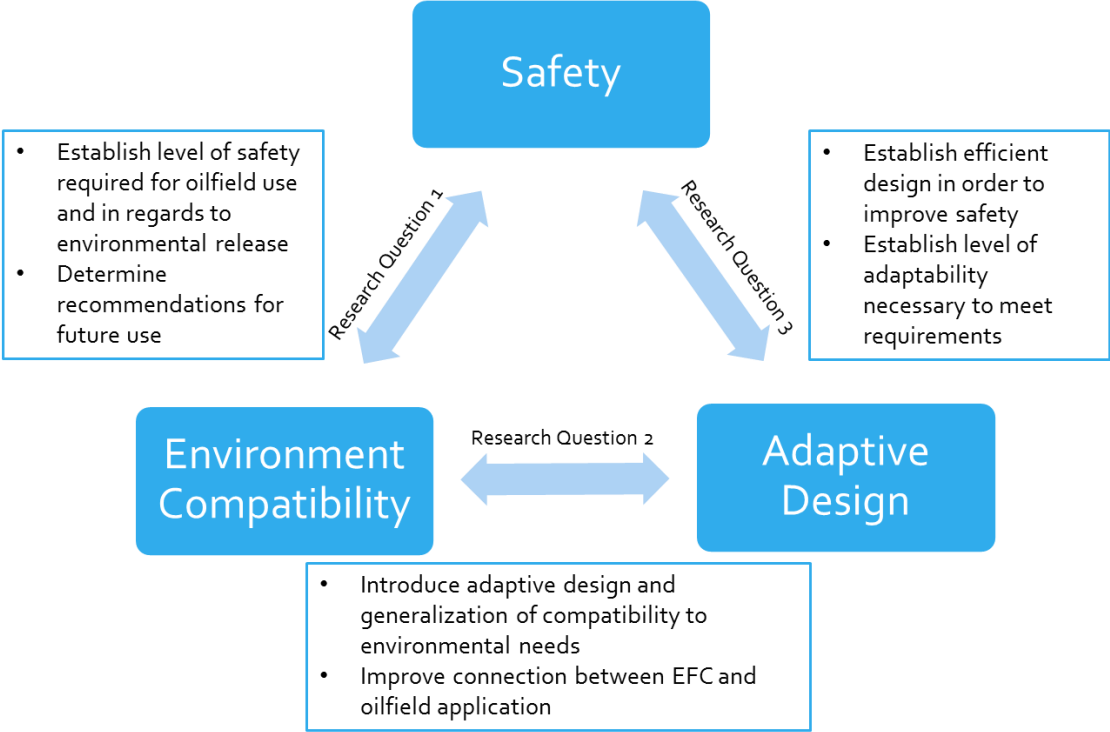


Figure 3.1 - Connectivity of Research Questions to Desalination needs in Oilfield

Specifically, the focus of RQ1 is on how freeze crystallization can be utilized to treat flowback and produced water from oilfield operations. This is in the domain of compatibility of the safety of freeze crystallization as a disposal method (safety) as well as its compatibility of the need of the oilfield and in place infrastructure (environment compatibility). Similarly, in RQ2 what changes need to be made to freeze crystallization technology for compatibility is addressed. Clearly, this is in the domain of environmental compatibility, but also is focused on the need for an adaptive design and needs for change if water quality and throughput change drastically. This adaptive design and mobility is discussed in detail in Section 5.2.2. Finally, the focus of RQ3 is on what

environmental benefits are realized by treating water with freeze crystallization specifically over underground injection. This addresses the dilemma between the feasibility of the design of a freeze crystallization treatment facility and the potential safety of treating water using EFC, which is elaborated further in Section 3.5 and Section 5.2.

### 3.2.1 Scaling Reduction

Scale is the bane of landholder and midstream operators alike. Scale is mineral deposits on pipe walls that reduces cross-sectional area and affects flow regime as well as fluid pressure in oil and water pipes. Scaling reduction of water recycling facilities and pipelines is a multimillion dollar per year business. Long distance transportation of high potential scaling brines that contain salts such as calcium carbonate or barium sulfate allows time for unfavorable depositions to form, leading to the need for costly pipe remediation or the use of expensive scale inhibitors. Scaling likelihood increases with increases in temperature and changes in pH [68]. Therefore, any method to control the scaling of waste water without the need for ancillary chemicals will reduce overall disposal and transportation costs, as well as prolong the lifetime of the piping and treatment infrastructure. Through freeze crystallization, it is shown that those salts which are most likely to cause scaling are removed first eutectically, thereby reducing future scaling by the same water stream [5]. This presents a major reduction in pipeline operating expenses if freeze crystallization is performed prior to long distance transport and also reduces the need for remediation which will limit non-productive pipeline time and associated costs.



### 3.2.2 Corrosion Reduction

Likewise, corrosive tendencies increase with increase in temperature and increase in salt ion concentration [69]. Since eutectic freeze crystallization is not capable of lowering the concentration of ions within a salt (except for those that initially exist above the eutectic concentration) it has limited effect on reducing corrosion through ion reduction. However, due to the low temperature of eutectic processes, the facilities performing freeze crystallization will be less prone to corrosive damage as compared to those of a thermal distillation plant that result in highly corrosive salts and caustic byproducts [70]. The implementation of local or small-scale freeze crystallization facilities would also reduce the impact of corrosion as it would minimize the water volumes moved through pipeline and are thus able to cause damaging corrosion. Discussion in Chapter 4, Section 4.2 further describes the benefits of corrosion reduction facilitated by treatment using freeze crystallization and the economics of regional treatment is discussed in Chapter 5, Section 5.2.

### 3.2.3 Low Energy Cost

While the applicability of using eutectic freeze crystallization (EFC) to remove multiple salts from complex multi-component, hypersaline brines has not yet been demonstrated [5], the thermodynamics of freeze crystallization are extensively known. Overall, EFC requires 6 times less non-renewable energy input than evaporative crystallization in a stand-alone process comparison [44]. This low energy requirement is realized by recalling that, for water, the latent heat of fusion is 333 J/g, while the heat of vaporization is 2256 J/g; a difference on the magnitude of 6 times the energy, all else

being equal. Various researchers have performed analysis on the energy reductions afforded by EFC for the separation of single species salts from solution to compare to evaporative crystallization and have determined energy reductions of 60-70% [7, 41, 71]. The cost of cooling energy is more expensive than that of heating, there is also energy benefits realized through the use of vapor-compression (Reverse-Rankine) chilling machines that have a coefficient of performance (COP) of 4.0 or more. The use of highly efficient chillers allows for additional energy savings that help reduce the total cost of the crystallization method. Van der Ham (1998) [41] outlines the use of the frozen water stream to precool the incoming brine stream, thereby reducing the energy requirement to cool the brine stream, as well as transform the water stream into a liquid form that could then be sent elsewhere with greater ease than in solid ice form. In conjunction with the lower energy costs, in Section 3.2.3 I discuss the potential cost savings realized from a freeze crystallization plant over that of a regional or mobile platform for EFC.

#### *3.2.4 Infrastructures Cost Assessment*

Increases in water consumption is causing water scarcity in many areas of the U.S. and indeed these problems are often exacerbated by discharge of polluted water [44]. In fact, the availability of fresh water is predicted to become more scarce [32, 36]. It is unclear what the cost of polluted water is economically, but there are estimates that the economic stimulus from recycling water for reuse rather than disposal is worth \$3-4/bbl [2, 5]. With aging pipeline infrastructure, injection wells being shut in at increasing rates, and crumbling roads caused by truck rumbling down dilapidated streets [47] the

time will come, and may already have arrived, that the cost of disposal may be as much as the cost of treatment. However, energy and disposal costs vary across the U.S. with injection into disposal wells averaging \$0.75-\$1/bbl in West Texas to \$6.50/bbl in the Northeast [8] due to regional differences in injection water volumes, disposal well availability, and transportation costs.

Himawan (2002) [7] estimates that the cost of a freeze crystallization system was 7% more costly than to evaporative crystallization, but could save up to 60% of the energy cost. The reality of this economic evaluation remains uncertain as freeze crystallization has only been used on a limited scale briefly for a pilot mining waste water processing in South Africa as I discuss in Chapter 2, Section 2.3.1. What that analysis does conclude, however, is that freeze crystallization is a new process with significant room for technological improvements and cost reduction as implementation occurs, while evaporative cooling and other processing methods is already established and has only incremental future cost savings only as a result of technological improvements [5].

One additional aspect to review in the analysis of freeze crystallization for the task of oil and gas waste water recycling is the realization that the pure salts produced have the potential to be a revenue stream to those companies operating freeze crystallization systems, as well as limiting disposal volumes and energy costs [5]. The possible economic stimulus realized from the sale of these pure salts to industrial chemical manufacturers is discussed in an economic analysis in Section 5.2.

### 3.2.5 Known Limitations of Freeze Crystallization

Adoption of freeze crystallization in the last decade has been small despite the fact that there are a variety of applications that could benefit from the specific advantages of freeze crystallization [69]. It is known in the oil and gas industry that major operators readily embrace new technology for the extraction and treatment of reservoir fluids, but are hesitant when it comes to implementing new technologies that are perceived to be mechanically complex, especially when established methods appear to be acceptable [72]. Case in point, the design for the pump-jack, an essential piece of oilfield machinery, is relatively unchanged since its introduction in 1925 [73]. Similarly, since disposal wells have been standardized and effectively operated for so many years, there is little incentive to invest in new infrastructure necessary to undertake recycling operations simply for the environmentally green initiative. Rather, the economic benefits of freeze crystallization are what will entice those major operators to embrace change. This economic benefit and impact to existing infrastructure embodies Research Question 4 and is elaborated in Sections 4.1 – 4.3 and Section 5.1.

Unfortunately for freeze crystallization, much of the cost for developing and construction is up in the air. Therefore, the most significant disadvantage of freeze crystallization is the capital expenditure to initially plan, design, and construct a facility capable of processing the volumes necessary in the oil and gas field which is on the magnitude of 10kbd+ (42 thousand gallons per day) [41, 74]. The cost for this facility is discussed in Section 3.2.3 and is also mentioned in Section 5.3. Johnson (1976) [75] concludes that a combination of freeze crystallization and a membrane process would

be a potent combination for brine disposal when other disposal methods become obsolete. The chemical make-up of oilfield brines (specifically from the Marcellus and Utica Shale play) is elaborated in Section 3.5.1, but the main component is a high concentration of NaCl which is deemed to be suitably treatable only with freeze crystallization [76]. Unfortunately, oilfield brines also include high concentrations of other salt species that are not adequately removed with EFC [5]. Herein lies another limitation of freeze crystallization in the realization that it can likely not be implemented alone and would thus have to be paired with other disposal methods.

It has been shown that the use of a wetland constructed to treat the produced water retentate of reverse osmosis is a viable alternative for water reuse [77], but it is unlikely that a large enough artificial ecosystem can be created to process the required daily volume of water co-produced with oil production. In-field recycling and water processing would require significant resources to deploy since treatment would have to occur continuously through the day [78].

While the combination of treatment of freeze crystallization and reverse osmosis allows water to meet most standards for irrigation use, it does not always meet toxicity standards and therefore cannot be released to the environment, except for some non-potable use, such as agricultural or landscape irrigation [2]. One of the toxins that is difficult to remove is boron. Not many oilfield brines exhibit boron, but those of the Marcellus and Utica Shale can have measurable levels which will require either water dilution to reduce the boron levels to non-toxic quantities or will limit all treated water from these streams for only agricultural use. While boron is not represented in Table 7.1

as a constituent of produced water, it is a low concentration contaminant that is often not measured, but commonly present. Other potentially toxic constituents of produced water include naturally occurring radioactive materials (NORM). These present a social and transportation concern since retentate from both reverse osmosis and freeze crystallization will have increased levels of radioactive ions which limits public acceptance of local water disposal [27]. With no requirement to report the levels of radioactivity in produced water, further research or government intervention to illuminate the quantity and quality of radioactive isotopes present is necessary to determine what effect, if any, these isotopes would have on the effectiveness of freeze crystallization and the purity of the crystallized salts. The sensitivity of the freeze crystallization process to the presence of specific impurities is addressed in Section 4.2 in the discussion of the goals for bench scale experimentation. Without bench scale EFC work, it is unclear whether appreciable amounts of NORM particles will become entrained in the nucleation of ice and salt crystals to influence the disposal and removal of these constituents, or whether the NORM will remain in the retentate water of the EFC process and could simply be removed in an ancillary manner through injection disposal or with RO.

Social tensions of NORM material will remain even with the introduction of freeze crystallization as an alternative away from potentially anthropogenic earthquake causing underground injection [53]. Additionally, the invisibility of injection wells from the public eye allows them to go unnoticed, except for the occasional earthquake whereas freeze crystallization or other water treatment options would require

centralized treatment locations to be viable [79]. These centralized facilities will be easily visible and the need for public education on the matter will be paramount to ensure a successful transition away from underground injection. Government-industry alliance organizations such as the OERB in Oklahoma would be suitable candidates to take public education forward regarding the use and benefits of water recycling were it to be implemented on a commercial scale.

### 3.3 SINGULAR SPECIES BRINE ANALYSIS

To adequately evaluate the efficacy of the OLI Systems software, analysis on a simple singular species brine is performed to compare the results of the simulation to those physically measured in a laboratory setting to ensure there is verification of accuracy before moving forward with more complex scenarios. Given that freeze crystallization may be an obscure topic to those unfamiliar with electrolytic chemistry, the single species brine analysis is taken as an opportunity to carefully outline the freeze crystallization method so that all readers can proceed and have a basic understanding of the subsequent Sections of Chapter 3. A single species salt refers to a brine that is made up of one cation and anion. Similarly, a binary system would contain two different and distinct cations and two anions.

#### 3.3.1 Salt Selection Criteria and Concentration

For single species analysis, a salt is needed that can accurately test the capabilities of the OLI software while simultaneously providing utility to the study at hand of oilfield produced water analysis. The analysis concentrations should only be those that are physical and realistic so as to ensure the software can handle that which will be present

in more complex systems as well as to evaluate the corroboration of published literature values of the same salt species under laboratory conditions. Multiple concentrations will be analyzed to describe and graphically show the various results that can be obtained for a brine system at concentrations above, below, and at/near the eutectic concentration.

Given that the most prevalent ions present in oilfield brines is  $\text{Na}^+$  and  $\text{Cl}^-$ , and the high eutectic point of a sodium chloride system, the selection of sodium chloride as the salt for single species analysis is justified through the plethora of literature published on freeze crystallization of sodium chloride and the utility a sodium chloride analysis will have for the thesis topic at hand. It is my intuition that given the high eutectic freezing temperature of NaCl brines ( $-21^\circ\text{C}$ ) that this crystal will likely be the first to form under crystallization conditions. The analysis I perform in Section 3.5 shows this is the case.

The modeled freeze crystallization is performed using temperature reduction steps of  $2^\circ\text{C}$  from a starting temperature of  $20^\circ\text{C}$  to  $-50^\circ\text{C}$ . The rationale for the selection of these temperatures for use in the simulation are given in Section 3.1 and pertain to the physical continuity limitations of the software ( $-50^\circ\text{C}$ ), the lower realistic limit of commercial chillers, and an arbitrary value of ambient temperature ( $20^\circ\text{C}$ ). From the literature, it is expected that no freeze crystallization will occur at temperatures above  $5^\circ\text{C}$  except for solutions that are previously supersaturated, or exhibit low solubility [5]. The  $2^\circ\text{C}$  temperature steps size is selected as there is no appreciable loss of accuracy when compared to incremental step sizes, but simulation time is reduced greatly. Each graph is representative of a 1L sample of brine with the qualities described, and



therefore a precipitation of 1 gram of any salt species indicates a reduction in the TDS by 1000ppm for each ion required for that salt species.

**3.3.2 Results from Software**

Three simulations are run on a single species NaCl brine using the OLI Stream Analyzer software [66]. Each simulation is executed at a different concentration of sodium chloride, in an effort to determine graphically the effects of being above, below, or at the eutectic point. The salt concentrations under study are 2.5%, 23.3%, and 51% weight percent respectively.

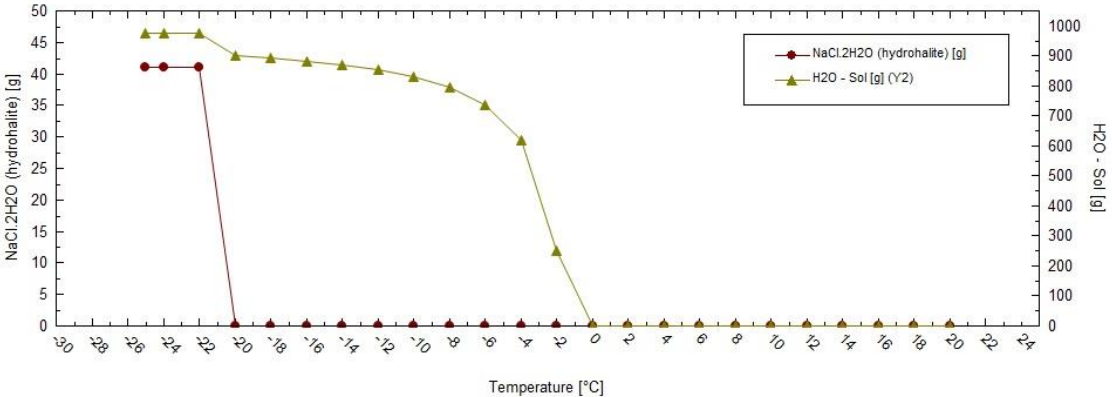


Figure 3.2 - Simulation of Freeze Crystallization on a 2.5 wt% NaCl brine

The simulation of freeze crystallization on the 2.5 wt% NaCl brine is shown above in **Figure 3.2**. The proper way to mentally observe the EFC graphic is by viewing right to left as that would be associated with a temperature reduction due to freezing. Ice begins forming at a slightly reduced temperature, but not significantly different than the known freezing temperature of water under atmospheric pressure of 14.69 psi of 0°C. Only ice is formed until a temperature of -20°C, at which point NaCl<sub>2</sub>H<sub>2</sub>O (hydrohalite) begins to form. By forming solely ice originally, the system is increasing in concentration of NaCl

until finally reaching the eutectic concentration at which point hydrohalite is formed. Hydrohalite is the stable form of halite (NaCl) at temperatures below  $-5^{\circ}\text{C}$  [80]. Hydrohalite melts under its own vapor pressure at  $0.1^{\circ}\text{C}$  indicating that any hydrohalite removed from the brine solution will subsequently melt and dry, resulting in pure water and halite. Shown below in **Figure 3.3** is a graphical representation of the process of freezing at concentrations below the eutectic concentration using a standard phase diagram for a NaCl brine operating under atmospheric pressure. Notice how the intersecting locations of the phase diagram coincide with the quantity of crystallized salt formed in **Figure 3.2**. Following the red arrow, we enter the phase diagram at a salt concentration. Following a depression in solution temperature, near  $-3^{\circ}\text{C}$  the solution would begin to exhibit the formation of ice.

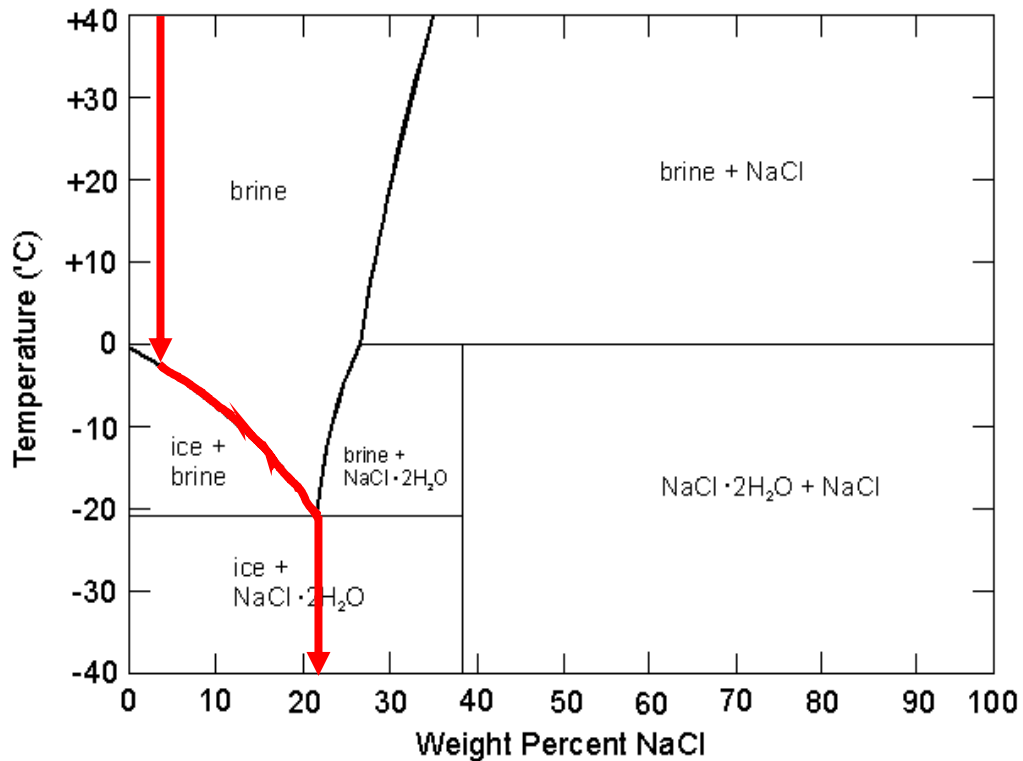


Figure 3.3 - Solubility Curve for Halite Brine Below Eutectic Concentration

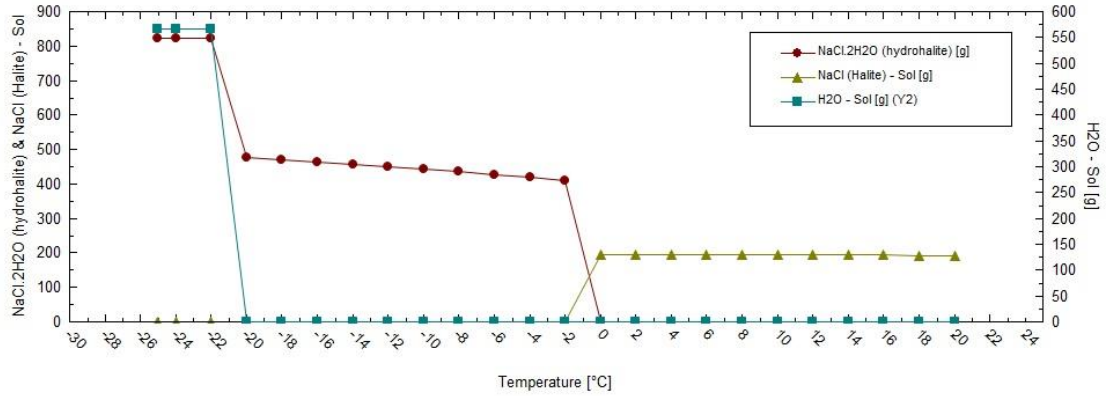


Figure 3.4 - Simulation of Freeze Crystallization on a 51 wt% NaCl brine

Under supersaturated conditions shown above in **Figure 3.4**, a 51 wt% NaCl brine first exhibits halite crystallization until sufficient reduction in the concentration of NaCl is reached, to approximately 22 wt%. Temperature reductions after initial halite crystallization result in only halite crystallization until after reduction in temperature to  $-2^{\circ}\text{C}$ . Halite forms due to the solution becoming supersaturated with NaCl. Hydrohalite is not formed at these temperatures as it is not a stable halite crystal until below  $-5^{\circ}\text{C}$ . Between  $-2^{\circ}\text{C}$  and  $-21^{\circ}\text{C}$  hydrohalite forms without the formation of ice, resulting in a decrease in the concentration of sodium chloride until the eutectic concentration is reached, at which point both hydrohalite and ice are coproduced simultaneously. This process is shown graphically below in **Figure 3.5**.

Freeze crystallization of a brine at a concentration near the eutectic concentration of a NaCl system is shown below in **Figure 3.6**. Almost simultaneously, the formation of hydrohalite and ice begins at  $-21^{\circ}\text{C}$ . Again, below in **Figure 3.7** this process is shown for freeze crystallization at the eutectic concentration. This is the phenomena that is exploited with the use of freeze crystallization as a waste water recycling method. By cooling brines to reduced temperatures, either ice or salt crystals are formed, thereby

effectively increasing or decreasing the wt% of salt in solution until the eutectic concentration is met. At this point, the brine is in a stable state and further reduction in temperature does not affect the system. At this concentration, the salt crystals and ice are coproduced. The salinity of the brine does not change at the eutectic concentration as water molecule and salt ions are removed in equal magnitude. This fact is imperative moving forward and will be discussed in Section 5.1 as a major limitation to the use of EFC as a water recycling method for oilfield waste water industry.

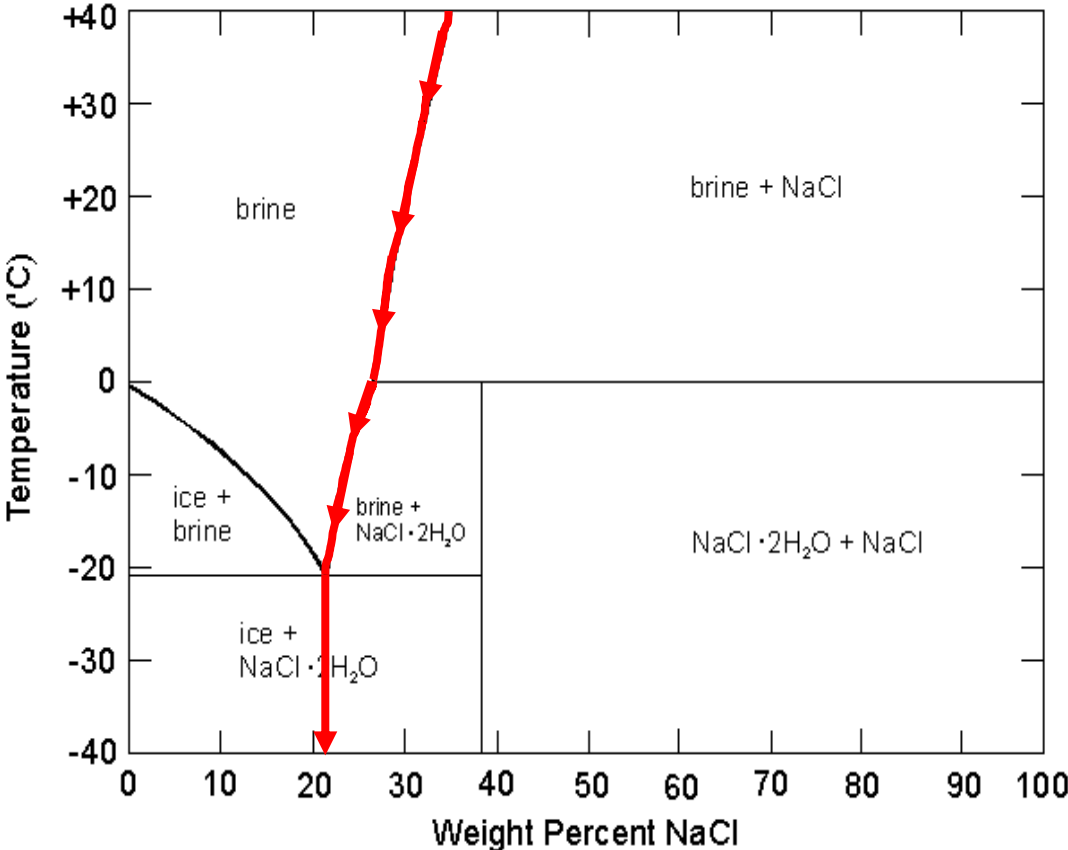


Figure 3.5 - Solubility Curve for Halite Brine Above Eutectic Concentration

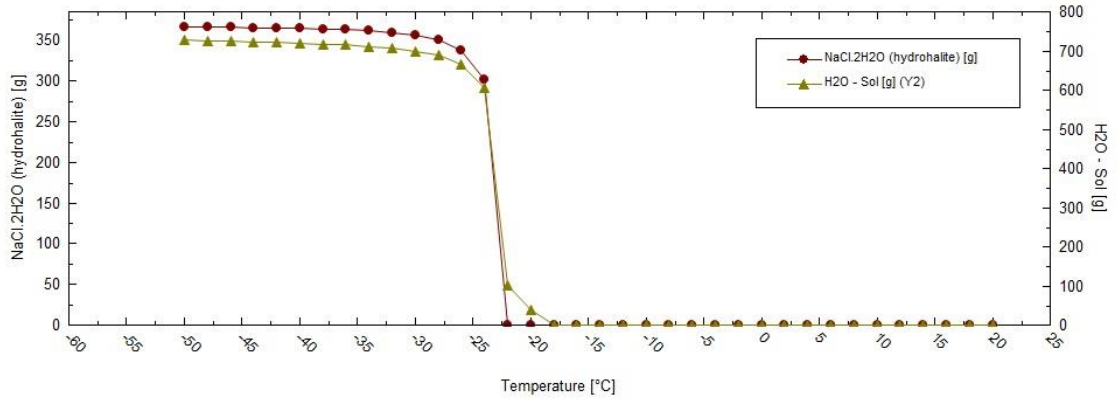


Figure 3.6 - Simulation of Freeze Crystallization on a 23.3 wt% NaCl brine

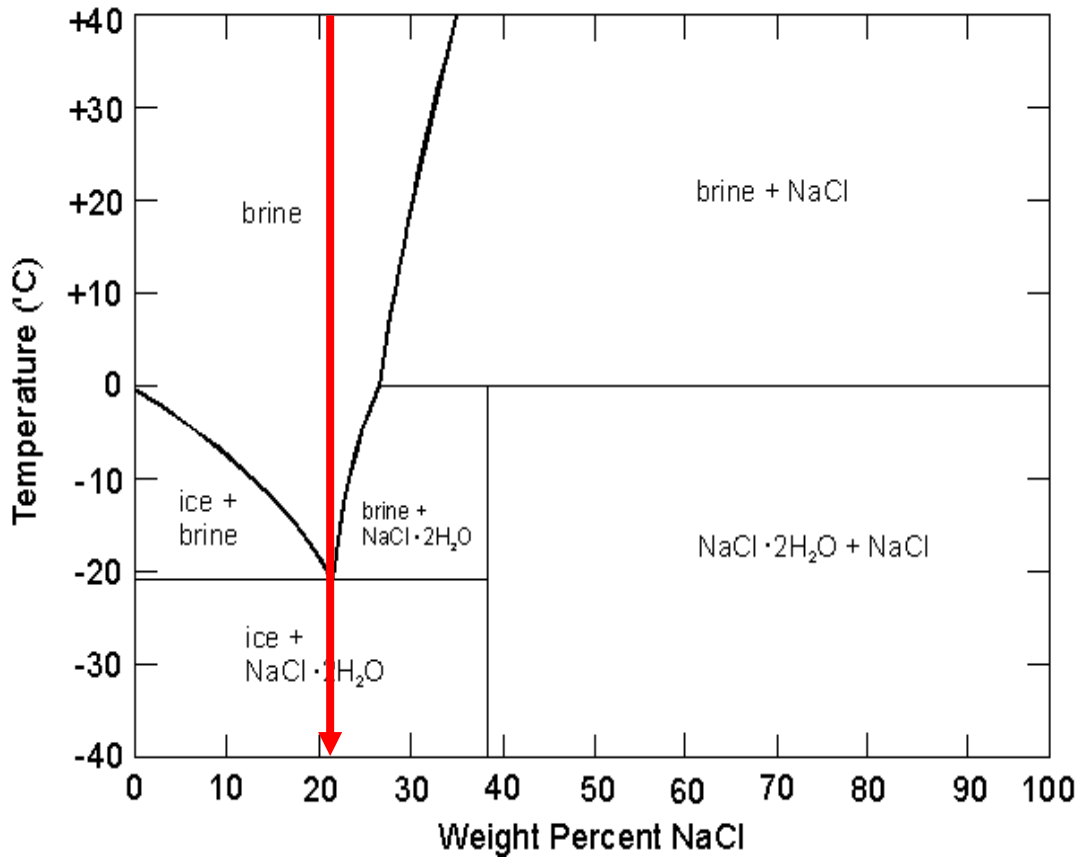


Figure 3.7 - Solubility Curve for Halite Brine at the Eutectic Concentration

### 3.3.3 Comparison to Published Data

The work of B.J. Verbeek [6] concludes experimentally that the Eutectic point of a NaCl brine system is  $-21.1^{\circ}\text{C}$  and corresponds to the theoretical value. This work also outlines

the sensitivity of the eutectic point for a NaCl solution to the presence of magnesium and other trace impurities, thereby necessitating the work in the proceeding section, Section 3.4.2 where we investigate the effect of barium sulfate on the eutectic point of a primarily NaCl system to determine if there is sensitivity to scaling salts that are commonly present in Marcellus and Utica waste water. The results of the analysis presented in Section 3.3.2 compare favorable to those presented in the preceding article and give confidence to the method employed in this thesis.

#### *3.3.4 Connection to Produced Water*

As I previously mention in Section 3.3.1, the use of NaCl as the brine species for single species analysis is conducted due to the prevalent nature of NaCl in waste brines from the oilfield [40] and overwhelming literature sources on the subject. In subsequent sections, we will delve into the realm not often covered in texts explicitly and that do not include peer reviewed published literature. Due to the stable nature of the Sodium-Chlorine bond, it is seen in many EFC simulations and studies that Halite or the stable Hydrohalite form before other salt species, including other sodium species. Much of freeze crystallization research is focused on treating Reverse Osmosis (RO) retentate brines and subsequently the scope of this thesis will primarily pertain to the validation and applicability of EFC for use in treating oilfield brines. In the scope of this thesis work focusing on the water treatment of the Marcellus and Utica Shale plays specifically, NaCl is especially important as it can make up most of the TDS in the brines from these regions as shown in **Table 7.1** in Appendix A. As mentioned previously, the sensitivity of the EFC process to the presence of impurities is addressed in Sections 4.1 – 4.3 and is validated

through the use of multiple examples to provide the theoretical performance validity necessary to validate this thesis.

### 3.4 BINARY SPECIES BRINE ANALYSIS

To determine the robustness of the simulation and to determine what effect, if any, the inclusion of other distinct salt species have on the reduction or increase in eutectic temperature, it is important to proceed with analyses using progressively more complex brines. A distinct salt species is one that contains two separate cations and anions. With appropriate selection of cation and anion, it is assured that only two salt crystal species will form. Following the singular species analysis then, is an analysis of a binary brine that should serve to introduce the complexity of freeze crystallization on complex brines and introduce concepts that are not covered in the discussion of singular species brines such as common ion effects. To design and simulate Eutectic Freeze Crystallization, it is important to have a detailed understanding of phase equilibria. However, limited availability of adequate examples in the literature and texts coupled with questionable data quality used in experimentation, using phase diagrams alone is of limited usefulness. Many authors have thus switched to using the extended UNIQUAC activity coefficient model to simulate freeze crystallization as the use of phase diagrams becomes impractical in systems with more than four types of ions [3]. It is with the UNIQUAC model that we proceed and gives justification to the use of the OLI Stream Analyzer in this thesis.

#### 3.4.1 Salt Selection Criteria and Concentration

Similar to single species salt selection, salts are now needed that can:

1. Accurately test the capabilities of the OLI software while simultaneously providing utility to the study at hand
2. Be separate and distinct without common ions to determine if the simulation can identify and proceed through multiple eutectic points
3. Build on the previous simulation of NaCl in order to evaluate what changes, if any, the presence of additional salt species has on the eutectic point of Na<sup>+</sup> and Cl<sup>-</sup> given they are the most prevalent ions in these hypersaline waste waters
4. Have applicability to the oilfield and the ions commonly associated with Marcellus and Utica waste water and have a eutectic temperature that is different enough from NaCl that it can be readily identified graphically.

For the above criteria, one salt is especially troublesome in the Marcellus and has a high eutectic point as evidenced by its scaling tendencies at very high (room) temperatures. Barium Sulfate, BaSO<sub>4</sub>, is an inorganic salt that has very low solubility in water and whose solubility is not appreciably temperature dependent [81]. While the eutectic temperature of BaSO<sub>4</sub> is not low (due to the low solubility of this salt there is no distinct eutectic point per se, but rather near 0°C there is ice formation and this ice formation contributes to an increase in the concentration of BaSO<sub>4</sub> in a single species Barium Sulfate brine) it is a salt that is present in all water quality reports that are provided for this thesis in the Marcellus and Utica Shale, and can be seen in **Table 7.1** in Appendix A. This salt also has applicability to addressing the scaling concerns mentioned as drivers for waste water recycling solutions in Section 3.2 and Section 2.2. Calcium carbonate is not included as the second salt for analysis as Marcellus shale produced waters exhibit



little calcium carbonate, compared to those wells of the Permian Basin and Eagleford shale.

The modeled freeze crystallization is performed using temperature reduction steps of 2°C from a starting temperature of 20°C to -50°C. The rationale for the selection of these temperatures for use in the simulation are given in Section 3.1, and pertain to the physical continuity limitations of the software (-50°C), the lower realistic limit of commercial chillers, and an arbitrary value of ambient temperature (20°C). From previously published literature, it is expected that no freeze crystallization will occur at temperatures above 5°C except for solutions that are previously supersaturated, [5] or exhibit very low solubility. The 2°C temperature steps size is selected as there is no appreciable loss of accuracy when compared to incremental step sizes, but simulation time is reduced greatly. Each graph is representative of a 1L sample of brine with the qualities described, and therefore a precipitation of 1 gram of any salt species would indicate a reduction in the TDS by 1000ppm for each ion required for that salt species.

**3.4.2 Results from Software**

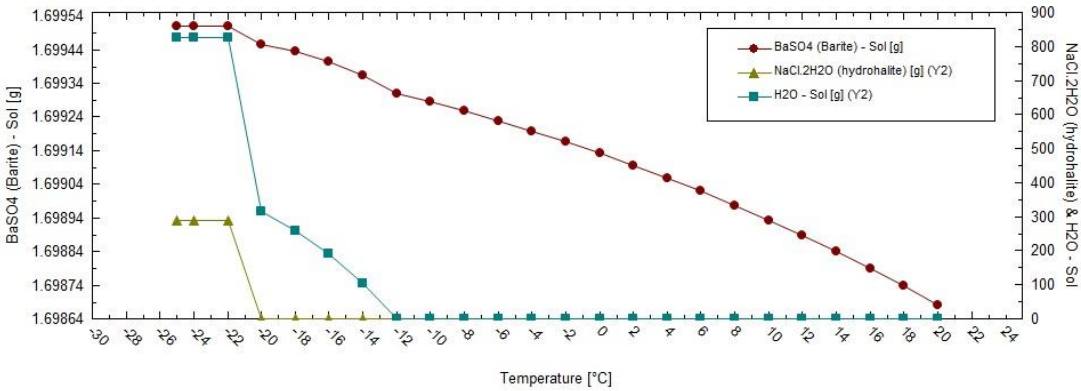


Figure 3.8 - Binary species brine of NaCl and BaSO<sub>4</sub>

The simulation of freeze crystallization on the binary brine of 2.0 wt% BaSO<sub>4</sub> and 23.3 wt% NaCl brine is shown above in **Figure 3.8**. The proper way to mentally observe the EFC graphic is by viewing right to left as that would be associated with a temperature reduction due to freezing. Due to the low solubility of BaSO<sub>4</sub>, Barium Sulfate gradually forms as temperature is reduced and the solubility is further reduced. Notice the low solids formation for BaSO<sub>4</sub> (~1.7g in total, but 1.698g is deposited prior to cooling) indicating that rapidly, almost all the Barium Sulfate is removed from solution and further chilling does not significantly alter the solubility of Barium Sulfate and therefore the produced quantity of BaSO<sub>4</sub> from EFC specifically is negligibly small. Ice begins forming at a reduced temperature of -12°C, significantly different than the known freezing temperature of pure water under atmospheric pressure of 14.69 psi of 0°C. Only ice (and negligible trace Barium Sulfate) is formed until a temperature of -20°C, at which point NaCl·2H<sub>2</sub>O (hydrohalite) begins to be formed. By forming solely ice originally, the system is increasing in concentration of NaCl until finally reaching the eutectic concentration at which point hydrohalite is formed. However, different than the ice formation of the 2.5 wt% NaCl brine in Section 3.3.2, the ice formation temperature is now -12°C instead of 0°C and the formation temperature for hydrohalite is now -20°C instead of -22°C. this indicates that the presence of Barium Sulfate even in small quantities has a significant effect on the phase diagram of the brine and can alter the expected properties and action of the brine under chilling. The consequences of this effect will be discussed further in Section 5.1.1., Feasibility of Implementation.

### 3.4.3 Comparison to Published Data

To date, there has been no published literature discussing the freeze crystallization of a Barium Sulfate and Sodium Chloride binary species brine. Relative to the plethora of available literature on Sodium Chloride brines, information on Barium Sulfate brines or crystallization is nonexistent. Likely this low availability of Barium Sulfate brine information is due to the low solubility of this salt and its propensity to be a salt crystal in nature, not necessarily be a brine species. Given the lack of information relating these two-salt species, there is little that can be said regarding their comparison to published information, whether experimental or simulated. Instead, this section will include remarks regarding the phenomena discussed in the proceeding section on the reduction in water crystallization temperature in a Sodium Chloride brine with the low concentration of Barium Sulfate relative to a single species Sodium Chloride brine and relating this back to known principles of electrolytic chemistry.

Mentioned previously in Section 3.4.1, the common ion effect is the phenomena when multiple salt species in solution share a common ion. For waste water brines an example would be NaCl and MgCl<sub>2</sub> both sharing Cl<sup>-</sup> ions for formation. Lewis et al. [3] determined that experimental results of a binary common ion brine are in agreement with the OLI Stream Analyzer model and that even in low concentrations, that impurities (such as Ba<sup>2+</sup>) have a clear effect on the eutectic temperature by depressing the freezing point of ice, and therefore the eutectic point of the system. Even though the hypothetical brine that is tested consists of Ba<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, the higher reactivity of the chloride ion over the sulfate ion causes the system to react instead as if it is solely a

NaCl, BaCl<sub>2</sub> brine and therefore there is an effect from the common ion, Cl<sup>-</sup>. This is an important consideration considering that Chloride ions are highly reactive and are also present in large quantities in oilfield waste brines. This implies that the common ion effect will similarly depress the freezing point of ice or salt in a complex brine simulation in Section 3.5.2.

#### 3.4.4 Connection to Produced Water

As I mention in Section 3.3.1 and 3.4.1, the use of NaCl and BaSO<sub>4</sub> in the binary species simulation is conducted due to the prevalent nature of these salts in brines from the oilfield, specifically the Marcellus and Utica Shale plays [40]. In the subsequent sections of this chapter, we will delve into freeze crystallization as it has yet to be studied; with the use of the OLI Stream Analyzer software to conduct simulation of EFC on multi-species complex waste water brines. The effect that the small amount of BaSO<sub>4</sub> had on depressing the freezing temperature of ice highlights clearly the importance of obtaining detailed and complete water quality reports for the waste water of the Marcellus if Freeze Crystallization is to be performed and that even small variations in composition might have profound effects on the sensitivity of the system. This could have implications on the ability of a Freeze Crystallization treatment facility to handle the volumes and rates of waste water necessary for commercial operation or impact the scaling of a system for mobile applications, as is discussed in Section 5.2.1. As well, the effect of the BaSO<sub>4</sub> still in solution in trace quantities is addressed in Section 5.3.3 when discussing the robustness of EFC as a standalone water recycling method and the potential need for additional water processing steps, likely with the use of RO.

### 3.5 COMPLEX WASTE WATER BRINE ANALYSIS

For the complex brine analysis, I am analyzing simulation of Freeze Crystallization using inputs from the water quality reports provided courtesy of Baker Hughes Inc. These water quality reports can be viewed in Table 7.1, Appendix A and are inclusive of 149 wells that produce from the Utica in Ohio, and 182 wells that produce from the Marcellus in West Virginia or Pennsylvania. Included in these reports are 19 unique measures of the water quality, given as mg/L (ppm) of ions of interest and biocides or scale inhibitors. A selection of these wells is used to simulate freeze crystallization on a variety of Marcellus and Utica brines. The potential limitations of analysis using only these 19 parameters are discussed further in Section 5.4.1. Given the broad range of TDS from these water quality reports, multiple simulations are performed on a variety of the reported samples from each play, as well as a simulation of a representative average brine from each play. These multiple simulations are performed to determine if there is significant sensitivity to the impurities reported, or whether all the brines have eutectic points that are similar enough to be processed together and wouldn't require individual processing systems for each specific well composition.

#### 3.5.1 Salt Selection Criteria and Concentration

The TDS of the Marcellus brine water quality reports ranges from 59,000-310,000 ppm indicating these are very saline brines that would not be capable of undergoing RO treatment (see Chapter 2, Section 2.3.2). Recall from Section 1.3 that one selection criteria for the Marcellus Shale play specifically for water disposal investigation is because this region is limited in the application of injection wells for disposal and has

high costs for transportation to disposal sites. While the hypersalinity would make it challenging to process for typical water treatment methods, freeze crystallization is well situated for the cool temperatures of the Northeast and the high concentration of salts in general would mean that with reduced energy input pure salt can be generated in copious amounts. As mentioned in Section 3.2.3 there is economic value that could be obtained through the sale of these pure crystallized salts from the EFC process. The economic value of this sale and the implications on supply EFC could have are explored further in Section 5.3.

For analysis, wells are selected that did not have reported quantities of SIs (scale inhibitors) or biocide as the specific chemical used is not listed and the effects these chemicals would have on the EFC process are unknown. SIs work by disrupting the formation of the crystal lattice structure of the salt by denying nucleation points or disrupting the active crystal growth sites [82]. Additionally, wells are selected that both did and did not exhibit net charges to test the robustness of the OLI Stream Analyzer in its ability to handle non-neutral charge. All the brine samples collect for analysis by BHI are collected from API separators [51] and should exhibit a minimal residual hydrocarbon or TSS. It is assumed in this thesis that any residual hydrocarbon or TSS are removed via an alternative processing method prior to EFC.

### *3.5.2 Results from Software*

In this section, I will proceed in detail over 5 simulations performed using the OLI Stream Analyzer on actual oilfield brines reported from the Marcellus, Utica, and Permian basins. These brines represent a small sample of the available brine data provided

courtesy of Baker Hughes Inc. but provide a representative dataset for the expected Freeze Crystallization (FC) cases that would be represented across the spectrum of brines from these plays. The analysis and commentary to proceed will first give salient information about the makeup of the brine (complete data information is available for each in **Table 7.1** in Appendix A, followed by an intuitive preliminary expectation that can be made regarding what we know from the preceding Sections 3.3 and 3.4 and then finally the simulation results are commented and explained. A discussion on the results from the simulation itself and the implications these results have on the design and implementation can be found in Section 5.1.

The first simulation performed using the water quality reports is for the Marcellus Shale well 104 (API 37-019-22194) that has an estimated TDS of 144,552 ppm, of which 91,881 is  $\text{Cl}^-$  and 34,142  $\text{Na}^+$ . This represents a brine that is approximately 7 wt% NaCl with approximately 7 wt% other ions, the majority of which are Chloride. Given that the brine consists primarily of NaCl and that main contaminants are Chloride ions (126,022 ppm is either sodium or chloride) this suggests that less than 2 wt% of the brine is other contaminants. Intuitively, if we proceed as if the brine is just a pure NaCl brine of 7 wt%, we can predict a high side estimate for the first freezing temperature of the brine. Recalling from Section 3.3 the known solubility curve for an NaCl brine of 7 wt%, we would predict it to exhibit the formation of ice at a temperature of approximately  $-5^\circ\text{C}$ . Since a pure NaCl brine of 7 wt% is below the eutectic concentration considerably, we would firstly expect ice to form with FC of the Marcellus 104 brine. Including the pertinent information from the water quality report for Marcellus 104, namely that

there are other cations that share a common ion (chloride) with sodium, we investigate what effect this would have on the observed ice crystallization temperature.

We would expect, based on the results of the analysis presented in Section 3.4 and the literature from Lewis et al. (2011), that the presence of these other species that the eutectic temperature is depressed. Whether significantly or only moderately we cannot be sure based on approximation and intuition alone, but if the pure brine would exhibit a first freezing point of  $-5^{\circ}\text{C}$ , then  $-10^{\circ}\text{C}$  to  $-15^{\circ}\text{C}$  wouldn't be abnormal. Therefore, the expectation we proceed with based on a very limited subset of information regarding the brine from the Marcellus 104, just TDS, Chloride and Sodium, we make the prediction that the results from the simulation will yield a case where:

1. Ice is formed prior to salt crystallization
2. The salt that will crystallize is NaCl, or rather hydrohalite as the stable species
3. The temperature of ice formation is depressed below that of a pure NaCl brine of  $-5^{\circ}\text{C}$
4. The Eutectic temperature of the system should be lower than that of a pure NaCl brine of  $-21.1^{\circ}\text{C}$

Presented below in **Figure 3.9** is the OLI Stream Analyzer FC simulation for the Marcellus 104. We conclude that our prediction from above given some limited information and assumptions is accurate. Specifically, we now identify the ice formation temperature to be near  $-8^{\circ}\text{C}$ , and a eutectic temperature for co-formation of hydrohalite and ice at approximately  $-30^{\circ}\text{C}$ .



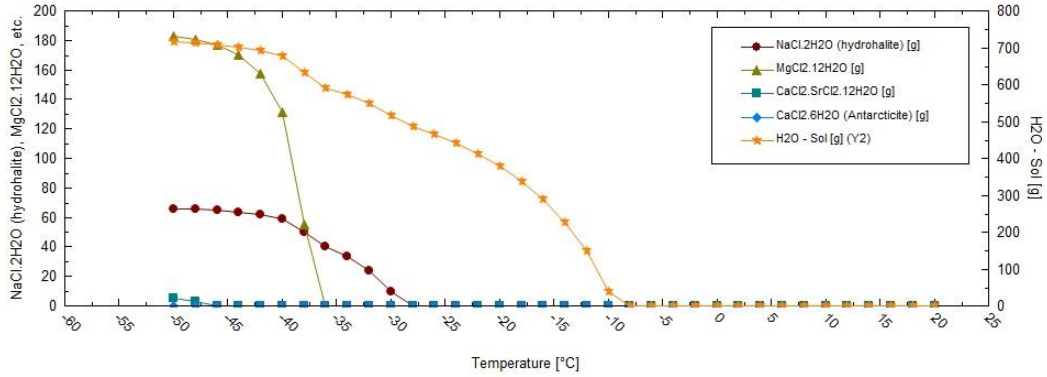


Figure 3.9 - EFC Simulation of coproduced brine from Marcellus 104

We see other eutectic points at much lower temperatures and associated with the formation of measurable salt crystallization, such as that of  $MgCl_2$  at  $-36^\circ C$  and minute crystallization of antarcticite ( $<10$  g/L or 10,000ppm). This FC graph has been simplified to reduce the number of formed salt species for clarification. Other salt species form, however they all exhibit a crystallization temperature substantially below that of hydrohalite, and each form in such minute quantities ( $\ll 1$  g/L) that they can be perceived as impurities in the formed solids and thusly be ignored. The cations of formation are not appreciably rare and do not include those that have significantly more economic value than NaCl, as is addressed in Section 5.2.

Specifically, from this first simulation analysis of a Marcellus oilfield brine we note that intuitive interpretation of water quality provided rapid realization if a sufficient amount of information regarding likely formation temperatures and crystallization products, and that for a brine of approximately 150,000 ppm TDS, we first see crystallization of ice. This first production of ice and its association with the brine TDS is further quantified in succeeding analysis of other Marcellus brines.

Moving now to the Marcellus 75 brine (API 37-031-25508) that has an estimated TDS of 310,161 ppm, of which 192,526 is  $\text{Cl}^-$  and 67,795  $\text{Na}^+$ . This represents a brine that is approximately 13.5 wt% NaCl with approximately 17 wt% other ions, the majority of which are Chloride. Given that the brine consists primarily of NaCl and that main contaminants are Chloride ions (260,321 ppm is either sodium or chloride) this suggests that less than 5 wt% of the brine is other contaminants, the majority being either Calcium ( $\text{Ca}^{2+}$ ) at 3 wt% or Barium ( $\text{Ba}^{2+}$ ) of 0.8 wt%.

Given the high TDS of this brine coupled with the very large total contribution of impurities in the form of Calcium, Barium, etc. we will not attempt to intuitively assess the outcome of FC on this sample as it is indeed, very complex. Instead, we will focus on interpreting the results of the FC for OLI Stream analyzer and the implications this would have on the formation of pure salts. The simulation for Marcellus 75 is shown below in Error! Reference source not found.. We identify that there are multiple eutectic points and the potential formation of 4 salt species. The crystallization temperature of the Calcium Chloride and Magnesium Chloride is too low for commercial freezing and is excluded from consideration of the EFC analysis. At  $-8^\circ\text{C}$  we see first formation of hydrohalite, followed by Barium Chloride at  $-18^\circ\text{C}$  and finally eutectic formation of ice,  $\text{BaCl}_2$ , and hydrohalite at  $-24^\circ\text{C}$ .

The formation of multiple salts at one eutectic temperature would indicate that the salt crystals formed are inseparable and would not be as marketable as if they are pure. Given for a 1 L sample it is predicted that 8 g of  $\text{BaCl}_2$  form with 200g hydrohalite, that would indicate salt formation that is 6%  $\text{BaCl}_2$  and 94% NaCl after dehydration of the

hydrohalite. 94% is still a relatively high purity and likely acceptable on an industrial reagents scale. This relative economic value is addressed in Section 5.2.

The relevance of including the Marcellus 75 brine in this discussion is due to its uniqueness in having two salts crystallize at the temperature. In the dozens of simulations performed, it is one of only a few that exhibited this phenomenon. The others (Marcellus 63, 68, 69, and 76) all exhibited the formation of the same two salts. This is caused by the high proportion of Barium ions in each brine which has a similar propensity to form chlorine salts as other Alkaline Earth Metals. Given that only 5 of the 332 brine samples exhibited considerably high levels of barium, the likelihood of this occurring during FC of a conglomerate brine from multiple sources is low. This is quantified later in this section by way of example using an average of all the Marcellus brines as one stream.

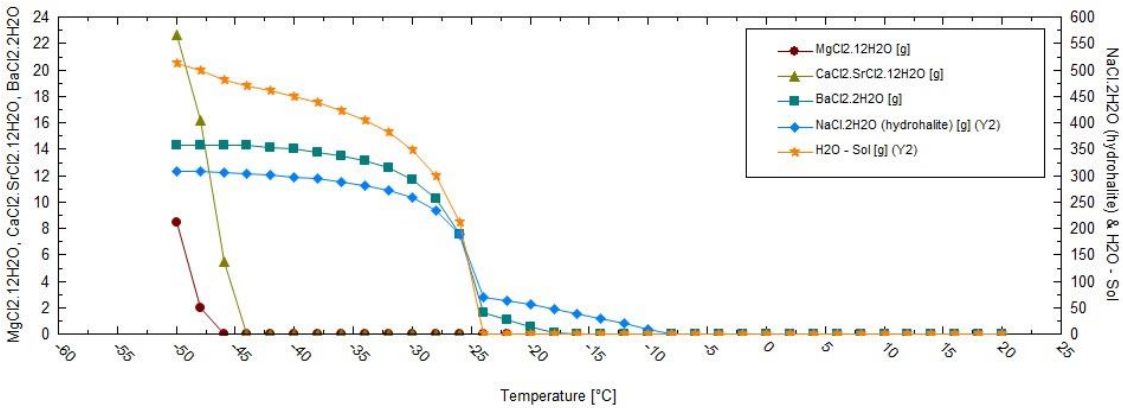


Figure 3.10 - EFC Simulation of Coproduced brine from Marcellus 75

The final Marcellus stream to be included is for an average of the 184 Marcellus brines reports in the water quality summary provide by Baker Hughes Inc This average would represent the comingling of many well produced water streams to one for central

treatment and processing. The average Marcellus brine has an estimated TDS of 221,451 ppm, of which 137,753 is  $\text{Cl}^-$  and 47,869  $\text{Na}^+$ . This represents a brine that is approximately 9.5 wt% NaCl with approximately 13 wt% other ions, the majority of which are Chloride. Given that the brine consists primarily of NaCl and that main contaminants are Chloride ions ( $\text{Cl}^-$ ) (185,622 ppm is either sodium or chloride) this suggests that less than 3.5 wt% of the brine is other contaminants, the majority being Calcium ( $\text{Ca}^{2+}$ ) at 2.8 wt%. This average Marcellus produced brine is generated using a weighted average of the stream volumes associated with the water quality reports provided courtesy of Baker Hughes Inc. Only those wells that did not indicate the use of biocides or scale inhibitors are included. The inclusion of this average brine in this analysis is to investigate what type of FC would be expected from the use of field wide processing. This field wide processing and related averaging should have the effect of reducing the contribution of individual wells producing large percentages of contaminants that could affect the sole formation of hydrohalite and ice at the eutectic temperature. For example, by averaging the Marcellus 75 brine in, the effect of Barium has been decreased. In fact, the Barium contribution to the average brine is now 0.08 wt% compared to 0.8 wt% in the Marcellus 75.

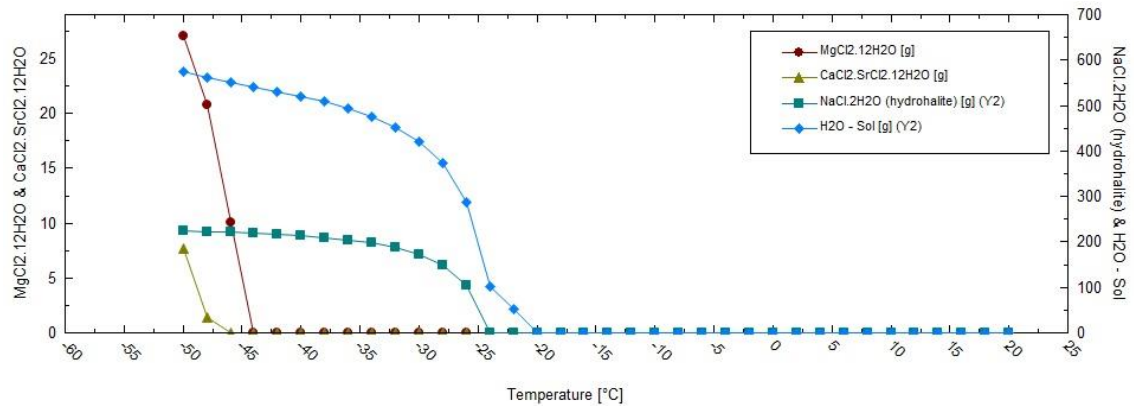


Figure 3.11 - EFC Simulation of coproduced average brine from Marcellus Shale

Shown above in **Figure 3.11** are the results of FC simulation using the OLI Stream analyzer on the Marcellus average brine. We see that we have the formation of ice crystals only from -20°C to -24°C and then eutectic co-formation of hydrohalite and ice at -24°C. There again are other eutectic temperatures of -44°C for magnesium chloride and -46°C for Calcium Chloride however these salts are present in minute quantities compared to NaCl and ice. The formation of ice only prior to EFC is discussed in further detail in Section 5.2 as it has economic implications for the feasibility of EFC and its incorporation as a viable water recycling method in the oilfield industry.

Following the average Marcellus (Pennsylvania) brine, we analyze an average Utica (Ohio) brine to determine if there is a distinctly different profile to be expected from this neighboring formation, or if similar EFC are present in all oilfield brines. Consequently, this analysis is followed by the analysis of a Permian Basin (West Texas) brine to eliminate potential regional and timescale concerns.

The average Utica brine has an estimated TDS of 169,089 ppm, of which 109,125 is Cl<sup>-</sup> and 34,677 Na<sup>+</sup>. This represents a brine that is approximately 8 wt% NaCl with approximately 9 wt% other ions, the majority of which are Chloride. Given that the brine consists primarily of NaCl and that main contaminants are Chloride ions (143,802 ppm is either sodium or chloride) this suggests that less than 2.5 wt% of the brine is other contaminants, the majority being Calcium (Ca<sup>2+</sup>) at 1.9 wt%. This average Utica produced brine is generated using a weighted average of the stream volumes associated with the water quality reports provided courtesy of Baker Hughes Inc. Only those wells that did not indicate the use of biocides or scale inhibitors are included. The inclusion of this average brine in this analysis is to investigate what type of FC would be expected from the use of field wide processing. This field wide processing and related averaging should have the effect of reducing the contribution of individual wells producing large percentages of contaminants that could affect the sole formation of hydrohalite and ice at the eutectic temperature.

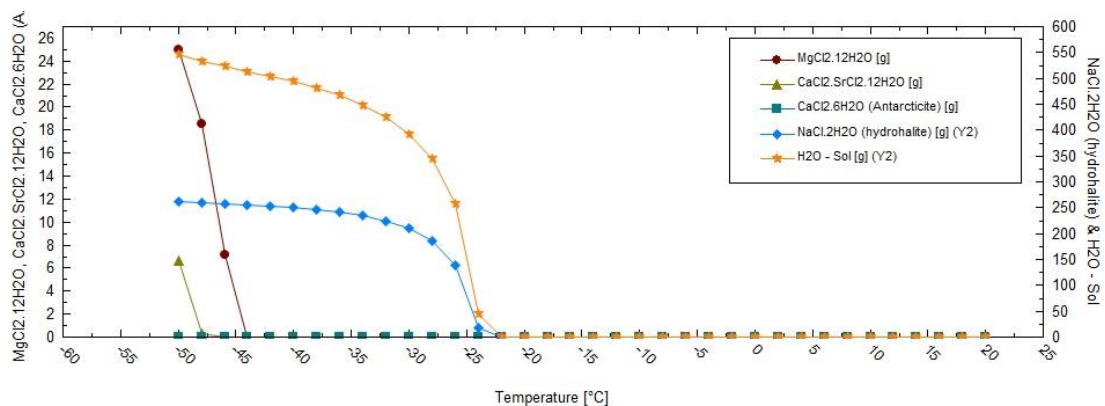


Figure 3.12 - EFC Simulation of coproduced average brine from Utica Shale

Shown above in **Figure 3.12**, are the results of FC simulation using the OLI Stream analyzer on the Utica average brine. We see that we have the co-formation of hydrohalite and ice at  $-24^{\circ}\text{C}$  indicating the brine is near the first eutectic concentration for the hydrohalite species. There again are other eutectic temperatures and  $-44^{\circ}\text{C}$  for magnesium chloride and  $-48^{\circ}\text{C}$  for Calcium-Strontium Chloride, however these salts are present in minute quantities compared to NaCl and ice. The implication of EFC without prior salt or ice crystallization and potential sensitivity is discussed in further detail in Section 5.2 as it has economic implications for the feasibility of EFC and its incorporation as a viable water recycling method in the oilfield industry.

Finally, we end the complex waste water brine analysis with a sample Permian waste water. The water quality report for this Permian stream comes from a different source than the Marcellus and Utica data. While much of the information provided remains the same, there are also many more ions reported. In general, these ions are present in minute quantities and likely will only have the effect of depressing the eutectic point of the mixture. Additionally, it should be noted that the Permian stream is much less saline than the brines of the Marcellus and Utica, as is to be expected, however the sample provided still seems remarkably low in TDS.

The Permian brine has an estimated TDS of 34,568 ppm, of which 21,200 is  $\text{Cl}^-$  and 12,200  $\text{Na}^+$ . This represents a brine that is approximately 2.5 wt% NaCl with approximately 1 wt% other ions, the majority of which are Chloride. Given that the brine consists primarily of NaCl and that main contaminants are Chloride ions (33,400 ppm is either

sodium or chloride) this suggests that less than 0.1 wt% of the brine is other contaminants, the majority being Carbonic acid ( $\text{HCO}_3^-$ ) at 0.09 wt%.

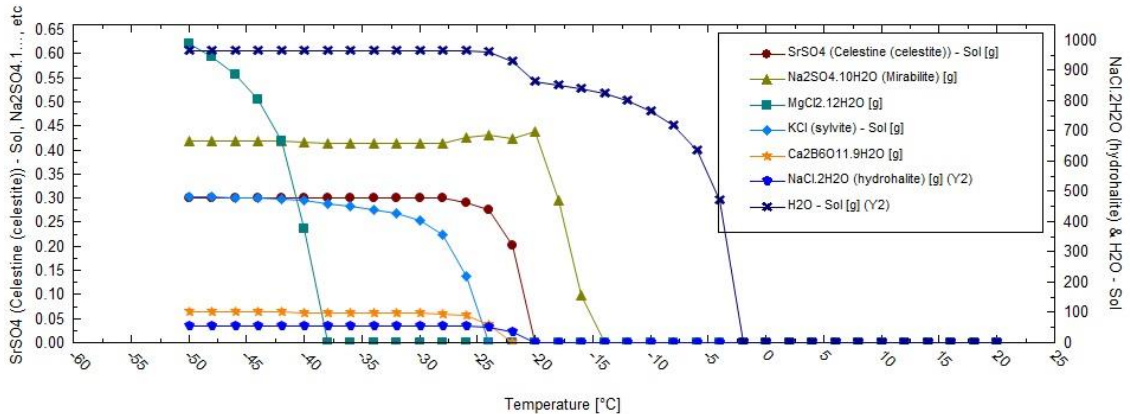


Figure 3.13 - EFC Simulation of coproduced brine from the Permian Basin

Shown above in **Figure 3.13** is the OLI Stream Analyzer simulation for the Permian waste water brine. As might be expected for a brine of such low TDS and predominately NaCl, we first observe the formation of ice. Of note, is the formation of Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) at  $-14^\circ\text{C}$ . This is interesting for the fact that the level of sulfate is low (284 ppm). Likely due to the high pH there is stability for this salt species to form. However as is the case in the Marcellus 75 and the formation of Barium Chloride, there formation of Mirabilite occurs in very minute quantities. Where FC to achieve  $-22^\circ\text{C}$ , we would be left with a salt portion that is  $\sim 55$  grams Hydrohalite and just 0.5 grams Mirabilite, or an impurity level of 2% after dehydration of the hydrohalite. We also observe that the eutectic point for this sample is approximately  $-22^\circ\text{C}$ , similar to that of a pure singular species NaCl brine. It is clear that the impurities are having little effect on depressing the eutectic point of this sample. This is due to the low TDS nature of this



salt and the very low level (<0.1 wt%) of impurities compared with other brines that have been analyzed.

### 3.5.3 Comparison to Published Data

There is no published data regarding the freeze crystallization of oilfield brines. Much of the literature for eutectic freeze crystallization is focused on identifying the costs of an EFC facility compared to that of an RO facility [3, 7, 74], identifying potential uses for EFC as a tertiary desalination method for other desalination processes [83], or as a potential technology for the use of disposal in the mining industry for a simple binary salt [84]. The effects of residual hydrocarbon and TSS is unknown for the EFC process [85], as are the effects of industry standard scale inhibitors and biocides. While the oilfield brines are complex in terms on containing many ionic components, the main component is a high concentration of NaCl which has been deemed to be suitably treatable only with freeze crystallization [76]. Identified in Section 3.4 that Lewis et al. [3] determined that experimental results of a binary common ion brine are in agreement with the OLI Stream Analyzer model and that even in low concentrations, that impurities (such as Ba<sup>2+</sup>) have a clear effect on the eutectic temperature by depressing the freezing point of ice, and therefore the eutectic point of the system. Similarly, the effect of Ba<sup>2+</sup> and its depression of the eutectic point to below that expected for a NaCl single species salt alone is also present in the complex oilfield brine as well. Section 5.3 will include a more detailed inspection of the published literature with regards to the implications of the transports, sale, and potential disposal of NaCl salt and brine retentate.

#### 3.5.4 Connection to Produced Water

The analysis presented above in Section 3.5.2 uses information provided courtesy of Baker Hughes Inc. from standard water quality reports generated in the field from samples collect from API water separators. In the reports are tabulate information including pertinent water quality information such as the TDS, use of biocides, scale inhibitors, etc. Also noted are the contributing proportion of 19 ions common in oilfield waters, such as sodium, magnesium, chlorine, etc. While not inclusive of all species present in these complex water systems, the water quality reports do include those ions that are present in measurable quantities and that are required by law. There is no current regulatory requirement to report the content or concentration of NORM in the waste water. Therefore, without further analysis the effects of NORM on the nucleation of salt and ice crystals can be speculated only. Further speculation into this effect are presented in Section 5.1.

### 3.6 SYNOPSIS OF CHAPTER THREE

In this Chapter, I have introduced potential benefits realized by the industry if EFC is to be incorporated as a recycling method for waste water over currently established methods. For information regarding current water disposal and recycling methods please see Section 2.3. Also included is the concept of Eutectic Freeze Crystallization with introductory examples to explain the phenomena and provided justification for the use of the OLI Stream Analyzer for the simulation work that is performed. Additionally, I have presented singular and binary species salt simulations to provide and illustrate the freeze crystallization process with reference to the current literature status of freeze

crystallization. Commentary on the gaps in the current EFC literature are mentioned explicitly in Section 3.4 and reinforce the research questions presented in Section 1.2 as well as the needs for further work that is expanded in Section 5.1. Finally, the Chapter is concluded with original simulation of complex multi-species oilfield brines provided by way of water quality reports courtesy of Baker Hughes Inc. in Section 3.5. The general implications of the results of this chapter are outlined below regarding the technical outcomes. For economic and system design implications please refer to Sections 5.2 and 5.3, respectively.

- The Eutectic temperature for singular species NaCl brine is  $-21.2^{\circ}\text{C}$  with the formation of hydrohalite
- Inclusion of other ions and chloride forming cations has the effect of depressing the crystallization temperature of hydrohalite, generally on the order of  $5\text{-}10^{\circ}\text{C}$
- The co-formation of other salts near the eutectic point of hydrohalite can be limited through the mixing of waste water streams from multiple wells
- Oilfield brines, composing mainly  $\text{Na}^+$  and  $\text{Cl}^-$  in the TDS, exhibit one realizable eutectic temperature (hydrohalite and ice) while the eutectic temperature for other salts is too low for commercial chilling operations
- An average Marcellus/Utica brine exhibit first the formation of ice, followed by eutectic co-formation of hydrohalite and ice

## Chapter 4 – Bench Scale Testing of Eutectic Freeze Crystallization

In this Chapter, given the immense cost associated with contracting EFC work or building an experimental testing apparatus for EFC at the University of Oklahoma, we discuss briefly a method for establishing a working bench scale design and discuss the possible outcomes from this type of testing and why it is necessary for answering the Research Questions (Empirical Performance Validity). Section 4.1 includes a discussion of the pertinent outcomes that are required of experimental work and are necessary for the proof of concept for EFC implementation. Also, in Section 4.1, the results of the EFC simulation work presented in Section 3.5 are compared to those that would be generated from experimentation. Section 4.2 approaches the information that is missing in the current literature and necessitates original research to be able to answer important Structural Validity questions regarding EFC. Section 4.3 includes the design and construction of a bench scale EFC testing apparatus. Also, in Section 4.3 is discussion on procurement and associated costs for the construction of a EFC laboratory bench for the parameters which we would be interested in collecting for analysis. The anticipated possible outcomes of experimentation tie to the third quadrant of the validation square for Research Questions 1 and 3, and the Structural Validity for Questions 2 and 4 are provided in Section 4.2 and 4.4. In Section 4.4 we discuss in more detail the importance and process of quantifying relevant effluent stream qualities for the validation of EFC for oilfield use. This Chapter is essential for validating the thesis through a purposefully designed method with commentary on the implications for use in industry and technological development. In conjunction with the economic evaluation provided in

Chapter 5, this Chapter is primarily of utility to industrial researchers that have funding greater than academic parties and could take the validation of EFC to the next stage to verify and narrow the estimates of feasibility and cost presented herein. This chapter relies heavily on the use of the validation square to verify and validate the concept presented in this thesis. Chapter 1, Section 1.4.2 contains more information regarding the verification and validation strategy and is heavily dependent upon the work done by Pederson et al. (2000) [25].

#### 4.1 CONFIRMATION OF SIMULATION

In this Section we discuss the pertinent outcomes that are required of experimental work and that are necessary for the proof of concept for EFC implementation. In Section 4.1.1 and 4.1.2, the results of the EFC simulation work presented in Section 3.5 are compared to those that are generated from experimentation. This is necessary given the lack of published literature concerning the efficacy of complex multicomponent freeze crystallization to physical results. Section 4.1.1 discusses the simplest verification necessary for EFC, determining the Eutectic Temperature of the brine, which relates to the work of Chapter 5, Section 5.2.2 and Chapter 3, Section 3.2.3. Section 4.1.2 has implications to the validation of EFC as a cost-effective water management solution in the oilfield, which is also discussed in more detail in Chapter 5, Section 5.2.2 and Chapter 3, Section 3.2.3. Finally, Section 4.1.3 is included as a primer for the Performance Validity for EFC and Research Questions' 1 and 2 that is presented in Chapter 5, Sections 5.2.3 and 5.2.5 which relate to the sale and disposal of the produced salt stream.

#### 4.1.1 Verification of Eutectic Temperature

In this Section, we discuss the use of bench scale experimentation to verify the structural consistency of EFC by comparing the results of EFC simulation to experimentation. This is a necessary step in the proof of concept for EFC as the nature of the complex multicomponent oilfield brines is largely unknown. As discussed in Chapter 3, Section 3.1.1, the OLI Systems is used to model theoretically the fractional crystallization due to temperature drops expected in a freeze crystallization system. Lewis et al. (2010) [3] first discussed the use of the OLI software for brine crystallization of multicomponent waste water streams. In their study, bench scale laboratory freeze crystallization of a 5 wt% Na<sub>2</sub>SO<sub>4</sub> brine is compared to that generated by the OLI Stream Analyzer, specifically the eutectic temperature and concentration. Using the validation square discussed in Chapter 1, Section 1.4.2., this agreement indicates a high level of confidence in the generated results of the OLI Systems software for simple multi component brines. However, their analysis does not accurately capture the high complexity and variability of waste water streams that are present in the oil and gas field, nor is there sufficient evaluation of freeze crystallization economics to justify further study of the matter at an industrial level. As mentioned in Chapter 1, Section 1.1.3, the hope is that the analysis presented in this thesis can fill these gaps and present clear validation for further examination as well as provide a potential avenue away from the use of waste water injection as a disposal method discussed in Chapter 2, Section 2.3.3. Much of the thermodynamic comparison that is discussed in this section is in relation to the work published by Verbeek (2011) [6].

Verbeek performs work using a cooled disk column crystallizer (CDCC) as first mentioned by vd Ham (1998) [41] and a scraped cooled wall crystallizer (SCWC) of 10L and 200L volume, respectively. A depiction of the CDCC used in his experimentation is included as for clarity.

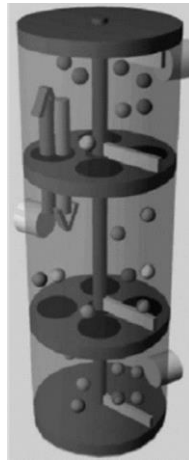


Figure 4.1 - Cooled Disk Column Crystallizer Design [41]

His work shows that the eutectic temperature of  $-21.1^{\circ}\text{C}$  corresponds to the theoretical value for a NaCl brine of 23.3 wt%, the eutectic concentration. This agrees with the OLI System Stream Analyzer Simulation results obtained and discussed in Chapter 3, Section 3.3.2 of a eutectic temperature of approximately  $-21^{\circ}\text{C}$  for a NaCl brine of 23.3 wt%. Verbeek also explores the effect of a contaminants, Mg at 1 wt%, on the crystallization temperature and purity of NaCl. He concludes that the contaminant suppresses the freezing point slightly, but also increases the rate of heat transfer by 30%. He attributes this increased heat transfer to the reduced scaling of precipitated salts on the vessel body. This result holds promise that the high level of contaminant ions present in oilfield

waste water could be beneficial to the EFC process and help the thermal efficiency of the design.

The crystallization model developed by OLI utilizes the revised Helgeson-Kirkham-Flowers (HKF) model for calculation of thermodynamic properties of aqueous solutions and modifies the framework of the Debye-Huckel model for other excessive terms [3, 67]. OLI Stream Analyzer uses the HRK method to carry out crystallization calculations to temperatures of  $-50^{\circ}\text{C}$ , which is the lower limit of that model. This model appears to be adequate for the analysis presented insofar by Verbeek and Lewis et al. by verifying the eutectic temperature and concentration of a simple singular and binary species brine. What is unclear and necessitates further experimentation, is the verification of the eutectic temperature of a complex multi-species brines. Determining the eutectic temperature alone would not justify the high cost of developing an experimental setup but is one piece of information that would be useful in the path to providing a proof of concept for EFC in the oilfield industry. As mentioned previously in Chapter 3, Section 3.5, the reduced eutectic temperature for the complex multi species brines is consistent with the results obtained by Lewis et al. showing a suppression of eutectic temperature in their experiments from the additional ions in solution and is consistent with the work of Verbeek. The magnitude of this suppression from simulation of oilfield brine is nontrivial as there is great difficulty in reaching  $-26^{\circ}\text{C}$  compared to  $-21^{\circ}\text{C}$ . Refer to Chapter 3 for more detail regarding the eutectic temperature and simulation of complex multi species brine.



#### 4.1.2 Verification of Thermodynamic Requirements

The main necessity for performing experimentation, then, is not for difficulty of determining the Eutectic Temperature of the brine mixture as in Section 4.1.2 we show that the OLI software has shown substantial evidence that the Eutectic Temperatures calculated are valid. Rather, the difficulty comes from determining the overall specific heat for the brine, as it is a complex calculation based on many physical phenomena – conductivity of slurries, contaminants, and penetration theory. The conductivity of the liquids and the contained solid particles is described by Tareef (1940). Ramires (1994) [86] provides the thermal conductivity for a sodium chloride solution based on temperature and concentration. His work does not discuss the role of contaminants on these constants. Verbeek assumes that given the small level of contaminants (<1 wt% Mg) in his test brine, that the deviation from the theoretical thermal conductivity will be small. Indeed, by his analysis the introduction of the contaminant could change the specific heat by the fluid by as much as 10% and result in only a 1% increase in total heat transfer for the crystallization chamber designs used. This is a sufficient assumption to be made under his circumstances but does not adequately describe the situation faced when using EFC for the produced water brine where contaminants account for upwards of 7 wt%. Finally the specific heat of the slurry of ice and salt in water is calculated by the process described by Meeuqisse and Infante (2001) [87].

There is no literature to be found regarding the effect of such high level of contamination that consists of multiple salt species. To provide a proof of concept for EFC in the oilfield, experimentation must be done to verify that the high level of

contaminant species in the NaCl dominant produced brine would not adversely affect the heat transfer of the process as heat transfer directly influences the capacity of the crystallizer.

The OLI Stream Analyzer calculates a specific heat for the NaCl brine at the eutectic concentration of  $3.4 \text{ kJ}/(\text{kg}\cdot^\circ\text{K})$  which does not correspond well to the specific heat Verbeek found to be  $10 \text{ kJ}/(\text{kg}\cdot^\circ\text{K})$ . This deviation is likely due to the HKF model calculating the specific heat as a static fluid parameter at the simulation starting temperature,  $24^\circ\text{C}$ . This is not a correct nor similar method to that outlined above and used by Verbeek to calculate the specific heat. Additionally, the flow regime and slurry nature of the brine mixture also leads the OLI estimate to be off.

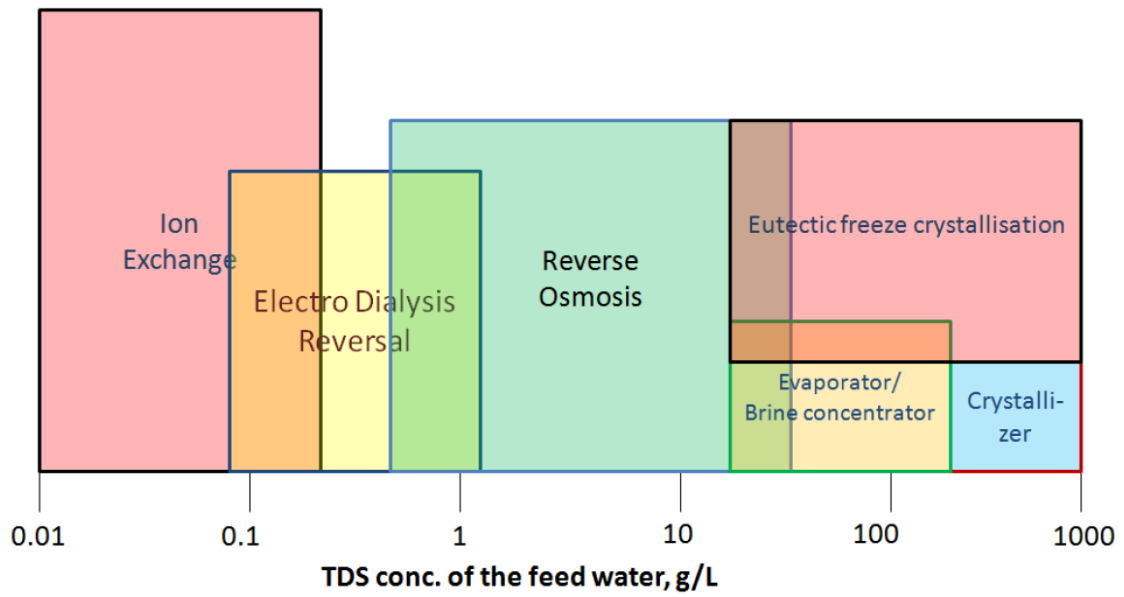
Examining much of the thermodynamic work for freeze crystallization is outside the scope of this paper in its detail but underscores the insufficiency for simulation to adequately model the physics behind the temperature and salinity dependent process without empirically derived constants from which to begin calculations, as Ramires does for pure NaCl solutions. The OLI Stream Analyzer could be updated to include this stepwise method of calculating specific heat, but this would be futile without the constants necessary given the high wt% contaminants present in the oilfield brines. Therefore, either calculations could be performed with greater accuracy after developing these constants, or bench scale work could be used to empirically arrive at the specific heat by working backwards from the overall measured heat transfer and the known transfer rates of the refrigerant and vessel wall.

The estimates for Eutectic Temperature and specific heat are thankfully very consistent across the 61 brines that were evaluated using the OLI Stream Analyzer. This occurs due to the almost independent nature of the solubility of NaCl from the temperature. This can be visualized on the phase diagram as the steepness of the solubility line. Because of this steepness in the initial freeze crystallization of the hypersaline brine, large quantities of salt will precipitate quickly. This could provide difficulties in the filtration and washing of the produced salt as the system will be inundated rapidly. By performing bench experimentation on these hypersaline produced brines, not only could the specific heat of the fluid be determined, the energy required to reach the eutectic temperature would be easily identified. This would allow for a potentially economic method of high purity NaCl generation. The purity of this stream is dependent on the washing and drying stages of the hydrohalite, which is the subject of the succeeding Section.

#### *4.1.3 Purity of Effluent Streams*

This Section is included as a primer for the Performance Validity for EFC and Research Questions' 1 and 2 that is presented in Chapter 5, Sections 5.2.3 and 5.2.5 which relate to the sale and disposal of the produced salt stream. Before the precipitated salt can be sold or marketed, a preliminary purity must be established with which to price it on the commodity market. The sale of the salt is necessary as it reduces the need to dispose of solid waste instead of a liquid waste, but also represents a valuable byproduct stream which offsets the higher energy cost of EFC over conventional injection disposal. In addition to the purity of the salt stream, the ice stream purity must be monitored. Water

with moderate salinity (between 1000 and 40,000 ppm) can be treated using Reverse Osmosis to a purity that makes the water potable or viable for release to the environment through estuaries and streams, as shown in **Figure 4.2**.



*Figure 4.2 - Desalination method by TDS, courtesy Shell Oil Company [6]*

If the water stream is natively low salinity, no treatment is necessary for reuse for hydraulic fracturing or agriculture. Finally, while EFC is marketed by many researchers to be a zero-liquid discharge recycling method (ZLD), it remains that this would be impractical given the high level of contaminants present in an oilfield brine. The risks and problems associated with NORM materials and the third effluent stream from EFC, the mother liquor retentate, is discussed in Section 4.2.3.

Verbeek finds that the ice slurry stream from EFC lost 42% of its mass from melting at room temperature as it was removed from the crystallizer and that the ice produced still contains 9 wt% NaCl. By washing the remaining ice with cooled water twice, nearly all

the contaminants and salts from the surface bound mother liquor was washed away. This washing step represented a 2-kW loss of heat. This heat loss to the environment is included in the economic evaluation of Chapter 5, Section 5.2.2. A viable method for secondary treatment is to remove the ice stream and rather than allow melting and washing, proceed to a secondary treatment to deal with the 90,000 ppm NaCl. By diluting this process stream 2:1, the salinity decreases to 45,000 ppm NaCl and be treatable with RO [69]. This in-series treatment option is addressed thermodynamically in Section 5.2.2 in a comparison with the energy requirements for multiple washings as mentioned previously.

The salt stream filter operates similarly in Verbeek's setup and any trace mother liquor present on the crystal surface is removed by creating a vacuum under the belt. The salt stream is allowed to heat from the  $-21.1^{\circ}\text{C}$  eutectic temperature to  $0.1^{\circ}\text{C}$  for recrystallization of the hydrohalite to halite, as mentioned in Chapter 3, Section 3.2. Verbeek finds that 0.73 kW of heat is lost to the environment for the warming of the filtrate to  $0.1^{\circ}\text{C}$ . 13% of the Mg contaminant of his experiment is present on the crystal surfaces. He finds the contaminant can be washed away easily implying that no contamination is built inside the NaCl crystals. Following a similar methodology, we can generate a preliminary estimate of the purity of the salt stream from EFC of produced water using the same 13% figure as a starting point. In the average Marcellus brine presented in Section 3.5, there is 3.5 wt% contaminants in 18.5 wt% NaCl brine, 2.8 wt% of the total contaminants is  $\text{Ca}^{2+}$ . After washing, the NaCl salt stream mass flow rate of 0.93 g/s, the 13% contaminant figure estimates that 1.05 g/s NaCl salt will be generated

with 0.12 g/s being contaminants, with no washing. Using a washing and water extraction mentioned above of 0.73 kW of heat is lost and the anhydrous salt is very clean NaCl, of greater than 95% purity. This 95% purity value is used in the economic evaluation Section 5.2.3 regarding the disposal and sale of the precipitated salts.

It appears that additional experimentation would not be necessary to confirm the purity of the effluent streams, however this is incorrect. As discussed in Section 4.2.2, the content of produced water with NORM and other common industrial chemicals such as scale inhibitors and friction reducers on the ice and salt nucleation process are not understood. Therefore, we cannot conclude that the phenomena witnessed of pure crystals being formed independent of contaminants within the crystalline body will hold when introduced to these alternative contaminants. In the succeeding Section, we discuss the larger research gaps that exist and what must be done to provide a proof of concept for EFC and why bench scale experimentation is crucial in this development.

#### 4.2 RESEARCH GAPS ADDRESSED THROUGH EXPERIMENTATION

In this Section we approach the knowledge information that is missing in the current literature and necessitates original research to be able to answer important Structural Validity questions regarding EFC. Of primary importance to the proof of concept is the unknown effect of hydrocarbon on the crystallization of salt and water, presented in Section 4.2.1 with commentary on expected outcomes and testing procedures and parameters for bench scale work. Section 4.2.2 includes the work that needs to be performed to better understand the anticipated corrosion and corrosion product problems the EFC facility should be aware of and includes common industry methods

used to control corrosion rates. Some discussion of corrosion and the potential of EFC is discussed in Chapter 3, Section 3.2.1 and 3.2.2. Finally, in Section 4.2.3 the unknown effect and product of radioactive isotopes that are naturally occurring in the produced waters is discussed. The social implications of NORM material have been discussed already in Chapter 2, Section 2.3.

#### *4.2.1 Effect of Hydrocarbon on Crystallization*

Produced water contains up to 1% hydrocarbons after separation in an API separator. The API separator works to separate bulk suspended solids, hydrocarbon and water gravimetrically. While most hydrocarbons can be separated gravimetrically using an API separator [51], micro emulsions and polar hydrocarbons often remain in solution after separation and pose a threat to life if released to the environment immediately. These components still entrained in the fluid are small oil droplets contained in the water-continuous phase are subject to the competing forces of dispersion and coalescence. For oil wells, the droplets can contain heavier hydrocarbons and asphaltenes as well as the aromatics such as benzene, toluene, etc. Additionally, microbes and other fine solids may remain suspended in the produced water after separation. Natural gas wells and condensate wells such as those common in many shale plays such as the Eagleford and Marcellus have a proportionately larger contribution from the lighter hydrocarbons. Dispersed gas and flotation units can be used in conjunction with API separators to reduce the proportion of hydrocarbons within the produced water stream, but this treatment comes at an additional cost. Electrocoagulation is used with success for the flocculation of the O&G portion of the

water. It has the benefit of sometimes making flocs of highly polar chemicals and ions in the water stream. For water that is subject to overboarding or planned for reservoir pressure control injection, these additional treatments are standard, as the presence of hydrocarbons is impermissible.

Little is known about what effect the trace hydrocarbons and aromatic present in produced water would have on freeze crystallization desalination. In general, there is too much hydrocarbon present in produced water (>15 ppm) to perform RO as the organic chemicals quickly degrade the osmotic membranes, not even mentioning the hypersalinity. From a freeze crystallization standpoint, this is a very minimal hydrocarbon content accounting for a minute level of contamination. The issue arises due to the fact that the type of crystallization that takes place in the crystallizer is heterogenous nucleation in which the formation begins around a nucleation site, such as salt, solids, or irregularities on the container surface [88].

The ramifications to freeze crystallization come in identifying the effect of salt and water crystal nucleation from its presence. Since nucleation is sensitive even to minute impurities in the system it is critical to understand these effects before design and construction of a freeze crystallization facility at an industrial level [89]. It is speculated that if nucleation occurred around the residual hydrocarbon remaining in produced water following separation and flotation that the reduction in nucleation temperature would be miniscule in comparison to the effect on nucleation of the dissolved solids contaminants as previously mentioned in Section 4.1. There are social implications of the water crystalizing around hydrocarbons in that the ice stream would then be unfit



for release into the environment, as the release of hydrocarbons is detrimental to ecologies and health. Offshore regulations allow for trace hydrocarbons at levels less than 15ppm, but this could prove fatal in large doses to agriculture and aquatic life in sensitive inland ecologies that contain limited available water for dispersion, such as rivers, streams, and lakes. These concerns are present in release of produced water at sea, but the larger volume of water at sea and the vast surface area allows for quicker degradation of the aromatics by UV radiation and microorganisms.

Alternatively, the hydrocarbon portion could contaminate the ice stream not through nucleation but through surface contamination. Since the hydrocarbons are less dense and do separate gravimetrically with time, like the ice stream in a crystallization settling chamber, it is feasible that the hydrocarbons form a surface film that is then transferred to the ice stream upon removal. Washing the ice stream should take place to remove the surface contamination of the mother liquor already, so this scenario would simply return the hydrocarbon back to the crystallization chamber with the returning washed fluid.

It is unlikely that the hydrocarbon portion present would form stable hydrates as the pressures are too low to remain within the stability zone, regardless of depressed temperature [90]. While the other favorable circumstances for hydrate formation are present in an EFC crystallizer (free water, low temperatures, agitation), the operating pressures would need to be a minimum quadruple that of atmospheric pressure to remain stable. Additionally, the miniscule hydrocarbon portion in the aqueous phase would not be sufficient to create damaging or plugging hydrates. In fact, the high salinity

of the brine retards the formation of hydrate by creating unstable impurities in the hydrate ice crystal lattice [91].

One potential issue with the reduction in temperature with hydrocarbons would be precipitation of heavier alkanes at the depressed temperatures [92]. In this case, the solid hydrocarbons would float to the fluid surface in the separator and then coat the exiting ice stream. It is again unlikely that there would be sufficient quantity of large hydrocarbon molecules remaining to be of concern or to constitute as a measurable contaminant in production. In fact, given one main application for this technology would be treating the produced water associated with Marcellus gas formation, there would be a very minimal volume of long chain alkanes in the oleic or condensate phase to begin with. However, the ability of the hydrocarbon to precipitate out, or to form a stable crystalline hydrate with the water phase should not be discounted as real possibilities with implications to the stability of the system. Additionally, there is a potential for stable micelle structures to form in the agitated, low temperature environment of a crystallization chamber. The micelle structure would not be separated gravimetrically and would likely serve as a nucleation point for crystal development. As state above regarding the minimal contribution of heavier hydrocarbons in a shale gas procued water stream, it is unlikely that long chain hydrocarbons would be present is significant quantity in a shale gas waste water stream. Were it to be shown that freeze crystallization was insensitive to the presence of hydrocarbons, this technology would potentially be much more valuable to operators as it would negate the need to treat

water using API separators, etc., and could be applied to condensate and heavy oil applications.

Additionally, the salt nucleation could be affected by the hydrocarbon. There are tens of thousands of chemicals added to fracturing fluid and many of these return in the flowback water. Given the proprietary nature of many of these chemical cocktails, it is difficult to ascertain their effect on freeze crystallization. Some of the chemicals that can be added to reduce the viscosity of the fracturing fluid are glycols such as propylene and ethylene glycol, common antifreeze agents. The agents prevent nucleation of ice close to the freezing temperature in three ways [93]:

1. They can maintain the supercooled state of body fluids by inhibiting the usual growth of ice.
2. They have the capacity to inhibit recrystallization
3. They may serve as plasma membrane protectors at low temperatures.

Generally, the scale inhibitors are targeted to such agents as calcium carbonate and barium salts as they represent the highest propensity for damaging hard scales. Because of their nature, chelant scale inhibitors are not effective against NaCl salts. While they are effective against removing Chloride ions, the large contribution of chlorine ions in solution makes it infeasible for their use in the brines associated with the Marcellus shale [94].

Most importantly, if these chemicals do reduce the temperature of ice crystallization, it is speculated that the crystal size will be reduced as well given the smaller mean log

temperature difference across the crystallization chamber [95]. This would represent an increased challenge of separation as the feeder belt away from the separation chamber would have to have a smaller screen to trap the reduced sized crystals. With too fine a screen there is a risk of plugging by contaminants that is not as pronounced at larger mesh sizes.

To this end, it is imperative that bench scale testing be performed to identify to what effect, if any, the presence of hydrocarbon has on the nucleation temperature of the system (Eutectic Temperature), the energy required for freeze crystallization (likely insignificant in relationship to other energy requirements) and the associated solid stream purity for system stability analysis. Without understanding first what will happen to the hydrocarbon stream, and other nucleating agents for that matter, it would be inadvisable to proceed to industrial scale investment in freeze crystallization.

#### *4.2.2 Corrosion Study of High Salinity Retentate*

A corrosion study of this high salinity produced brine should be performed as carbon steel is prone to pitting and crevice corrosion from the acidic components and the chloride ions in solution. High levels of chlorine hasten the corrosion and can render even a stainless-steel vessel defunct in a matter of months to years depending on wall thickness. Additionally as corrosion occurs in the crystallizer vessel, surface crystallization of NaCl can lead to the development of “crystallization pressure” exerted by the growing crystal onto the walls, eventually causing disintegration or catastrophic damage [96].

Since eutectic freeze crystallization is not capable of lowering the concentration of ions within a salt (except for those that initially exist above the eutectic concentration) it has limited effect on reducing corrosion through ion reduction. However, due to the low temperature of eutectic processes, the facilities performing freeze crystallization will be less prone to corrosive damage as compared to those of a thermal distillation plant that result in highly corrosive salts and caustic byproducts [70]. The implementation of local or small-scale freeze crystallization facilities would also reduce the impact of corrosion as it would minimize the water volumes moved through pipeline and are thus able to cause damaging corrosion.

Measuring corrosion rates has been unpredictable and empirical for many companies in the oil and gas industry. A long-standing practice has been the use of iron ( $\text{Fe}^{2+}$ ) counts from produced water to measure the corrosion rate of production casing. It is assumed that the iron present is primarily a byproduct of the corrosion process [97]. However, the Marcellus and Utica shale have iron counts from the water itself and therefore the iron count is an unreliable predictor of corrosion. Additionally, by only measuring iron concentration, there is only relative magnitude of corrosion processes available for analysis, rather than type, location, and extent of the corrosion process. By monitoring and accurately measuring the corrosion of the vessels used in the process of EFC water management, the system can be made more resilient to corrosive zones and a holistic facility cost better estimated that includes replacement and redundancies for piping and containment.

A coupon corrosion study is a relatively inexpensive method to test the corrosivity of a fluid on carbon steel. Given that the corrosion rate is dependent of temperature, contact time and fluid properties such as pH, it is imperative that through testing these parameters be controlled. Specifically, when testing the corrosion rate, it would be invaluable to have the rate near the reduced eutectic temperature of  $-25^{\circ}\text{C}$  for the oilfield samples. Like the discussion in Section 4.2.1, the chemical cocktail included to fracturing fluid also includes corrosion inhibitors. However, since these inhibitors are usually proprietary it is unknown what their efficacy is at low temperature or under which physical method they operate to reduce corrosion. A coupon corrosion study could be performed on native oilfield brine samples and retentate brine samples following EFC to determine the properties of the hereto unknown retentate water from treatment.

A corrosion study that would yield more information than a coupon study would be a dynamic flow test since an additional corrosivity parameter is the flow regime of the fluid. As the flow rate becomes less laminar and more turbulent and dynamic, the rate of corrosion increases as the kinetic fluid energy is increased and the rate of contact increases. A dynamic flow corrosion test is more expensive than a simple coupon analysis and should only be performed if the results of coupon analysis indicate high corrosion rates ( $>300\ \mu\text{m}/\text{year}$ ).

#### *4.2.3 Salinity and Radioactivity of Retentate*

Public perception of radioactivity in produced water is not very balanced. While many polled individuals agree and accept that the process of producing oil and gas comes with

risks and uses water for drilling and pressure maintenance, they are less receptive to disposal and water management when informed that produced water contains radioactive isotopes [98]. The work performed by Torres et al. (2017) indicates that those outside of the O&G industry perceive and understand the risk of radioactivity and produced water less than that of industry insiders. This risk perception is an effective tool be used by operators in developing and delivering a holistic safety measurement and management schema in and outside of the production fields. To increase the trust between producers and communities, there needs to be transparency in water management that reassures necessary precautions are being made to protect the community as well as realistically protect companies' financial interests in economic water management. To this end, the disposal or saline, radioactive produced water is necessary, but should be done as safely as possible within the given constraints.

The radioactive isotopes that are present in produced water are mainly uranium, radium, and radon. These NORM isotopes are dissolved in low concentrations in ground waters and are concentrated in reservoirs over time with the catagenesis of kerogen desorption of rock material, and radioactive decay from minerals [99]. Because of the richness of chloride ions in oil-field waters, other elements including radium exhibit enhanced solubilities [100]. Measuring the radioactivity and reporting of radioactive isotopes is not regulated by law. Since much of water is reinjected for pressure maintenance or as in UIC wells, there is little risk by low level NORM radiation from exposure. Measuring the retentate water volume, salinity, and radioactivity are imperative for proper water management and disposal. Some evidence exists that the

radiation waste from drilling and disposing of water in the Marcellus is more pervasive than other areas [101]. While EFC is touted as a ZLD water treatment method, there will be retentate water from processing oilfield brines since the Eutectic Point for some salts is drastically lower than that of NaCl. For reference, refer to Section 3.5 and note that the Eutectic Point for Calcium and magnesium Chloride are near  $-45^{\circ}\text{C}$ , much lower than that of Hydrohalite near  $-25^{\circ}\text{C}$ .

Additionally, it is speculated that the radioactive isotopes that might be in solution will not form salt crystals in meaningful quantities to be of importance other than as a minor contaminant in the NaCl stream from EFC. However, as the liquid volume decreases with continued treatment, the concentration of the radioactive isotopes and the minor contributors as calcium and magnesium will increase. As the contribution of Calcium and Magnesium increase, the risk for scaling or formation of these less desirable radium salts to form increases. More importantly, increasing concentration of radioactivity could present a health risk from over exposure or add to anticipated disposal costs. For perspective, the drinking water standards are 5 pCi/L combined radium-226 and 228. The concentration in brine for natural gas wells in the Marcellus are shown to have up to 3000 times this concentration. Because of this, the practice of recovering salt or applying brine directly to highways as a de-icing solution has been suspended in many New England states [102].

The current methods used to manage the radioactive waste are avoidance, consolidation and volume reduction [103]. Clearly, avoiding radioactive material is not possible if exploitation of the Marcellus gas is to take place, nor is it possible to reduce



water production rates easily in fractured gas wells unless a water zone is detected and shut-in. Consolidation and volume reduction are both radioactive water management methods that are well suited to the freeze crystallization precipitation of brines. By decreasing the total volume of irradiated waters, consolidation allows for more manageable control of the contaminated waters and ensures more effective control of proper disposal will take place. The disposal of the radioactive retentate water is not regulated under Pennsylvania or Ohio law. This implies that if bench scale experimentation confirmed the radioactive isotopes remained in the retentate solution, their disposal could remain underground injection with minimal regulatory changes. However, if the isotopes form radioactive salts (solid waste) the gamma radiation exposure rate cannot be over 10  $\mu\text{R/hr}$  [104]. Beginning In 2013 Ohio facilities that accept scales and solid wastes for oil field use (TENORM) must have a radiation concentration no higher than 5 pCi/g. In Texas this same solid waste could be disposed of by conventional means as it is considered a byproduct material, not a radioactive source material that is regulated differently [105].

To this end, it is imperative that bench scale testing be performed to identify to what increase in radioactivity can be expected using EFC as a treatment method for produced water, and what happens to these radioactive components. By creating more data on the sources and levels of radiation from fractured gas well produced water, the regulations controlling its disposal can be crafted more congruent to the desires of affect communities as well as the producers. Additionally, this is an important validation step for the efficacy of EFC for treating produced water as if it represents an increase to

human exposure it shouldn't be pursued cautiously. Additionally, the quality, and therefore the value, of the produced salt and water streams of EFC are directly dependent upon whether the radioactivity is disassociated efficiently.

### 4.3 TEST CHAMBER DESIGN

In this Section, the design and construction of a bench scale EFC experiment is outlined and discussed. This builds on the motivation and inadequacies of previous testing presented in Section 4.1 and 4.2 that necessitate further experimentation for validation of EFC. First is a discussion of the design inspiration and construction followed by the requirements for design and Requirements List for experimentation. This Section includes the design and construction of a bench scale EFC testing apparatus. Also, there is discussion on procurement and estimated associated costs for the construction of a EFC laboratory bench for the parameters which we would be interested in collecting for analysis, as mentions in Section 4.2. The anticipated possible outcomes of experimentation tie to the third quadrant of the validation square for Research Questions 1 and 3, and the Structural Validity for Questions 2 and 4 are provided in Section 4.4. Finally, the section is concluded with the testing procedure that should be in place for measuring the pertinent testing parameters, the subject of Section 4.4. By including a design and testing section in the thesis, we aim to have a near ready-made project proposal created for anyone who wishes to take the concept of eutectic freeze crystallization forward for validation for oilfield use.

#### 4.3.1 Design Requirements

We propose that in order to review fully the applicability of EFC to desalination in the oilfield that further testing is necessary. As outlined in the preceding Sections, there exist research gaps in the current literature regarding fundamental aspects of the safety and quality of brine from produced water. Namely, further testing is necessary to:

1. Determine the effect of hydrocarbon on crystal nucleation
2. Validate the claims regarding reduced corrosion from EFC
3. Investigate the effects of TENORM on the safety of retentate brines

In performing experimentation for EFC, we desire a design that is capable of testing the brine in batch and in continuous operation in order to test under applicable conditions in implementation (continuous) and for testing the claims of ZLD (batch). Batch testing would be beneficial for limited supply testing as it allows for the experimentation with a small sample volume of brine, likely taken in the field, to be used, limiting transportation and storage costs. As well as testing simply for the eutectic temperature, we require a design that can adequately separate the effluent streams of water and salt so that they might be further quantified in purity through secondary testing. This testing could take the form of FTIR, IR, or GCMS testing to determine the makeup and purity of the crystals. Most research campuses in the United States have the facilities on hand to test crystal purity.

The design for an EFC crystallizer should be easy to manufacture and operate, requiring little in the way of specialized equipment or technology to construct. It is speculated

that the most expensive single piece of equipment necessary for EFC is a refrigeration unit capable of reaching and holding temperature in the neighborhood of  $-25^{\circ}\text{C}$  reliable and with a high level of accuracy. For long term testing and validation of EFC for desalination of oilfield brine, it is beneficial to have a design that can be operated in series at multiple eutectic temperatures so that serial continuous flow operation can be achieved. While this would yield similar results to batch testing in reaching ZLD product, it is an important step along the path of validation and eventually implementation. The design selected should also be insensitive to the highly saline and corrosive nature of the brine samples. Aluminum would be a good material of choice for the crystallizer as its corrosion resistance is high, and it exhibits beneficial machining qualities.

Any testing of EFC for oilfield use should also be accompanied by sensitivity testing of the EFC process by the presence of hydrocarbon and for testing the enhanced radioactivity of the mother liquor brine as salt and water are precipitated. For testing hydrocarbon, it is recommended that heptane be available for making up synthetic brines that have higher levels of hydrocarbon contamination. Heptane is the hydrocarbon of choice for simulating oil contamination as it is readily available and is the dominating constituent of the oleic phase of most sweet, light crude. Additionally, Minute amounts of  $\text{H}_2\text{S}$  could be used to test the effect of souring on the process, although it is speculated that there would be little except enhanced corrosion. For determining the radioactivity of brines either an ionization chamber or scintillation crystal device should be readily available, depending on the level of radiation that is present. Every precaution should be taken to minimize human contact with the

potentially enhanced radioactive retentate brine, so an EFC crystallization chamber should have a valve for remote removal of a mother liquor sample for radiation detection.

Below in **Table 4.1** we outline the necessary equipment and process for construction and testing EFC for oilfield application. The Requirements List is inclusive of the demands for validation of EFC and the wishes of the authors to perform necessary testing for socially responsible engineering.

In the following Section, we discuss a potential design that could be used in this experimentation of EFC. The design recommended has been used with success in the past and can be adapted to meet the needs of produced water validation with minor alterations.

#### *4.3.2 Design Inspiration*

The EFC crystallizer and design discussed herein is adapted from Verbeek (2015) [6] and vd Ham (1998) [41]. Vd Ham introduces the column type crystallizer with cooling disks, which he calls the cooled disk column crystallizer (CDCC), shown in **Figure 4.3**. This design removes heat through the cooling disks and allows for the gravimetric separation of salt and ice crystals from the mother liquor by allowing crystals to move between cooling compartments through orifices on the cooling disks. This design represents a simplistic approach at studying EFC as the crystalizing chamber is simple enough to manufacture using aluminum billet and a CNC machine. Additionally, surface area for cooling is increased with the inclusion of many cooling disks in parallel. The symmetrical

central design also allows for one motor to operate scrapers that facilitate agitation, and migration of the brine, and detachment of scale from the cooling disks and crystallizer walls. Verbeek (2015) uses this design for his small (10L) bench scale freeze crystallization and a larger (200L) skid mounted scraped cooled wall crystallizer (SCWC). Both designs allow for batch or continuous operation. The SCWC exhibits a higher cooling efficiency and helps validate the scalability of the technology but is more complex to manufacture. For basic research to answer questions regarding to oilfield brine desalination using EFC, the CDCC is sufficient. The design Verbeek uses is equipped with a potassium formate cooling solution to reach freezing temperatures to  $-60^{\circ}\text{C}$ . The refrigerant is cycled through the cooling disks that operate like a shell and tube type heat exchanger. Vd Ham recommends a one-stage refrigeration system for high salinity brines as the large amount of salt produced leads to a decrease in COP and the increased energy cost for two-stage refrigeration isn't recovered by the increased COP. For greater efficiency, he also recommends using  $\text{CO}_2$  refrigeration for cooling. It is important to recognize that the temperature between the cooling disks and the cooling brine shouldn't be too large otherwise extreme scaling can occur on the cooling disks and unfavorable crystal shape is caused which can affect their purity. Some preliminary testing has been performed using liquid nitrogen as a cheap cooling liquid that doesn't require refrigeration, but the cooling is too rapid to facilitate uniform crystal sizes and the scaling is too great for reasonable operation.

Table 4.1 - Requirements List

<b>Requirements List</b> <i>EFC Experimentation for Produced Water</i>	
<b>Wish/ Demand</b>	<b>Requirement</b>
----- Design Criteria -----	
W	Batch Processing
D	Continuous Processing
D	Low Cost Construction
W	Corrosion Resistant Material
W	Ability to Be Run in Series
D	Compatibility with Common Oilfield Water Processing Equipment
D	Minimize Thermodynamic Heat Losses
-----Evaluation of Solution-----	
D	Includes Laboratory Monitoring Software and Equipment
D	Availability of Crystal Purity Determination by FTIR or GCMS
D	Availability of Ionization or Scintillation Type Radiometer
-----Administration-----	
W	Be Useful for Many Iterations of Testing
W	Manageable by Technicians
D	Low Operational Cost
W	Easily Sourced Produced Water Samples
-----Outcomes-----	
D	Identification of Effect of Hydrocarbon on Crystallization
D	Identification of Radioactivity of Retentate Water from NORM Material
W	Corrosion Study of High Salinity Brines on Crystallization Chamber
D	Thermodynamic Requirement for Complex Multi-Species Brine Sample

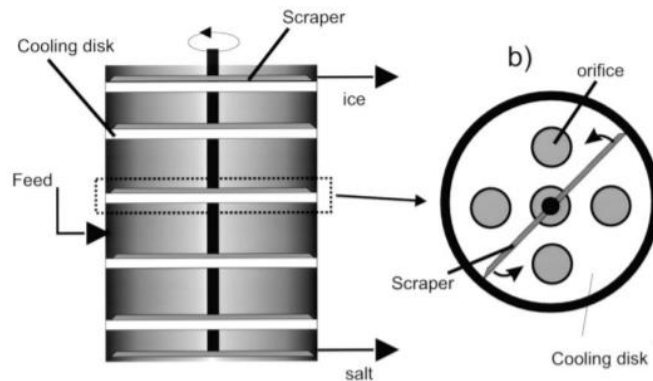


Figure 4.3 - CDCC crystallizer proposed by vd Ham [41]

Verbeek does not denote any inadequacies of the CDCC design to the process of EFC. Indeed, its simplistic nature allow for a basic, low cost build that can be used on a variety of fluid and applications. The CDCC operates by flowing refrigerant through the cooling disks of the crystallizer. This cooling encourages crystal formation at the eutectic temperature. The rotation and agitation of a scrapper serves to detach the precipitated crystals from the cooling disk. Orifices located in the cooling disks then allows for the gravimetric separation of the crystallized salt and water from the brine, with ice being less dense separating to the surface and salt the bottom.

Some minor modifications that should be made to the CDCC design are:

1. decreasing cooling disk spacing to increase agitation and nucleate crystals
2. increasing cooling disk number to increase cooling area
3. decrease energy for scrapers by using single speed motor with variable gearbox
4. decrease heat loss by applying permanent polyurethane foam coating
5. limit plugging of migration orifices by limiting cooling disk refrigeration nearby
6. Install valve near bottom of the crystallization chamber for retentate removal
7. Install CDCC design in series to operate at multiple eutectic temperatures for ZLD

By implementing the above changes, the crystallizer can be operated with more efficiency while limiting all changes to very minor modifications. By increasing cooling area, the rate of cooling can be maintained constant at a lower temperature difference across the cooling disks. This would reduce the load on the refrigeration units but come at the cost of an increased refrigerant volume. Additionally, the freezing chamber



volume could be increased for constant temperature difference across the cooling disk if more disks are used.

By installing a gearbox for the scrapper not only can turbidity of the brine be maintained and changed, but different motors can be installed based on the anticipated motor torque due to scaling that ensures the motor is operating in its most efficient region. Verbeek has insulation installed around the CDCC during testing, but we speculate that by using a spray foam insulation, the rate of heating due to the external environment can be limited even further, thereby reducing the cooling needed per volume of brine.

Verbeek mentions that higher processing rates could cause plugging due to salt volumes in the SCWC. To that end, in order to limit the possibility of plugging at larger temperature difference across the cooling disks, the 'tubes' of refrigerant that run through the cooling disks should be direct away from the migration orifices to limit scaling in the neighborhood. If too much scaling occurs in the orifice, it becomes plugged and manual remediation must take place.

A valve installed near the center of the crystallization chamber would allow for periodic testing of retentate water for composition and radioactivity, were it to be necessary during sample testing. While a minor improvement, the installation of this valve would be nontrivial as it would represent a major location of heat transfer to the CDCC with foam insulation installed. The use of a low heat transfer material such as plastic might be advisable.

Finally, installing the CDCC design in series would allow for testing at multiple eutectic temperatures and validation of the ZLD claim for an oilfield sample. For Marcellus samples similar in composition to those simulated in Section 3.4, there would be 3 total eutectic temperatures for complete brine elimination. While likely not cost effective for industrial application, it would be academically prudent to verify the ZLD claim under real time conditions.

Other process changes that should be incorporated to test the feasibility of EFC for produced water processing would be the inclusion of common oilfield processing equipment (small scale) in series as well to have the option to run EFC experimentation with or without pre-processing. The below flow diagram **Figure 4.4** is a simplification of the mentioned process. This design would represent a modest increase in cost but increase the complexity of testing situations that could be performed.



*Figure 4.4 - Process EFC Testing Procedure*

In the succeeding section we discuss the requirements of the design for testing EFC. This includes discussion about the above design and what should be measured at each step along the process testing. This testing design is low cost and allow for the option to run EFC experimentation with or without pre-processing.

#### 4.4 EXPERIMENTAL PROPOSAL

Having now shown the parameters that we are interested in measuring with the use of EFC and the recommended construction and design method for the EFC crystallization chamber, we now introduce the proposal for EFC validation testing for produced water disposal. This section is not intended to discuss the necessary criteria of the measured properties or how to measure them. Instead, it is included as a rough outline of the organization for testing and testing order to proceed through the validation of the method. The rationale and motivation for testing these parameters is indicated in the preceding Sections 4.1 and 4.2, respectively. Implications of these parameters and their financial impact on the implementation of EFC are discussed in Chapter 5. Connection of these parameters to the simulations of Chapter 3 and the social impacts of waste water management of Chapter 2 can be found in Section 4.1.

##### 4.4.1 *Introduction*

Managing wastewater is likely to become a defining challenge for the shale gas industry to confront [39]. Extracting and marketing shale gas requires large volumes of water and produces even larger volumes of flowback and produced water over the life of the well. While Marcellus wells produce much less wastewater per MCF than other natural gas wells, the total wastewater generated in the region is on the rise. One of the current limiting factors to Marcellus gas exploitation is the overwhelmed current wastewater disposal infrastructure. Current waste water disposal methods in the oil industry primarily include water injection into disposal wells, with limited utilization of electrocoagulation for in-field reuse and thermal distillation at refineries. Brine

hypersalinity and residual hydrocarbon has limited the application of membrane technology and simple environmental expulsion is heavily regulated by the EPA [2]. The problems associated with injection disposal, coupled with a lack of nearby Class II injection wells has limited the development of the Pennsylvanian Marcellus shale gas due to economic constraint imposed by the cost of water disposal and transportation. The challenge gas producers must now face is how to preserve the economics of shale gas production while simultaneously upholding responsible stewardship of resources and protecting public health. With increased concerns regarding induced seismicity and the safety of that type of disposal, the need for water recycling methods has grown.

Eutectic Freeze Crystallization has the potential to treat complex, hypersaline coproduced brine and represents a sustainable water treatment technology towards achieving a near zero waste by producing potable water and pure salts [3]. Given that the hypersaline brines of the Marcellus Shale are sodium and chloride rich [4], EFC can be used to selectively recover the sodium as a pure sodium chloride salt while simultaneously producing pure ice crystals. The pure ice would have innumerable uses; reuse for hydraulic fracturing, release into estuaries, and agriculture being only a few. The sodium chloride salt represents a potential revenue stream for water treatment companies and its sale to industrial chemical synthesizers could offset the cost of water treatment. While the applicability of using EFC to remove multiple salts from complex multi-component, hypersaline brines has not yet been demonstrated [5], the thermodynamics of freeze crystallization are extensively known. Verbeek shows that the overall efficiency an EFC crystallizer is 59% and that the energy requirement per unit

feed is comparable to that of typical commercial evaporative crystallizers [6]. The cost of a large-scale freeze crystallization facility is estimated to be equitable to that of evaporative crystallization [7], but to be competitive EFC would need to be comparable to the injection disposal cost of \$1.00 - \$6.50 to be of interest to Exploration and Production companies [8].

While industrial treatment facilities often employ methods to precipitate and flocculate suspended solids, few facilities currently have the capacity to remove ions and therefore address water management in a comprehensive and holistic manner.

#### *4.4.2 Statement of Problem*

Produced water contains up to 1% hydrocarbons after separation in an API separator. The API separator works to separate bulk suspended solids, hydrocarbon and water gravimetrically. While most hydrocarbons can be separated gravimetrically using an API separator [51], micro emulsions and polar hydrocarbons often remain in solution after separation and pose a threat to life if released to the environment. Little is known about what effect the trace hydrocarbons and aromatics present in produced water would have on freeze crystallization desalination. In general, there is too much hydrocarbon present in produced water (>15 ppm) to perform RO as the organic chemicals quickly degrade the osmotic membranes. Since nucleation is sensitive even to minute impurities in the system it is critical to understand these effects before design and construction of a freeze crystallization facility at an industrial level [89].

Additionally, there are tens of thousands of chemicals added to fracturing fluid and many of these return in the flowback water. Given the proprietary nature of many of these chemical cocktails, it is difficult to ascertain their effect on the freeze crystallization process. Some of the chemicals that are added to reduce the viscosity of the fracturing fluid are glycols such as propylene and ethylene glycol, common antifreeze agents. Added scale inhibitors are targeted to such agents as Calcium Carbonate and Barium salts as they represent the highest propensity for damaging hard scales, but by their nature they could affect the crystallization of Sodium Chloride salts. Most importantly, if these chemicals do alter greatly the temperature of crystallization away from the modelled Eutectic Point, an implement design could have inferior cooling properties and not be effective at separating the brine stream to salt and water.

Some evidence exists that the radiation waste from drilling and disposing of water in the Marcellus is more pervasive than other areas [101]. As the liquid volume decreases with continued EFC treatment, the concentration of the radioactive isotopes will increase. Increasing the concentration of radioactivity could present a health risk from over exposure or add to anticipated disposal costs by requiring adherence to stricter governmental regulations. In order to better understand these perceived health risks, further testing with actual oilfield brine samples is necessary.

It would be inadvisable to proceed to industrial scale investment in freeze crystallization without addressing the above concerns regarding trace hydrocarbon, fracturing chemicals and radioactive isotopes on the freeze crystallization process. To do so, it is

recommended that further bench scale EFC testing be performed to answer the above questions.

#### *4.4.3 Objectives*

We propose that to review fully the applicability of EFC to desalination in the oilfield that further testing is necessary. There exist Research Gaps in the current literature regarding fundamental aspects of the safety and quality of brine from produced water and how those aspects relate to the EFC process. Further testing is necessary to:

1. Investigate the effect of hydrocarbon and chemicals on crystal nucleation
2. Validate the claims regarding reduced corrosion from EFC
3. Investigate the effects of NORM on the safety of retentate brines

By performing bench scale testing specifically to address the above concerns, we will add to the knowledge that exists on EFC to date and validate its effectiveness at addressing real world complex water management in the oil industry. Without this additional bench scale testing, there would be insufficient evidence to rationalize EFC as an applicable technology to address waste water in the oilfield adequately.

#### *4.4.4 Testing Procedure*

Here we outline the procedure for testing oilfield brine samples using a designed EFC crystallizer after the work of vd Ham (1998) and Verbeek (2015). This process is not meant to be inclusive of all testing or steps that should be taken, but rather to serve as an outline of the major milestones of verification through experimental testing and what the outcome should be at each step along the way.

1. Construct Cooled Disk Column Crystallizer (after vd Ham) from billet aluminum
2. Verify thermodynamic accuracy by freeze crystallizing 21.1 wt% NaCl
3. Test supplied oilfield brine sample of known quality with no hydrocarbon or TSS
4. Compare and validate tested sample to results of EFC simulation
5. Test supplied oilfield brine with TSS and hydrocarbon
6. Take and measure radioactivity of retentate brine
7. Assess effect of hydrocarbon, suspended solids and fracturing chemicals on EFC process
  - a. If no effect of above, validation complete, proceed to cost estimation for oilfield water management with EFC
  - b. If measurable and ill effect of above, perform testing of CDCC in series with API separator and flotation unit to remove hydrocarbon and suspended solids
  - c. If ill effects continue, re-evaluate position of EFC as technology with applicability to oilfield industry

A simplified representation of the equipment and process is included in the figure below, **Figure 4.5**.



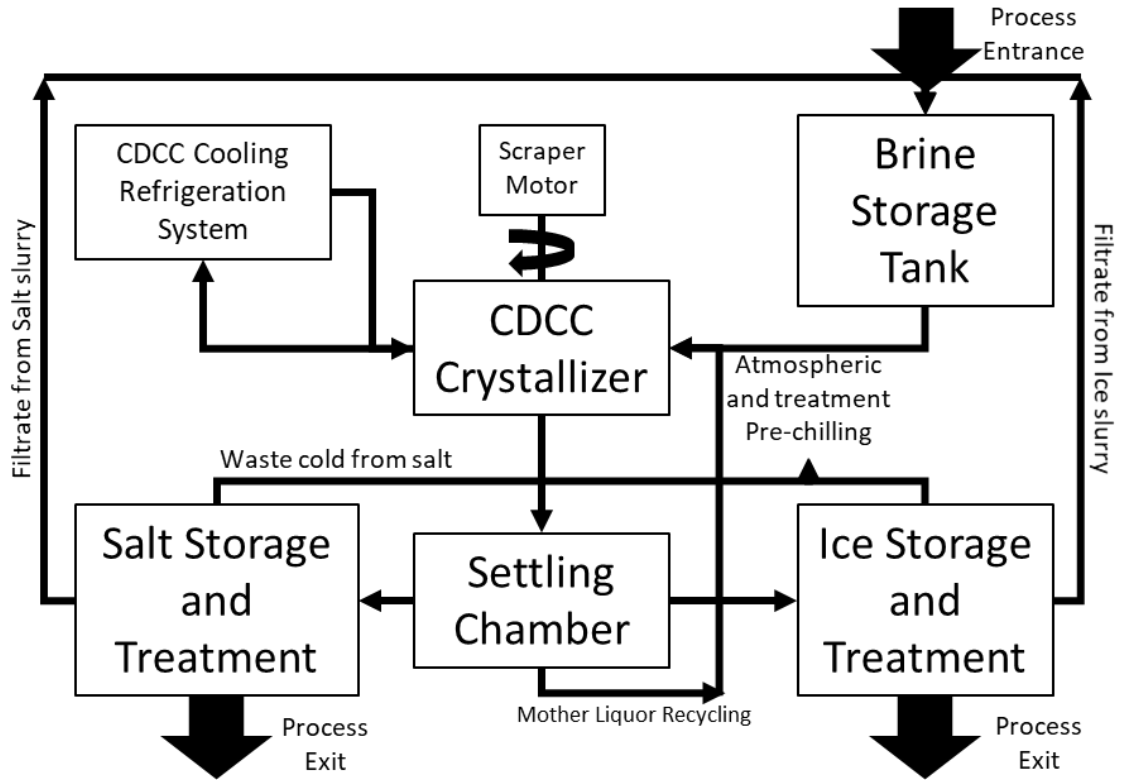


Figure 4.5 - EFC Process Flow Diagram

By following the general outline above, the major milestones of validation are met. Steps 1 and 2 are crucial to the Empirical Structural Validity of EFC as they ensure what has been constructed and achieved are in line with the published literature. Steps 3 and 4 are critical in testing the Empirical Performance Validity of the method by applying it now to a specific example problem and comparing that with accepted simulation modelling. Finally, steps 5-7 are specific Theoretical Performance Validity steps aimed at addressing if EFC is suited for applications outside the example problem and its robustness to change. This proof of concept experimentations relies heavily on the use of the validation square to verify and validate the concept presented above. This

verification and validation strategy and is heavily dependent upon the work done by Pederson et al. (2000) [25].

#### 4.4.5 Concluding Remarks

The experimentation outcome will be new knowledge that will result in the connection and evaluation of a new desalination method (EFC) to the problem of sustainable oilfield water disposal. By addressing the effects that hydrocarbon, hydraulic fracturing chemicals, and the effects of NORM radiation have on the EFC process, we can better understand what changes, if any, need to be made to ensure compatibility of EFC with oilfield waste water management processes.

### 4.5 SYNOPSIS OF CHAPTER FOUR

In Section 4.1 we discuss the use of further bench scale experimentation as a method for validating the performed EFC simulation work of Chapter 3. Additionally, the gaps that remain for empirical structural validation of EFC for compatibility in the oilfield are discussed in Section 4.2 as research gaps that can be closed with further experimentation. By providing both of these preceding sections as motivation, we proceed to Section 4.3 with a proposal for experimentation that includes the bench scale design and equipment requirements along with a testing procedure for experimentation of actual oilfield brine samples. Incorporating the feasibility aspect of EFC for oilfield use, the next Chapter includes discussion on preliminary cost estimation for EFC as well as estimated produced water stream in the Marcellus shale play for the next few years. In conjunction with the economic evaluation provided in Chapter 5, this Chapter is primarily of utility to industrial researchers that have funding greater than academic

parties and could take the validation of EFC to the next stage to verify and narrow the estimates of feasibility and cost presented herein. This chapter relies heavily on the use of the validation square to verify and validate the concept presented in this thesis. Chapter 1, Section 1.4.2 contains more information regarding the verification and validation strategy and is heavily dependent upon the work done by Pederson et al. (2000) [25]. In this Section, the research opportunities identified through critical literature review are presented and the connection between the identifies Research Opportunities and Research Questions proposed in Chapter 1 is established.

***RQ 1. How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?*** In this Chapter, we discussed the rationale behind the need for an alternative water treatment method for the Marcellus shale as adequate geology does not exist for injection disposal at economic rates and the cost of truck transportation is high. We propose that EFC can be used as an alternative water treatment method in conjunction with industry standard techniques such as flotation and API separation to remove suspended solids and organics prior to desalination. The use of EFC explicitly is not the subject of this Chapter, but the idea of applying this technology to produced water and its complete validation are discussed.

***RQ2. What changes need to be made to freeze crystallization desalination technology for compatibility with oilfield operations?*** The core of Chapter 4 is devoted to answering this Research Question. By investigating in which ways produced water differs from the test examples used by previous researchers, we have identified several key components of a produced water stream that must be addressed in order to validate

EFC for oilfield brine treatment. Section 4.1. is devoted to the verification of simulation work performed in Chapter 3 and how that is important in successful implementation of the technology in industry. In Section 4.2 we discuss the preliminary speculations as to the effects of different qualities produced water might have on the EFC process, namely the effect of hydrocarbon, corrosion of high salinity brines on the crystallization chamber, and the potential radioactivity of the retentate brines. In Section 4.3 we introduce a proposal for the building of a test apparatus to answer these Research Gaps identified in 4.2. By answering these Gaps, we can better answer the question of which changes are necessary to insure the success of EFC in industrial desalination treatment for the oilfield.

***RQ3. What environmental benefits will be realized by treating water for reuse and release over underground water injection?*** In Section 2.3.5, the potential release of water extracted from effluent brine back into the environment is discussed. Many areas with developed oilfields in the U.S. are in areas deemed as vulnerable to drought and there is an alarming history of mega-droughts lasting 300 years or longer in many western U.S. states. In Section 1.3.4 it is shown that the main work that needs to be done to prove there is an environmental benefit to the release of this water is largely outside the scope of this thesis. However, what is discussed in Section 2.3.7 and Section 5. 2.4 regarding the release of water and the sale of crystallized salt provides motivation that there is clear environmental significance of the work by reducing the ecological footprint of other industries. Similarly, a reduction of pre-treatment equipment represents a reduction in the ecological footprint of oilfield water management itself.

***RQ4. How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?*** This Research Question is addressed preliminarily in this Chapter and Chapter 2. By recommending testing of EFC in series with API separation and flotation chambers, we can determine if the methods are compatible in rates of flow as well as determine whether pre-treatment is necessary for desalination, or if one can simply proceed directly to the EFC treatment with no ill effects caused by the organics and suspended solids. This Research Question is addressed in the succeeding Section 5.3 with regards to the implementation of this technology with a discussion on the availability of equipment, technicians and the robustness of the process.

## Chapter 5 – EFC Cost Evaluation and Implementation

In this Chapter is a discussion of the estimated treatment and implementation cost of EFC using a field level treatment schema. The assumptions of future water production associated with Marcellus shale development and the scalability of EFC are discussed in Section 5.1. Following this is a cost analysis based on a simple thermodynamic analysis of EFC and regional industrial electrical costs for the Marcellus Shale play are found in Section 5.2. This per barrel estimate of cost is the culmination of careful statistical engineering analysis and is inclusive of the fixed and variable costs associated with treatment via EFC, as stated in Section 5.1.2. A comparison of this estimated cost of treatment compared to other common disposal methods is given in Section 5.2.4 and is a vital component of propelling this technology forward by providing motivation for industry research and further necessary validation, as discussed in Chapter 4. Finally, in Section 5.3 recommendations and considerations to the ability of this technology to be incorporated into current waste water disposal schema is evaluated and commentary on the complexity of the method to aid in preliminary managerial level discussion of the technology. In this Chapter the answer to the below Research Questions are provided:

**RQ1:** How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?

**RQ2:** What changes need to be made to freeze crystallization desalination technology for compatibility with oilfield operations?

## 5.1 PRODUCED WATER VOLUMES IN PENNSYLVANIA SHALE PRODUCTION

Produced waters come from a variety of sources; conventional wells, unconventional shales, flow back water, drilling fluids, etc. Waters from conventional wells are generally reinjected to provide pressure support within the formation of interest and poses little water management challenges outside of treatment, transportation, and injection for disposal of the residual volume. The unconventional shale waters, both produced and flowback, are problematic as there is no benefit in injecting these waters into the shale formation and limited management solutions existed outside of UIC II well injection. Indeed, the treatment and disposal of produced water from the unconventional shale wells is our concern in this Chapter, as discussed in Section 1.3.2. In attempting to address the water problem in Pennsylvania, we must look to predict the quantity and quality of the produced water to adequately manage treatment options and expectations. Since EFC is a new and unimplemented solution, it would be useful for any interested in taking the technology further to have an appreciable scale of the situation. In this Section, we attempt to provide an estimate for the water production in Pennsylvania through 2024 from unconventional sources only by performing simple statistical regression analysis given the limited available data and largely market controlled nature of the natural gas commodity. Additionally, in Section 5.1.2, we discuss the optimization and up scaling of EFC to address this future water stream.

### 5.1.1 *Expected Marcellus Volumes*

The Marcellus Shale is a primarily gas producing play. By many estimates it is the single largest gas field in the United States and the second largest worldwide [106]. As early as

2002 the USGS deemed the Marcellus shale to be capable of only 1.9 Tcf recoverable reserves; small by most measures. By 2011, the EIA had updated the estimated unproved recoverable reserves to 400 Tcf using current technological capability [107]. In 2016, the Marcellus shale produced an astounding 5.1 Tcf of natural gas in Pennsylvania alone, with every indication that the production rates will increase for the foreseeable future [108]. With this increased exploitation comes the challenges of water management. Contrary to common perception, the Marcellus gas wells produce much less water per unit of gas (approximately 35%) compared to the conventional natural gas wells [39]. The problem lies in the overwhelming quantity of gas, and therefore water, the region has generated in recent years, coupled with an inadequate infrastructure. Since 2004 the total wastewater generated in the area has increased by 570%. As of 2016, Pennsylvania has only 8 native UIC II wells for produced water with pending permits for 2 more. To begin laying the groundwork for EFC as an effective solution to water management, outside the technical difficulties that are yet addressed in previous EFC research (refer to Chapter 4), we need to discuss the scope of the problem with quantitative information. In Section 3.5, we discuss the water quality that is associated with Marcellus and Utica unconventional. The complete water quality information provided for these wells by BHI can be found in Appendix A.

An exceedingly difficult number to assign a point value is the water cut for wells. The water cut (WC) is the ratio of water produced compared to the volume of total liquids produced. The water cut in water drive reservoirs can reach very high values as reservoir depletion and coning occur over the life of the well. Similarly, for gas wells, the water



gas ratio (WGR) is equally difficult to assign a value. The number changes over time as wells initially flowback fracturing waters, then increases with time via similar mechanisms as those listed above for conventional oil wells. Additionally, the WGR is a function of well technology (downhole equipment) and simply natural random variability as no two wells exhibit the same reservoir conditions, and indeed WGR. Without spending an exorbitant amount of time with data collection and processing, a simple average of WGR is provided in the literature by observing the total volume of gas produced in the Marcellus Shale in 2012 and dividing that by the total produced water under the same conditions. Veil 2015 reports this data for 2012 as 17,406,287 bbl of produced water and 2,041,753 Mmcf of gas [109]. With appropriate unit conversions, this becomes 8.5 MMbbl/Tcf for the year 2012. As a global average of the data, this will prove to be sufficient as a first pass as the estimated mean WGR for Marcellus unconventionals for further analysis. More recent data was not easily available in conjunction between the two necessary values. On an individualistic basis, the WGR for unconventionals can be generated in the Marcellus by observing individually reported production rates of gas and water on a per well basis using platforms such as Drillinginfo. This tedious analysis is compounded as the reporting standards maintained by the state vary across The Union. States such as NM, WV, and PA require reporting of water, while OK, TX, and others do not.

Having now pinpointed preliminarily the WGR for Marcellus shale gas production, we must identify the quantity of gas that is expected to be produced yearly to identify the requisite quantity of produced water. The historical information regarding shale gas

production from the Marcellus are collected from the Pennsylvania Department of Environmental Annual Report [108]. This report clearly denotes the quantity of gas produced in the state that is sourced from unconvencionals. Shown in **Figure 5.1** is the historical annually reported information from the PDEP that is the basis for the regression analysis of gas forecasting.

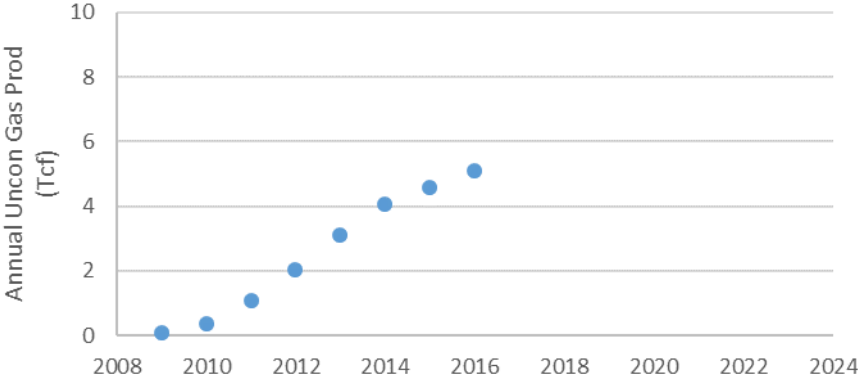


Figure 5.1 - Annual Unconventional Gas Production in Pennsylvania 2009-2016

As can be seen in the figure above, prior to 2009 insignificant quantities of natural gas were produced in Pennsylvania through unconventional sources (< 0.5 Bcf), but gas rates steadily rose until 2014, followed by flattening production increases year over year. This change in rate of production in 2014 is largely due to the market collapse of 2013 and 2014 reducing natural gas prices from \$5.17 to \$3.96 per MMBtu [110]. Post 2014, we also see a flattening in the annual production rates, indicative of a saturated market with growth now controlled by increase in demand rather than lack of supply induced inflated prices. Given that natural gas is a commodity and prices fluctuate daily, we must also realize that regulatory and population demands are likely to have effects on the ultimate yearly output of gas from the Marcellus shale. Pennsylvania doesn't

currently have a gas severance tax, although that is subject to change in upcoming legislative sessions [111]. This severance tax could change producer’s decisions in this area and lead to a decrease in natural gas production. World energy organizations, such as ExxonMobil, are predicting increases in demand for natural gas through the 2040 (World Energy Outlook **Figure 5.2**). It is important to remain critical of the role this commodity has in predicting the water management needs of the future for the Middle-Atlantic Region of the U.S.

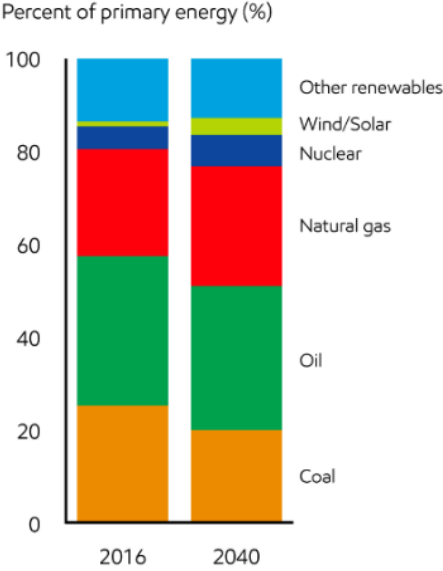


Figure 5.2 - ExxonMobil's World Energy Outlook [112].

For the above reasons, it is prudent to be conservative in estimating natural gas rates in the region. For our analysis, we turn to simple statistical regression analysis to attempt to make an estimation into the future without introducing or taking into consideration changing political or demand climates. Below in Figure 5.3 the forecast of annual gas production from unconventional sources in Pennsylvania is shown. The regression

technique employed was combinative linear-logarithmic. This combinatory approach served to minimize the mean absolute percentage error (MAPE) of the model to the historical data for the years 2009-2016 while also conforming to intuitive reasoning that market forces would not likely sustain a linear increase in gas production into such large annual outputs were simple linear regression forecasting employed. The associated 95% forecast confidence interval is given in green.

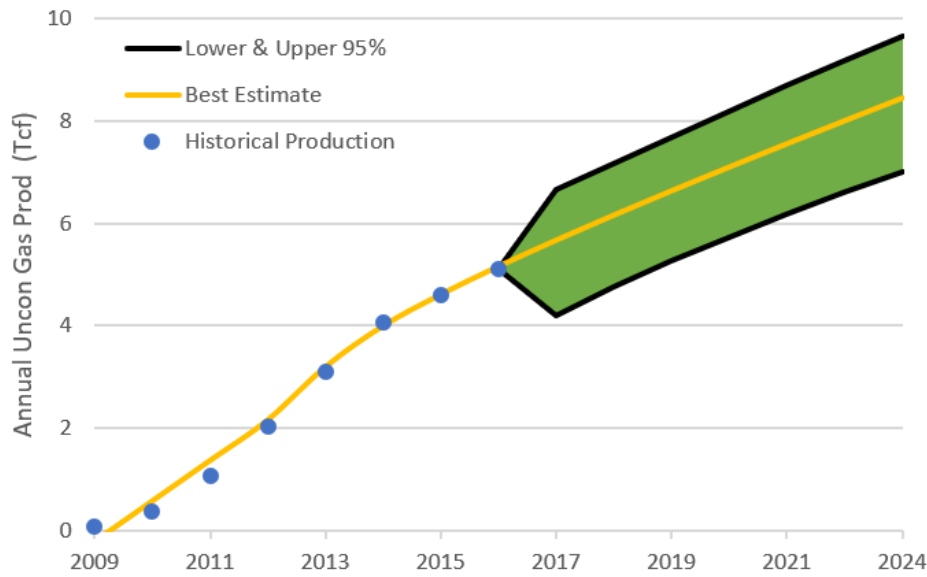


Figure 5.3 - Forecast of Pennsylvania unconventional gas production through 2024. This regression forecasting in conjunction with the above calculated WGR will be used in Section 5.1.2 as the basis for the projected water desalination needs in Pennsylvania in the coming years. Additionally, this scale of use will be useful in the economic analysis of Section 5.2.

### *5.1.2 Scalability of EFC to Industrial Level*

Water management is the new paradigm of oil and gas exploration. Elevating effective water management solutions is a key strategic concern for sustainable production in unconventional plays in the U.S. and worldwide. Companies should not only focus on cost reduction, but on mitigating risks. The Green Economy Initiative states that the payback for every dollar invested in sustainably developed water treatment on health, societal, and environmental benefits is between \$3.00 - \$4.00 [113]. The ultimate goal of produced water management, especially in areas of rapid development and those traditionally unaffected by the oil industry, is to remove dissolved components and use the desalinated water for beneficial uses that can effectively alleviate environmental impact and water shortage. Unfortunately, to date no large-scale application of produced water desalination by membrane technology or EFC processes has not yet been built at industrial scale [44, 49]. Conventional desalination attempts in the industry have been through the use of evaporative or thermal distillation. One of the most significant disadvantages of are the capital costs necessary for an effective large scale system (2-3x those of the former), but these costs can be overcome as the technology develops [69].

A critical step in the validation of a new process or method is involved in the transition for lab-scale model to full-size plant processing. Not only are there technical engineering problems to be overcome, there are ethical and social implications in the building and regulation of such a facility. Outside of the tangible efforts that must be made on the siting and permitting of a facility, the energy and process requirements for EFC are highly

dependent on the location in which it operates. A plant in West Texas will natively have less waste cold (heat sink) available for preprocessing when compared with one in the Northeast. Additionally, the products of EFC can be used and processed to recycle and recover the available cold for cooling the incoming process streams.

In the coming Section, we will discuss the estimated costs associated with building an industrial scale EFC plant and a cost comparison of EFC to the other typical industry water treatment methods. This analysis is performed to address if and how EFC can be utilized in the oil industry for desalination of produced waters.

## 5.2 ECONOMIC EVALUATION

In this Section is a cost analysis for EFC based on a simple thermodynamic analysis of EFC and regional industrial electrical costs for the Marcellus Shale play. This per barrel estimate of cost is the culmination of careful statistical engineering analysis and is inclusive of the fixed and variable costs associated with treatment via EFC, as stated in Section 5.1.2. The potential for sale or disposal of precipitated salts is discussed in Section 5.2.2. This is an important consideration when evaluating the cost of EFC treatment as it provides a potentially substantial windfall to operators to offset energy costs associated with treatment through sale. The per barrel cost estimate of Section 5.2.3 includes values for both sale gains and disposal costs of precipitated salt to provide a high and low bound to the treatment cost. Section 5.2.3 also includes a comparison of this estimated cost of treatment to other common disposal methods in the industry. This is a vital component for propelling this technology forward be incentivizing and

providing motivation for further industry led research. Further research is necessary for validation of EFC to the task of produced water desalination, as discussed in Chapter 4.

### 5.2.1 Thermodynamic Energy Efficiency

Verbeek (2015) calculates an energy cost for EFC of a 23 wt% NaCl brine from 10°C to -21°C and a 3.0 COP refrigeration cycle to be 132 kWh/m<sup>3</sup> of feed stream, which is nearly 3 times the theoretical energy requirement of 51 kWh/m<sup>3</sup> for a 5wt% brine, indicating substantial engineering gains are possible in the future with efficient design. His theoretical analysis for the 51 kWh/m<sup>3</sup> figure is described with a 20% return of the effluent water for washing liquid and that an ice slurry with 20% solid fraction is sent to the washing column, which is a good estimate of the requirements for EFC processing and washing.

These same parameters will be used below in estimating the theoretical energy requirement for EFC of produced water. This estimated ideal energy is the requirement using a chiller with a COP of 3.0 and doesn't include thermodynamic heat loss and other inefficiencies. This tabulated data below is for the West Texas Permian Basin brine described in Section 3.5, as well as the Marcellus average brine and Marcellus 75 using the treatment of 1 m<sup>3</sup> of feed water.

The difference in cooling required for the feed streams in the Marcellus Shale region and the Permian Basin are due to differences the in regional yearly ambient temperature in West Texas of 18°C and in the Middle-Atlantic Region (including Pennsylvania) of 11°C [114, 115]. While only mildly significant, the increase in energy require to cool the feed

stream in West Texas accounts for an increase in the total process of 4%. This is an increase that no optimization would be able to recover as it is an artifact of the environment. This also highlights some benefits that would occur through the employment of EFC in the Marcellus shale play. Not only are natural gas prices higher in the winter, and subsequent production on natural gas wells is increased, the outside ambient temperature is drastically reduced, which is beneficial in energy savings for EFC processing.

Table 5.1 - Energy Requirements for Ideal Process Permian Basin Brine

<b>Permian Basin</b>	kWh
Crystallization of Water	106
Crystallization of Salt	2.7
Cooling of feed from 18 to -21°C	<u>44</u>
	153

Table 5.2 - Energy Requirements for Ideal Process Marcellus 75 Brine

<b>Marcellus 75</b>	kWh
Crystallization of Water	156
Crystallization of Salt	9.1
Cooling of feed from 11 to -25°C	<u>38</u>
	203

Table 5.3 - Energy Requirements for Ideal Process Marcellus Average Brine

<b>Marcellus Ave</b>	kWh
Crystallization of Water	134
Crystallization of Salt	7.3
Cooling of feed from 11 to -25°C	<u>38</u>
	179

The estimates for thermodynamic energy required for EFC on the three brines provided is in agreement with the results obtained by Verbeek of 132 kWh/m<sup>3</sup> for his brine near



the eutectic point of a NaCl brine. The Permian Basin brine has a salinity near that of sea water and therefore exhibits a lower energy requirement when compared to that of the Marcellus brines which have concentrations near and above the eutectic concentration of a halite brine, respectively.

These energy costs summarized in **Tables 5.1-5.3** above should be used cautiously, as they do not include the energy required for transportation of brines within a facility, the energy for operating refrigerators, or other machinery necessary for the process. These energy figures simply are the non-recoverable heat loss for the crystallization process to occur. In Section 5.2.3 this preliminary energy requirement for EFC processing will be converted to a per barrel cost by combining the above figures with statistically relevant regional industrial electricity costs.

### *5.2.2 Sale of Precipitated Salts*

As previously mentioned in Section 4.3, the purity of the salt is crucial in identifying a market and marketable price for this portion of the effluent stream. Low purity salt is not a valuable commodity as there are readily available sources of pure salt on the market that are lower in cost than the purification necessary to treat low grade product. Subsequently, a high-grade salt would require little processing before use and in fact would have multiple marketable end users as a very pure salt is more difficult to find. In the case of EFC for produced water, the salt we are discussing is NaCl. Van der Ham (1998) asserts that EFC is able to produce pure water and salt crystals from a waste water stream [41]. Verbeek (2011) also reports high purity salt effluent when performing EFC experimentation with NaCl brines with magnesium as a contaminant [6].

As discussed in Section 4.3, until otherwise disproven, given the consensus of published research on EFC of the high purity of salt products from EFC of >95%, we will proceed with the speculation that produced water treated in this manner will similarly yield a salt that is 95% pure, which is a very high-grade salt. Worldwide, 62% of all salt is used in the manufacturer of industrial chemicals and for industrial purposes. Only 6% of salt that is used is food grade [116].

Salt has commercial markets as it is a required material in the manufacturing of a great deal of consumer products. Some examples would be the production of paper, dye setting in clothing, soaps, brass, tires, steel, and even bleach [117]. Today, the main production method for salts is through evaporative crystallization using the sun on seawater, brine extraction from deep salt domes by thermal liquefaction, and mining of near surface deposits. Finally, a subset of the salt produced is table quality salt. This is salt that is 97%+ pure and often contains anticaking materials and potassium iodide, an essential macronutrient. Of course, there are also specialty salt markets for consumption, such as sea salt, kosher salt, and specialty salts that are colored due to mineral impurities, such as black and pink salts. The published literature anticipates that EFC can produce this quality of salt.

Other uses for salt are oilfield direct applications. When drilling near salt formations, it is imperative that drilling muds be stabilized with the use of salt to maintain borehole integrity and reduce the chance for collapse or failure of the well [118]. In the event that the salt effluent from produced water via EFC is not to the quality necessary for

industrial precursor or table salt, it could still be used within the oilfield for mud weighting and stability purposes.

It is difficult to assess the market price of an NaCl salt when realizing it is a commodity with fluctuating price that is based on purity and location. This analysis becomes even more difficult when the purity of the hypothetical salt is unknown, as is the location of production. Nevertheless, we press forward and will present some general market value information that is accurate to date. In this way, we will show that there is value in the sale of the salt that could potentially offset the cost of treatment of produced water in this manner. Global salt demand is expected to grow 1.9% annually through 2020 [119]. In 2020, the global average price per metric ton is expected to be USD 42. This is in consensus with other economic analysis that state that the average selling price is USD 40-50 in 2018 [120]. The Economist also reports that this figure of USD 40-50 is for lower grade salts, and that higher grade (precursor level) used for table salt manufacturing and the pharmaceutical industry has an upward value of USD 150/ton. Therefore, it is reasonable to expect that the value of EFC effluent salt to be within the range of USD 40-150, likely on the high side, conservatively on the low. This price is not inclusive of transportation costs, only market value. In the Northeast U.S. this salt would have a seasonal value for road gritting and pharmaceutical use, depending on the respective purity.

### *5.2.3 Per Barrel Cost for EFC Treatment*

In order to calculate a per barrel cost of EFC treatment of produced water, first a preliminary energy requirement for treatment is necessary. This analysis is presented in

Section 5.2.1. Next, any cost recovery from sale of products should be included. The main product, salt, and its recovery cost is the subject of the preceding Section. It is here that we combine the preliminary recovery cost and energy requirement for treatment into a per barrel treatment cost. We then compare this number with literature published values for treatment of produced water via other methods.

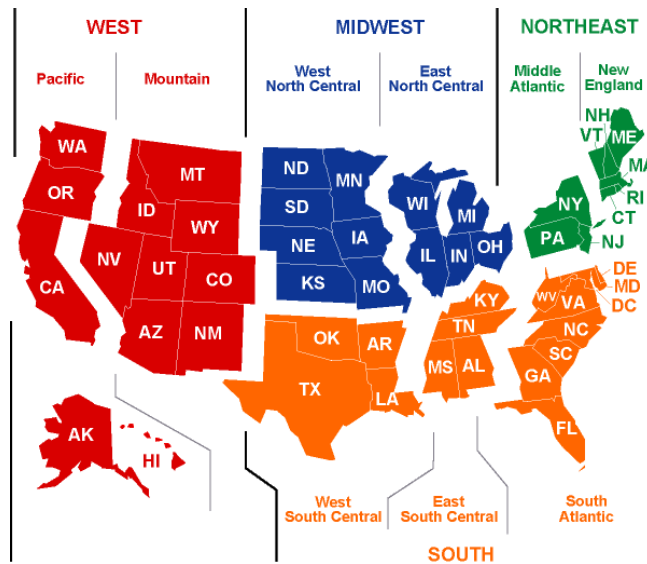


Figure 5.4 - EIA Electric Regions for Contiguous U.S.

The cost of electric energy varies yearly in the U.S. and across several distinct economic and geographic regions as show in **Figure 5.4**. We speculate that the applicability of EFC to the treatment of produced water will be viable across all U.S. regions and have therefore included the cost of electricity for the contiguous U.S. The electricity cost for industrial electric consumers in the U.S. in 2017 is graphically depicted below in **Figure 5.5** as a normal distribution. The source of region electric cost for industrial users was sourced from the EIA [121]. The cost by region was determined to be normally

distributed by the Shapiro-Wilke test with significance  $p = 0.034$ . The mean cost is 6.76¢/kWh.

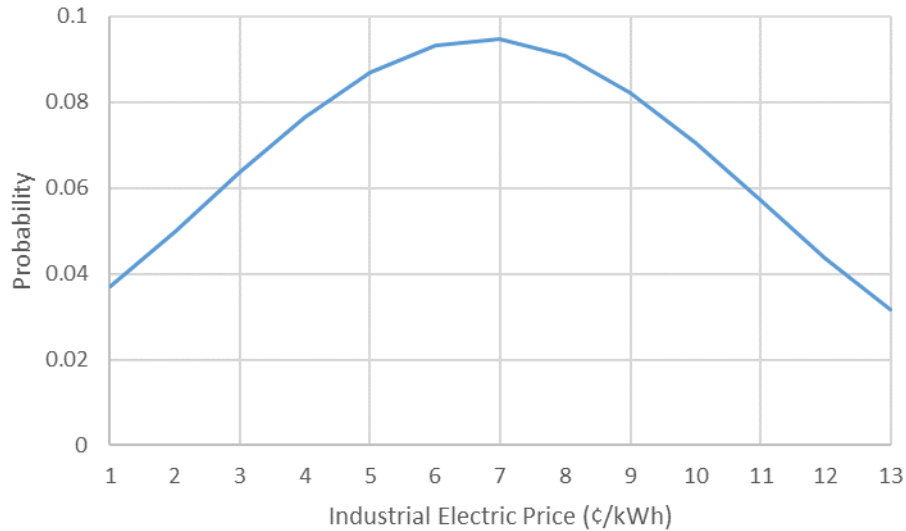


Figure 5.5 - U.S. Industrial Electric Energy Cost in 2017

Subsequently, it appears that the regional electric cost in the Middle-Atlantic Region (which is inclusive of the Marcellus Shale in Pennsylvania) is on the decline with significance  $F = 8.32 \times 10^{-5}$ , as shown in **Figure 5.6**. In fact, the two figures show an astonishing level of agreement in that it appears the mean industrial electric cost for the U.S. is similar to the expected industrial electric cost in the Middle-Atlantic Region for the years 2018-2020. By combining this cost of electricity with the anticipated energy requirements to treat the average Marcellus produced water in Section 5.2.1 of 179 kWh/m<sup>3</sup>, we can generate a reasonable estimate for treatment cost for the contiguous U.S. with the best estimate being the most likely cost for the Middle Atlantic Region today.

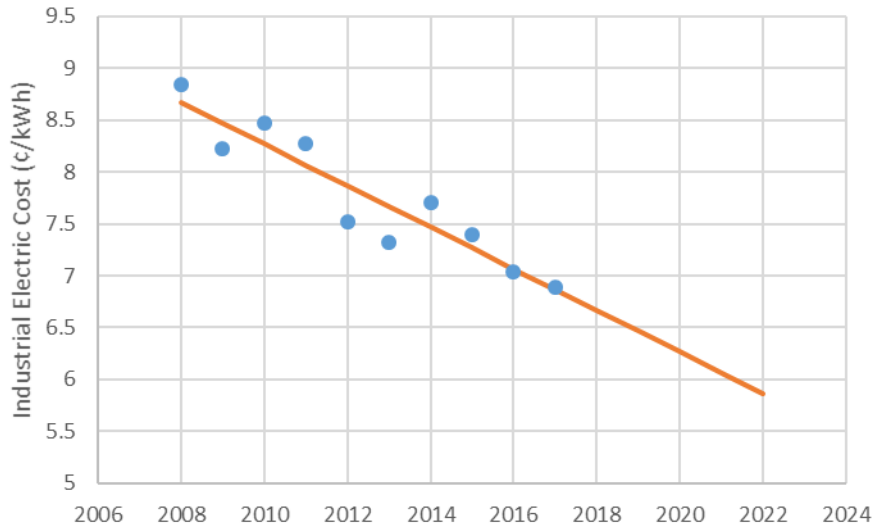


Figure 5.6 - Mean Industrial Electric Cost for Middle-Atlantic Region

Shown in **Figure 5.7** is the anticipated treatment cost for produced water via EFC in the contiguous U.S. using regional industrial electric costs from the EIA as of 2017 and with a treatment energy requirement of  $179 \text{ kWh/m}^3$ , the Marcellus Shale average from the analysis presented in Section 5.2.1. This results in a mean treatment cost of \$1.93/bbl.

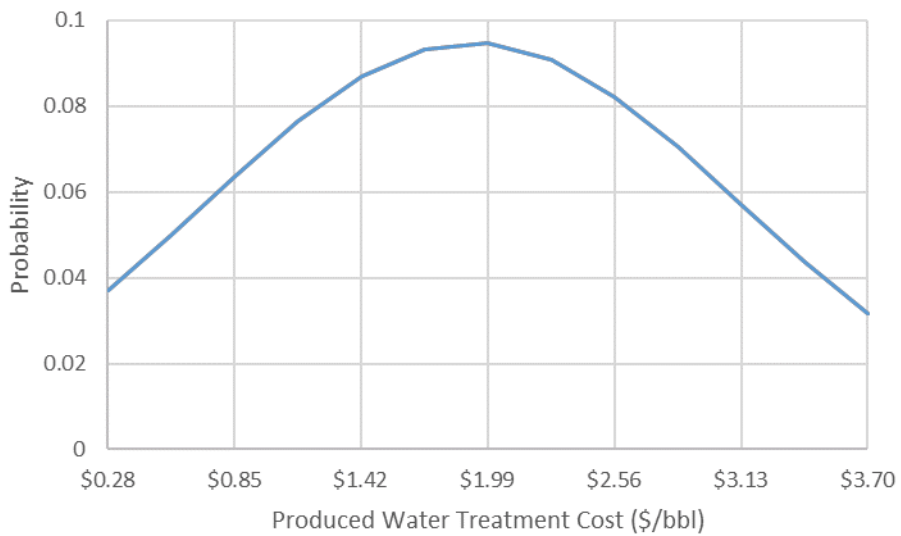


Figure 5.7 - Anticipated Treatment Cost for Produced Water via EFC

Comparing then this cost to those of other treatment methods in the U.S. shown in Table 5.4 - Comparison of Desalination Technologies [116] **Table 5.4** for the produced water, we see that the energy cost is quite large. However, the analysis presented herein is not indicative of theoretical energy requirements as those listed in the table below and is instead a realistic depiction of the energy necessary to treat the produced water using EFC with the technology available today. EFC has the potential to use less energy than other thermal processes and being at an early technological stage, has numerous opportunities for energy optimization.

*Table 5.4 - Comparison of Desalination Technologies [116]*

Technology	Feed Quality TDS (mg/L)	Process Recovery (%)	Energy Consumption (kWh/m <sup>3</sup> )	Energy Cost (\$/bbl)*	Product Quality TDS (mg/L)
Reverse Osmosis (RO)	< 45,000 <sup>b,e</sup>	40–65 <sup>b</sup>	4–6 <sup>d</sup>	0.04–0.06	< 250 <sup>f</sup>
Membrane Distillation (MD)	> 50,000 <sup>i</sup>	65–95 <sup>g</sup>	20.5–66.7 <sup>j</sup>	0.19–0.63	< 50 <sup>i</sup>
Multi-Effect Distillation (MED)	< 100,000 <sup>e</sup>	20–35 <sup>b</sup>	14–21 <sup>d</sup>	0.13–0.20	< 10 <sup>d</sup>
Multi-Stage Flash (MSF)	< 100,000 <sup>b</sup>	10–20 <sup>b</sup>	19–27 <sup>d</sup>	0.18–0.25	< 10 <sup>d</sup>
Mechanical Vapor Compression (MVC)	< 200,000 <sup>c</sup>	40 <sup>a,b</sup>	10.4–13.6 <sup>a</sup>	0.10–0.13	< 10 <sup>b</sup>

Additionally, when the potential value of the effluent salt is added to the economic analysis, we see that the picture for treatment costs changes drastically. The Marcellus average water quality report indicates that the brine contains approximately 60 lb/bbl of NaCl. With recovery of this salt and selling it at the \$40/ ton figure is a recovery of \$1.11/bbl. This would significantly lower the overall cost of treatment to a mean value of approximately \$0.82/bbl and is then similar to the cost of membrane distillation.

This economic analysis is useful in estimating a preliminary cost for treatment and is a vital component for propelling this technology forward by incentivizing and providing motivation for further industry led research. There is much room for improvement through technological advances of EFC that can further reduce anticipated energy requirements and the sale price for the effluent salt is very low given the anticipated quality. For both these reasons it would not be at all surprising if the cost of treatment, with some significant engineering work, would be approaching null. In the next Section we discuss the steps remaining between implementation of EFC technology for desalination of produced waters and continue to frame the technology around the needs of the oilfield industry.

### 5.3 EASE OF IMPLEMENTATION

This Section is included in conjunction with Section 5.2 to discuss the topics of considerations that must be addressed before implementation of EFC can be achieved. In Section 5.3.1, The considerations for construction of an EFC facility are discussed along with some preliminary, order of magnitude, cost estimates to help facilitate initiating ideation for industry. Section 5.3.2 is supplemental to 5.3.1 by discussing the rates that should be considered in the construction of a facility. Finally, tying back to Chapter 3, Section 5.3.3. includes discussion on the ability of EFC to meet the changing brine composition within and between regions. In conjunction with the economic analysis presented in Section 5.2 and the anticipated scale of problem from 5.1, this Section is necessary to frame the solution (EFC) to the problem in a meaningful, yet open direction.



### *5.3.1 Fixed Facility Construction and Cost*

As can easily be imagined, estimating the cost of water treatment systems is complicated; not only due to the factors and variables that are involved in the system design, but also due to the requirements of the system that are imposed by designers. The cost of an industrial treatment system is only one part of the entire equation, the other being the main factors that govern the cost and the target goals of the treatment design. These are:

1. Required flow-rate of the system
2. Quality of influent stream
3. Target quality of effluent stream
4. Construction material and design

The construction and design of the system is a critical first step in conceptualizing the planning phase for water treatment. Generally, the largest capital expenditure is required in purchasing and constructing the necessary facility and equipment. However, engineering costs should not be underestimated as for novel and new technologies the engineering solutions for a facility can typically run 10-15% of the total project cost. Likely for EFC these engineering costs will be higher as it is less developed than many water treatment methods. Some of the important factors to consider in the material and design of the system would be space requirements, installation, automation, regulatory costs, waste disposal costs, and other fees and costs that might require additional capex.

The target purity should be understood early in the planning phase. For EFC and for a sustainable recycling endeavor, that target can be pushed relatively low, with clean releasable water as the inevitable outcome. Clearly, a target is to comply with the regulatory standards and meeting minimum contaminant thresholds that are imposed by the locality and state. By working backwards from the target purity, secondary and tertiary processing equipment can be included in the technological assessment to determine what is necessary in conjunction with EFC. For this reason, additional testing is necessary for EFC to determine the purity of its effluent stream from the processing of produced water, as discussed in Section 4.3.

Next the quality of the influent stream should be well understood. This is the easiest portion of the pre-planning phase as it includes only the sourcing and evaluation of data from operators in the target area (in our case the Marcellus shale gas play) and creating a robust model for the expect water qualities. A first pass of this has been done in this thesis and is included in Appendix A which includes an estimated average water quality of Marcellus Shale gas well produced water. A more in-depth study should be performed that includes quality and quantity of flowback water from these wells to determine what effect that would have on the total water quality stream incorporated for processing. In general, the greater the contamination level of the influent stream, the more costly and greater number of steps required to treat the water for the target effluent quality. It is speculated that EFC may be able to negate this dilemma and reduce significantly the capex for water treatment of produced brine. For this reason, additional testing is

necessary for EFC to determine the purity of its effluent stream from the processing of produced water, as discussed in Section 4.3.

Generally, flow rates are a sliding measure of facility costs. Lower flow rates translate to lower capital costs, etc. This is a general truth, but there are cost differences between low and high flowrate systems. For example, an increase in flow rate of 50% cost increase costs by 20%, etc. The scalability of EFC is one uncertainty of the design of a full-scale treatment facility and is the subject on conversation in Section 5.1.2. By continuing testing of EFC at larger scales, the efficiency of the method and the expected flow rates can be better understood. Verbeek using the 200L SCWC crystallization chamber discussed in Section 4.2 has an influent flow rate of approximately 37 g/sec which is equivalent to a substantial 11,679 GPD at a brine density of 1036 kg/m<sup>3</sup> [6].

Finally, cost estimates for most industrial applications follows. SAMCO (2017) estimates that the capital cost for a 150 kGPD system for general industrial applications would cost 1.5 million USD [122]. Considering that the cost of EFC is estimated to be about 2-3x that of thermal distillation, this raises a preliminary capex of 3-4.5 million USD for the 150 kGPD application [69]. Remembering that the quantity of waste water produced daily by Marcellus shale gas sources in Pennsylvania alone is approximately 5 million gallons, we can see that the estimated cost for a treatment facility capable of this total stream volume is infeasible. However, SAMCO does estimate a 1000 GPM (1.5 million GPD) capacity ZLD system to cost 50 million USD, which is a realistic and feasible cost for a production company to be able to source.

Having discussed the relevant factors and issues to be considered in the design and construction of an EFC facility for industrial water treatment of produced brines, we next discuss the potential throughput of EFC discussed by other authors to facilitate to which degree these values are congruent with those provided above by SAMCO in generating a realistic and feasible rate to be anticipated by an EFC facility using currently available secondary and tertiary equipment.

### *5.3.2 Potential Throughput Through Upscaling*

As mentioned previously, most reuse in the oilfield is done on treating produced and flowback water for refracturing. This makes sense as 41% of wells in the U.S. are in regions of extreme water stress or drought and in some counties in Texas, more than 80% of municipal water goes to industrial and agricultural use [31]. Some municipalities do take cleaner flowback fluid as a waste stream for sewage plant treatment. This policy is largely being reverted in much of the country as the plants struggle to sufficiently treat the water for release. Given the large use of freshwater in hydraulic fracturing new wells (2-6 million gallons per well) and the high cost of water handling in the Marcellus shale (\$3+/bbl for disposal or \$7-10/bbl for transport), there is a new way for companies to profit from water management in this area if they can provide reliable, available produced water disposal. With thousands of wells projected to be drilled through Pennsylvania, West Virginia, and Ohio in the next decade with targets in the Marcellus Shale [65], it will be a major revenue source for someone. Experts also agree that public pressure and regulation to pressure producers for more recycling are coming

Himawan (2002) [7] estimates that the cost of a freeze crystallization system was 7% more costly than to evaporative crystallization, but could save up to 60% of the energy cost. The reality of this economic evaluation remains uncertain as freeze crystallization has only been used on a limited scale briefly for a pilot mining waste water processing in South Africa. What that analysis does conclude, however, is that freeze crystallization is a new process with significant room for technological improvements and cost reduction as implementation occurs, while evaporative cooling and other processing methods is already established and has only incremental future cost savings only as a result of technological improvements [5].

Unfortunately for freeze crystallization, much of the cost for developing and construction of a large-scale treatment facility is up in the air. Therefore, the most significant disadvantage of freeze crystallization is the capital expenditure to initially plan, design, and construct a facility capable of processing the volumes necessary in the oil and gas field which is on the magnitude of 10k bbl/d (42 thousand gallons per day) [41, 74]. The main operational expenditure for treatment is electricity. Given the lower industrial energy costs in the Northeast and the increased disposal costs, this appears to be the most logical location to pilot test new produced water disposal techniques.

Verbeek's 200L SCWC processes a stream of 11,679 GPD, so several similarly sized crystallizers could be used in parallel to provide sufficient brine processing power for produced water needs. Additionally, singular, larger crystallizer could be manufactured to allow for greater throughput volumes. A static crystallizer heat transfer rate of 0.18 – 0.25 kW/m<sup>2</sup>/°C is recommended to reduce scaling but still maintain sufficiently low

freezing times to make crystal size optimal for filtration and not induce undesirably high scale formation.

To be an appreciably effective force on the market with EFC, a daily treatment capacity of 40 kbd, or 168,000 GPD process volume should be considered. Using the numbers Verbeek generates in his analysis this would require an expected 14 SCWC to achieve the desired flowrate. Ideally the design would be upscaled to contain fewer, larger volume crystallizers working in parallel and series to optimize the characteristics of the EFC process and minimize waste heat. A benefit of operating multiple crystallizers at a singular eutectic temperature would also be further thermodynamic enhancement by the use of larger, more efficient chillers with COP of 4.0 or more. It is speculated that the cost to construct an EFC facility as described would be well within the capex estimate of 3-4.5 million USD.

This Section is supplemental to 5.3.1 in discussing the rates that should be considered in the construction of an EFC facility. And the scale of treatment water available in the U.S. and Marcellus shale for potential market capitalization.

### *5.3.3 Robustness of Method to Different Brine Species*

During simulation work using the OLI stream analyzer presented in Section 3.4 and 3.5, it is clear that the many salts exhibit eutectic points below NaCl, which is in agreement with published literature [123]. Because of this, if EFC treatment is performed holding only a temperature of -21.1°C, only halite salts and ice will be created. Remaining salt species will be entrained in a reduced water volume. Previously we express that in

conjunction with EFC other technologies can be employed to result in an efficient, ZLD stream for produced water. In this section we briefly reintroduce those previous concepts and reiterate why they are necessary and how this could potentially change the implementation cost for a scale EFC treatment facility.

With the high salinity retained brine after EFC processing to remove halite salt species, there will remain many ions, mainly calcium, magnesium and other chloride forming salts. These all exhibit a eutectic temperature lower than halite and will not be removed unless treated to a further reduced temperature. If water processing for bulk salt removal is the goal, then further processing is not necessary; simply discard the remaining retained brine in the conventional manner using injection disposal or evaporative crystallization. Each of these is associated with a historically known price and exhibits little technological gain or engineering work.

Alternatively, other technologies could be used to further reduce the volume of water necessary for disposal. Reverse Osmosis is a potential technology with a proven history and known concerns based on brine salinity. As mentioned in Section 4.4.2, there are questions regarding the applicability of RO for treating brines of this nature as the osmotic membranes are highly susceptible to deterioration if organics and hydrocarbons are present in measurable quantities. If shown to pose no threat to continued treatment by RO, then the two technologies can be used well in conjunction with each other, given the retentate salinity is not unduly high. In instances where the retentate salinity is too high for treatment with RO, the water can be disposed of in with conventional means, or instead diluted considerably with the processed fresh ice stream

from EFC. With halite composing most of the TDS in produced brines, when remade without the halite portion, the produced water can exhibit a low enough salinity for potential release. This is unlikely in the case of Marcellus produced waters as they exhibit a high level of contamination. For cleaner, low salinity brines this is a distinct possibility.

This could have implications on the ability of a Freeze Crystallization treatment facility to handle the volumes and rates of waste water necessary for commercial operation or impact the scaling of a system for mobile applications, as is discussed in Chapter 2, Section 2.3.5. As well, the effect of salts such as  $\text{BaSO}_4$  still in solution in trace quantities mentioned in Section 3.4 could necessitate the need for additional water processing steps to reduce scaling of equipment in the stages after EFC takes place. No pre-treatment of the waters for EFC should be necessary [75].

By using these technologies in series, reduced volumes of brines can be created that require less injection disposal, thereby reducing the impact of induced seismicity and lowering the overall cost of water management. Additionally, by treating the brine in such a fashion, the fresh stream of water can be used for agriculture or oilfield use thereby limiting the effect of industry on local municipal water supplies. The crystallized salt can also be sold on the market which would be financially rewarding and present a major incentive for implementing these technologies [5].



#### 5.4 SYNOPSIS OF CHAPTER FIVE

In this Chapter we discuss the implications of implementing EFC to industry scale level and provide a cost estimate for the treatment of produced brines from Marcellus shale gas wells to that of other desalination and disposal methods that are commonly used in the industry. In initiating this analysis, we provide insight into the scale of the problem by performing statistical analysis to forecast the volume of produced water from unconventional sources in Pennsylvania through 2024. Using this volume as a metric for water necessitating treatment, we perform analysis regarding the scale up of EFC in Section 5.1.2. Section 5.2 is primarily a economic evaluation for EFC to relate generally the cost of treatment and disposal of crystallized salts into a per barrel estimate for produced water disposal. This cost is then compared to other disposal methods to show favorably that EFC exhibits a reduced water management cost if implemented in this region under the given constraints. Finally, in Section 5.3 we discuss in more detail what the constraints are for the given analysis and the causes and concerns that will be faced in the implementation phase of EFC, were it to be undertaken. In doing so we have bounded our analysis within the context of the oilfield industry as stated in Chapters 1 and 2. The analysis present in Chapter 5 address mainly Research Questions 2 and 3.

***RQ2. What changes need to be made to freeze crystallization desalination technology for compatibility with oilfield operations?*** The core of Chapter 5 is devoted to answering this Research Question. By investigating and identifying the cost and manner of treatment utilizing EFC at an industrial scale, we have shown that potential changes need to be made in the expectations of EFC for desalination and that likely it is with

multiple technologies employed in conjunction in which successful water management lies. By addressing preliminarily a cost for EFC treatment, we can invite more minds to investigate and add to the knowledgebase of EFC for further development and to address compatibility concerns that the author didn't or was unable to address with his experience.

***RQ3. What environmental benefits will be realized by treating water for reuse and release over underground water injection?*** In Section 2.3.5, the potential release of water extracted from effluent brine back into the environment is discussed. Many areas with developed oilfields in the U.S. are in areas deemed as vulnerable to drought and there is an alarming history of mega-droughts lasting 300 years or longer in many western U.S. states. In Section 1.3.4 it is shown that the main work that needs to be done to prove there is an environmental benefit to the release of this water is largely outside the scope of this thesis. However, what is discussed in Section 2.3.7 and Section 5. 2.4 regarding the release of water and the sale of crystallized salt provides motivation that there is clear environmental significance of the work by reducing the ecological footprint of other industries. Similarly, a reduction of pre-treatment equipment would represent a reduction in the ecological footprint of oilfield water management itself. Additionally, the sale of crystallized salt and a source of fresh water would be instrumental in providing benefits for field development.

The main results from this Chapter are:

- The cost of EFC treatment in the Middle-Atlantic Region is estimated to be \$1.93/bbl
- Cost of EFC treatment can be reduced from selling crystallized salt worth greater than \$1.11/bbl
- Marcellus produced water volumes in Pennsylvania are expected to raise to 71 MMbbl by 2022
- The nonrecoverable energy requirement for an average Marcellus Shale produced water stream is estimated to be 179kWh/m<sup>3</sup>

## Chapter 6 – Concluding Remarks

In the previous Chapter, the results of a statistical analysis of the anticipated per barrel cost of EFC treatment of produced water and anticipated produced water volumes for the Marcellus Shale play of Pennsylvania were evaluated and compared to other literature published results. It was found that currently, EFC would exhibit a higher cost for treatment than other existing treatment technologies, but that with the potential for sale and reuse of salt and water effluent streams respectively, that the cost of treatment can be offset to be low or null. In this Chapter, a summary of the work is provided, and the main points of the chapters are highlighted in Section 6.1. The Research Questions and their answers are briefly mentioned in Sections 6.2. Then the relevant achievements and contributions of this thesis are presented in Section 6.3. The remaining questions and research gaps for future work are the subject of Section 6.4, bringing this work to a close.

### 6.1 A SUMMARY OF THESIS

My main goal through this thesis regards the potential benefits of utilizing freeze crystallization for desalination and recycling of oilfield produced water, while considering the trade-off between economic and environmental costs. A large part of this is to fill the gaps that exist in current research of EFC and present clear validation for further examination, as well as provide a potential avenue away from the use of waste water injection for the oilfield that is economically feasible and environmentally beneficial.

In Chapter One, the foundation for the thesis is laid. I begin with an introduction to the oil and gas industry and a review on the process of oil generation and cohabitation of brine in oil systems. A review into the necessity of technological advance in the industry is followed by a background and a motivation section that describes the 18-month long process of working with the Baker Hughes Challenge Problem, and the process of identifying and refining my research area. From this process, four Research Questions are developed and the connectivity to the overall theme of the thesis is identified. The connectivity between the Research Questions and the Challenge Problem are further substantiated in Chapter 2 through the critical literature review.

In Chapter Two, a critical evaluation of current waste water disposal methods, desalination, and water recycling literature are presented. In Section 2.1 this review of the literature is summarized and connectivity between the Research Questions and review established. In Section 2.2 principal concepts are introduced and the Research Gaps connection to the motivation presented in Chapter 1 are discussed. Section 2.3 contains an analysis of the waste water disposal methods currently in use and their limitations, as well as the requirements for released water that will be expanded in Section 5.3. In Section 2.4, the utility of Eutectic Freeze Crystallization to the industry and specifically Baker Hughes is established. This chapter is beneficial to those outside the industry unfamiliar with common practices, and their rationale.

In Chapter 3, I introduce potential benefits realized by the oil industry if EFC is to be incorporated as a recycling method for waste water over currently established methods discussed in detail in Chapter 2. Also included is the concept of Eutectic Freeze

Crystallization with introductory examples to explain the phenomena and provide justification for the use of the OLI Stream Analyzer for the simulation work that is performed. Additionally, singular and binary species salt simulations are presented to provide and illustrate the freeze crystallization process with reference to the current literature status of freeze crystallization. Commentary on the Gaps in the current EFC literature are mentioned explicitly in Section 3.4 and reinforce the Research Questions presented in Chapter 1, Section 1.2 as well as the needs for further work that is expanded in Chapter 5, Section 5.1. Finally, the Chapter is concluded with original simulation of complex multi-species oilfield brines provided by way of water quality reports courtesy of Baker Hughes Inc. in Section 3.5. The main findings of Chapter 3 are:

- The Eutectic temperature for singular species NaCl brine is  $-21.2^{\circ}\text{C}$  with the formation of hydrohalite
- Inclusion of other ions and chloride forming cations has the effect of depressing the crystallization temperature of hydrohalite, generally on the order of  $5\text{-}10^{\circ}\text{C}$
- The co-formation of other salts near the eutectic point of hydrohalite can be limited through the mixing of waste water streams from multiple wells
- Oilfield brines, composing mainly  $\text{Na}^+$  and  $\text{Cl}^-$  in the TDS, exhibit one realizable eutectic temperature (hydrohalite and ice) while the eutectic temperature for other salts is too low for commercial chilling operations
- An average Marcellus/Utica brine exhibit first the formation of ice, followed by eutectic co-formation of hydrohalite and ice

In Chapter 4, I discuss the use of further bench scale experimentation as a method for validating the performed EFC simulation work of Chapter 3. Additionally, the Gaps that remain for empirical structural validation of EFC for compatibility in the oilfield is discussed in Section 4.2 as Research Gaps that can be closed with further experimentation. By providing both of these preceding sections as motivation, we proceed to Section 4.3 with a proposal for experimentation that includes the bench scale design and equipment requirements along with a testing procedure for experimentation of actual oilfield brine samples. The work of Chapter 4 is done to be of use to industrial researchers and are maintained as independent of the original work done in this thesis for the purpose of being a take-away document that can be used to explain the current Research Gaps that exist in the literature and solicit funding for industrial and academic sources to close these gaps. To further motivate these positions for their support, a preliminary cost analysis is the subject of Chapter 5.

In Chapter 5 I discuss the implications of implementing EFC to industry scale level and provide a cost estimate for the treatment of produced brines from Marcellus shale gas wells to that of other desalination and disposal methods that are commonly used in the industry. In initiating this analysis, I provide insight into the scale of the problem by performing statistical analysis to forecast the volume of produced water from unconventional sources in Pennsylvania through 2024. Using this volume as a metric for water necessitating treatment, I perform analysis regarding the scale up of EFC in Section 5.1.2. Section 5.2 is primarily an economic evaluation for EFC to relate generally the cost of treatment and disposal of crystallized salts into a per barrel estimate for

produced water disposal. This cost is then compared to other disposal methods to show favorably that EFC exhibits a reduced water management cost if implemented in this region under the given constraints. Finally, in Section 5.3 we discuss in more detail what the constraints are for the given analysis and the causes and concerns that will be faced in the implementation phase of EFC, were it to be undertaken. In doing so we have bounded our analysis within the context of the oilfield industry as stated in Chapters 1 and 2.

In Section 6.2, I will discuss explicitly my take-away that embodies the answers I have formed to the posed Research Questions developed in Chapter 1. These Research Questions were first introduced in Section 1.3.2. The content of Section 6.2 is not intended to be accurate in a scientific sense and is intended to be opinionated in nature. For the explicit facts relating to each Research Question as discovered through the work of each Chapter, please refer to the Chapter synopsis sections.

## 6.2 ANSWER TO THE RESEARCH QUESTIONS

My primary research question was “How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?” To answer this question, there are several other questions that need to be answered first. The four secondary Research Questions are presented in Section 1.3.2, and the support and answers to these Research Questions are presented in the Chapter synopses. I have stated those Questions and answered each one of them as the following:

**Research Question 1: *How can freeze crystallization be utilized to treat flowback and co-produced water form oilfield operations?***



The ability of EFC to desalinate complex brines is explored through Chapter 3 via simulation to determine if the technology is capable of separating multi species brines that are common of produced water. Sections 4.1 and 4.2 include discussion on future bench scale work that should be performed to validate EFC through physical processes. Finally, economic considerations are included in Section 5.2 to evaluate if the method of EFC desalination could be implemented commercially.

The current EFC freeze chamber design that F. vd Ham [41] presents is of utility only for bench scale experimentation due to size (10 L). he outlines the design of a scraped cooled wall crystallizer (SCWC) capable of separating ice and salt crystals gravimetrically and the recycling of the mother liquor for further processing. Verbeek [6] builds on this original SCWC design and investigates the EFC process on a skid mounted EFC design that is capable of treating 200 L at a time. While this is a substantially larger volume, it is still not adequate in addressing whether EFC can accommodate the substantial ( $\geq 1,500,000$  L) stream that can be associated with a moderate (5 wells) sized advanced age oilfield. However, their work into the scalability of the EFC process can be expanded to address the gap of whether freeze crystallization desalination technology can be upscaled enough to handle the waste water streams. The compatibility of EFC to oilfield operation is primarily investigated to address any deficiencies or roadblocks that would delay implementation of this technology into the current infrastructure of treatment facilities in the industry, such as refineries or injection wellhead locations where significant infrastructure already exists. Lu [43] addresses the use of EFC for treating coproduced water from Kuwait and the treatment of low salinity flowback water from

Shale gas fracturing in the Marcellus. Unfortunately, Lu does not address what effect, if any, the presence of minute contaminants such as NORM, or solid contaminants such as residual hydrocarbon and suspended solids would have on the EFC process. He acknowledges that “In order to be able to make better cost calculations and compare them with evaporative crystallization, a more thorough study of all parameters involved in the EFC and recrystallization process is necessary. Some examples of important aspects to investigate are continuous operation (a commercial process will be continuous) and scaling up to larger scale. Also, EFC of produced waters from different origin and composition have to be studied.” He hints on an important issue. The driving factor for adoption of this technology by the oil industry is precisely the cost of a commercial operation and the robustness of the method to be applied to waters of varying qualities and origin. The latter is addressed through Research Question 1, while the former relates to the changes that need to be made to the technology for commercial upscaling.

By all accounts it appears that EFC is a compatible candidate for treatment of co-produced water from oilfield operations. This water is high in salinity and primarily NaCl, which has a relatively high eutectic temperature when compared to other salt species. This compatibility of the technique and the availability of current technology capable of cooling this water to the desired temperatures with competitive energy requirements insinuates that in the near future this technology can have rapid success in the oil industry, even with the significant research that still needs to be performed, as outlined in Chapter 4.

**Research Question 2: *What changes need to be made to freeze crystallization desalination technology for compatibility with oilfield operations?***

This gap is further explored in Section 3.5 by investigating the effect of common waste water stream contaminants on the EFC temperature for streams from the Marcellus and Utica shales. Additionally, Section 5.2 contains a discussion into the economics of EFC and preliminary work into cost estimation for treatment via EFC (in \$/bbl) is presented.

Many areas with developed oilfields in the U.S. are in areas deemed as vulnerable to drought [33] and there is an alarming history of mega-droughts lasting 300 years or longer in many western U.S. states [32]. This disturbing potential future of little potable water is underscored dramatically by the use and disposal of > 20,000 gallons per well of fresh water for hydraulic fracturing of new wells in these states. In many cases, the solution means recycling flowback or produced water to limit the need for fresh water in the production of hydrocarbons [31]. However, the recycling or release of produced water is often met with unintentional ecological consequences. Current regulation in Eastern Shale gas states (Pennsylvania and West Virginia) is heavy on regulating underground injection as a legacy of existing legislation passed in historic oil producing states such as Oklahoma and Texas, but have failed in implementing meaningful legislation regulating the release of tainted waters to the environment [30]. Given that there are little Class II brine disposal wells associated with the Marcellus Shale Gas production states, it is likely that recycling will be the way forward for development, but that underground injection is currently the only long term viable option for a future of gas production in the area. Arthur, Dutnell, and Cornue [28] acknowledge that there is

an associated infrastructural cost to the disposal through injection in the form of road damage, minor releases, and traffic related casualties that should be considered in an injection schema. Because of the potential detriments associated with injection are so many, Gupta and Hlidek [29] speculate that there is potential for an optimized recycling operation for the recycling of frac fluid as the cost of sourcing fresh water and disposal of waste water increases with water scarcity that will reduce the dependence on injection for disposal and water management. Recently in Oklahoma a connection between Class II injection wells and earthquakes (hereto referred to as induced seismicity) has been noted [53].

Few changes need to be made. If the outcomes of the further research in Chapter 4 reveal that EFC is insensitive to hydrocarbons and the radioactivity of the effluent water and crystallized salt is reasonably low, the technology can be implemented with little to no pretreatment required. Indeed, it would seem that EFC would be easily compatible with oilfield operations and readily adopted by many operators for use in water treatment facilities and for refining water treatment.

**Research Question 3: *What environmental benefits will be realized by treating water for reuse/release over underground water injection?***

A gap exists regarding whether there is a current recycling method that can help hydrologically impacted areas while simultaneously reducing anthropogenic seismic activity and associated environmental destruction such as roads and bridges by overuse of heavy disposal trucks and machinery and whether these recycling methods can

reduce unforeseen environmental damage in the form of detrimental releases of toxic salts into estuaries and streams.

This research question is evaluated through Section 3.5 in a discussion regarding the reduced water volumes associated with freeze crystallization and the potential energy savings realized through the use of the crystallization method over others. Additionally, in Section 4.2 commentary on the economic value of pure crystallized salt is presented and what impact this could have on national anhydrous NaCl production and associated environmental impact. Finally, in Section 5.2 a holistic economic analysis of freeze crystallization is performed that highlights the usefulness of the technology in reducing water injection disposal and the potential release of fresh water to the environment.

Refineries on average use 2.5 gallons of water for every gallon of crude processed. This combined with the introduction on entrained water from crude delivery means that the typically refinery deals with upwards of 10 million gallons of 'dirty' water daily. Typical dirty water processing at the refinery level includes membrane technologies (RO) and thermal distillation for water reuse [54]. Thermal distillation is the most common water treatment technique as it is economical and technically simple, the plants already have the necessary permits to use this technology. New refineries are stressed to reduce costs and consumption by adopting new lower energy desalination and treatment methods while minimizing discharges. Haddaway [55] mentions that the key is [to] "use existing waste or low-value streams from oil and gas exploration (and other industrial processes) to reduce the amount of effluent generated." By recycling water again and again for use in the refinery, the newer plants are able to reduce their environmental footprint,

reduce costly permitting and consumption costs, while simultaneously reducing energy consumption with energy efficient new equipment. What hasn't changed however, is the technology that is in use. Thermal distillation, while appropriate for refinery use, is at the edge of what is theoretically possible through energy efficiency, and there are little gains to be had from further optimization at this point. EFC has the potential to use less energy than a thermal process while simultaneously allowing for the continued recycling of water within the refinery and being at an early technological stage, has numerous opportunities for energy optimization.

By allowing for central treatment of unconventional water sources, injected volumes can be decreased. This decrease will have direct environmental benefits through reduced induced seismic events. Additionally, there are indirect benefits to the recycling of this water such as limited strain on water resources from operators reusing water rather than purchasing it fresh, and reduced mining and sourcing operations for the generation of high quality NaCl. These environmental impacts should be included in any LCA and would have resounding implications on a global scale.

***Research Question 4: How can freeze crystallization be utilized with minimum impact to existing water treatment infrastructure?***

While it is clear that there is need for efficient water treatment at the refinery level, and indeed waste water treatment from crude production as well, it isn't certain what changes would need to be implemented at the refinery level to have compatibility with freeze crystallization, given refineries have been utilizing thermal distillation for so many years.

This research question is developed in Section 4.4 with discussion on the sensitivity analysis of EFC temperature and this implication on the design of a EFC treatment facility. Through Section 5.3, future research needs for EFC and discussion about other problems for which EFC can be applied are covered to strengthen the relationship between EFC as a water treatment method and refinery operations.

This question is more difficult to answer pre-implementation. Likely this technology would be disruptive and decrease the demand on many water treatment equipment such as API separators, electro-coagulators and others. Additionally, the reduction in water injection volumes and other changes to the economics of well drilling and production would change the scope of the industry altogether. While these changes are broad and might be overreaching, at the minimum this technology represents an opportunity for an ambitious entrepreneur to enter the market and take a large share away from conventional management sources.

### 6.3 ACHIEVEMENTS AND CONTRIBUTIONS

The principal question for this thesis is as follows:

*“How can freeze crystallization be utilized to treat flowback and produced water from oilfield operations?”*

Current waste water disposal methods in the oil industry primarily include water injection into disposal wells, with limited utilization of electrocoagulation for in-field reuse and thermal distillation at refineries. Brine hypersalinity and residual hydrocarbon has limited the application of membrane technology and simple environmental

expulsion is heavily regulated by the EPA [2]. The problems associated with injection disposal, coupled with a lack of nearby Class II injection wells has limited the development of the Pennsylvanian Marcellus shale gas due to economic constraint imposed by the cost of water disposal. The challenge gas producers must now face is how to preserve the economics of shale gas production while simultaneously upholding responsible stewardship of resources and protecting public health. With increased concerns regarding induced seismicity from injection wells and the safety of that type of disposal, the need for water recycling methods has grown.

Eutectic Freeze Crystallization has the potential to treat complex, hypersaline coproduced brine and represents a sustainable water treatment technology towards achieving a near zero waste by producing potable water and pure salts [3]. Given that the hypersaline brines of the Marcellus Shale are sodium and chloride rich [4], EFC could be used to selectively recover the sodium as a pure sodium chloride salt while simultaneously producing pure ice crystals. The pure ice would have innumerable uses; reuse for hydraulic fracturing, release into estuaries, and agriculture being only a few.

The sodium chloride salt represents a potential revenue stream for water treatment companies and its sale to industrial chemical synthesizers could offset the cost of water treatment. While the applicability of using EFC to remove multiple salts from complex multi-component, hypersaline brines has not yet been demonstrated [5], the thermodynamics of freeze crystallization are extensively known. Verbeek shows that the overall efficiency an EFC crystallizer is 59% and that the energy requirement per unit feed is comparable to that of typical commercial evaporative crystallizers [6]. The cost



of a large-scale freeze crystallization facility is estimated to be equitable to that of evaporative crystallization [7], but to be competitive EFC would need to be comparable to the injection disposal cost of \$1.00 - \$6.50 per barrel to be of interest to Exploration and Production companies [8].

Original simulation research of eutectic freeze crystallization of produced water using OLI Stream Analyzer was performed on various brine compositions generated from water quality reports provided by Baker Hughes and indicated EFC is suited for desalination of co-produced waters. These results indicate that EFC has a high level of compatibility with the task of co-produced water desalination and can be applied under favorable economic situations. A statistical cost estimate for water treatment by EFC is performed and concludes that:

Additional research needs to be performed to complete the validation of EFC for the task of treating brines for release. Namely, it is unclear to date whether the presence of hydrocarbons and NORM material would interfere or contaminate the pure effluent streams of EFC. In Chapter 4 a research proposal to finish the validation of this method is included.

The major findings are:

- The co-formation of other salts near the eutectic point of hydrohalite can be limited through the mixing of waste water streams from multiple wells
- An average Marcellus/Utica brine exhibit first the formation of ice, followed by eutectic co-formation of hydrohalite and ice

- Marcellus produced water volumes in Pennsylvania are expected to raise to 71 MMbbl by 2022
- The nonrecoverable energy requirement for an average Marcellus Shale produced water stream is estimated to be 179kWh/m<sup>3</sup>
- The cost of EFC treatment in the Middle-Atlantic Region is estimated to be \$1.93/bbl
- When accounting for recovered costs from the potential sale of crystallized salt the treatment cost is reduced to \$0.82/bbl /bbl, similar to that of membrane distillation [9]

#### 6.4 PERSONAL REFLECTION

This Section is included at the bequest of my committee chair. By including a personal reflection section to the thesis, I am allowing myself a platform from which to now speak subjectively about my research and how it has shaped my thinking and understanding, rather than only objective evidence and insight.

In this thesis, I have identified that EFC treatment is applicable to produced water desalination and can do so within the neighborhood treatment cost of other methods. What remains is to complete the validation process of EFC from what has been previously published to ensure compatibility with actual oilfield water samples, not just simulated waters utilizing modelling software.

Some evidence exists that the radiation waste from drilling and disposing of water in the Marcellus is more pervasive than other areas [101]. As the liquid volume decreases with

continued EFC treatment, I believe the concentration of the radioactive isotopes will increase. Increasing the concentration of radioactivity could present a health risk from over exposure or add to anticipated disposal costs by requiring adherence to stricter governmental regulations. In order to better understand these perceived health risks, further testing with actual oilfield brine samples is necessary. It would be inadvisable to proceed to industrial scale investment in freeze crystallization without addressing the above concerns regarding trace hydrocarbon, fracturing chemicals and radioactive isotopes on the freeze crystallization process. To do so, I recommended that further bench scale EFC testing be performed to answer the above questions.

I believe that further examination and exploration of EFC as a viable recycling method over UIC wells for produced water management is necessary. Many industries in the U.S. are increasingly aware of their environmental footprint as well as economic footprint in their supply chain generation. Refineries are reducing carbon emissions, governments are subsidizing renewable energy research, and municipalities are encouraging citizens to reduce, reuse, and recycle to limit the strain on the environment from anthropogenic causes. Much of what is done in the petroleum industry occurs downhole. Out of sight and out of mind, nevertheless the difficulty of truly measuring subterranean contamination in a meaningful way. Unfortunately, the effects of injection wells have come into view of the public perception. Rather than add mystery to the process of hydrocarbon recovery, we as an industry should welcome public scrutiny and be open to discussion. While many of the engineering concerns might be outside of common

understanding, it is our duty as engineers to simplify our work to make it understood by everyone.

All of this to say, we should be focusing now on greener alternatives to necessary petroleum activities, such as waste water management, so that when regulatory or social bodies demand change we are ready. It is unfortunate that many companies operate under the fleece of environmental compliance but refuse to do all that is possible and conform only to the prescribed regulations. While permissible, it is this attitude that doesn't garner sympathy from society and is not conducive to disruptive breakthroughs. It is my belief that as we continue to strive for environmental equilibrium, that it is necessary to look ahead of the regulations and prepare for the good of posterity without sacrificing quality of life today. We should allow our social conscience to guide us to engineering solutions, not just fiscal conscience. While my research presented herein shows that EFC represents a costlier disposal alternative to injection or other recycling methods, that does not mean it is less viable from an implementation standpoint. No one wishes to pay more for fuel or petroleum derivatives, but if a slight increase in cost is necessary for greenproofing future work, it is worthy of the investment. It is our commitment to ourselves and our beliefs that makes us human. Let's not take the humanity out of engineering.

## References

- [1] EIA, "Annual Energy Outlook," Energy Information Administration, Washington, D.C. February 6 2018, Available: [www.eia.gov/aeo](http://www.eia.gov/aeo), Accessed on: March 27 2018.
- [2] Department of Interior. (2008). *EPA 909-F-98-001, Water Recycling and Reuse: The Environmental Benefits*. Available: <https://www3.epa.gov/region9/water/recycling/pdf/brochure.pdf>
- [3] A. E. Lewis *et al.*, "Design of a Eutectic Freeze Crystallization Process of Multicomponent Waste Water Stream," *Chemical Engineering Research and Design*, vol. 88, no. 9, pp. 1290-1296, 2010.
- [4] K. B. Gregory, R. D. Vidic, and D. A. Dzombak, "Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing," *Elements*, vol. 7, no. 1, pp. 181-186, 2011.
- [5] D. G. Randall, J. Nathoo, and A. E. Lewis, "A Case Study for Treating a Reverse Osmosis Brine Using Eutectic Freeze Crystallization- Approaching a Zero Waste Process," *Desalination*, vol. 266, no. 1-3, pp. 256-262, 2011.
- [6] B. J. Verbeek, "Eutectic Freeze Crystallization on Sodium Chloride," Master of Science, Delft University of Technology, 2015.
- [7] C. Himawan, R. J. C. Vaessen, H. J. M. Kramer, M. M. Seckler, and G. J. Witkamp, "Dynamic Modeling and Simulation of Eutectic Freeze Crystallization," *Journal of Crystal Growth*, vol. 237-239, Part 3, pp. 2257-2263, 2002.
- [8] C. Irwin. (2013, March 27). *Wastewater Recycling Part III: Costs and Challenges*. Available: <https://breakingenergy.com/2013/05/15/wastewater-recycling-part-ii-how-its-done/>
- [9] K. E. Murray, "Quantity and Quality of Produced Water in Oklahoma," D. Milligan, Ed., ed. University of Oklahoma MCEE: Produced Water Working Group Oklahoma Geological Survey, 2016.
- [10] J. Gerard, "The State of American Energy," American Petroleum Institute 2018, Available: [http://www.api.org/~media/Files/Policy/SOAE-2018/SOAE2018\\_Report.pdf](http://www.api.org/~media/Files/Policy/SOAE-2018/SOAE2018_Report.pdf).
- [11] Ranken-Energy. (2017, March 27). *A Partial List of Products Made from Petroleum*. Available: <https://www.ranken-energy.com/index.php/products-made-from-petroleum/>
- [12] Huffington-Post, "Oil Is In Everything, From Shampoo To Vitamins," in "The Huffington Post," The Huffington Post, The Huffington Post 2011, Available: [https://www.huffingtonpost.com/2010/06/11/oil-is-in-everything-from\\_n\\_608751.html](https://www.huffingtonpost.com/2010/06/11/oil-is-in-everything-from_n_608751.html), Accessed on: March 27 2018.
- [13] IEA. (2016, March 23). *Oil Market Report*. Available: <https://www.iea.org/oilmarketreport/omrpublic/>
- [14] PSAC. (2016, March 27). *Petroleum Services of Canada Industry Overview*. Available: <https://www.pfac.ca/business/industry-overview/>
- [15] D. Suzuki, "Transporting Fossil Fuels: Rail vs. Pipeline is the Wrong Question," EcoWatch2014, Available: <https://www.ecowatch.com/transporting-fossil-fuels-rail-vs-pipeline-is-the-wrong-question-1881851845.html>, Accessed on: March 27 2018.
- [16] M. S. Vassiliou, *Historical Dictionary of the Petroleum Industry*, 3 ed. Lanham, Maryland: Scarecrow Press, 2009.

- [17] J. Meisenhelder, "Shale 2.0: From Efficient to Effective Shale Development," *Journal of Petroleum Technology*, 2013.
- [18] E. Crooks. (2015). *The U.S. Shale Revolution* [Online News Article]. Available: <https://www.ft.com/content/2ded7416-e930-11e4-a71a-00144feab7de>
- [19] R. Staff. (2015). *U.S. Fracking Boom Added 725,000 Jobs* [Online News Article]. Available: <https://www.reuters.com/article/usa-fracking-employment-study/u-s-fracking-boom-added-725000-jobs-study-idUSL8N13159X20151106>
- [20] EIA. (2012). *Potential of Gas Hydrates is Great, but Practical Development is Far Off*. Available: <https://www.eia.gov/todayinenergy/detail.php?id=8690>
- [21] M. Schriber. (2009, March 27). *The Chemistry of Life: Where Oil Comes From*. Available: <https://www.livescience.com/3400-chemistry-life-oil.html>
- [22] J. A. Veil and C. E. Clark, "Produced Water Volume Estimates and Management Practices," presented at the International Conference on Health, Safety, and Environment and Production Rio de Janeiro, Brazil, 12-14 April, 2010.
- [23] S. Earle, *Physical Geology*, First Ed. ed. British Columbia: Steven Earle, 2015.
- [24] F. Mistree, J. H. Panchal, D. Schaefer, J. K. Allen, S. Haroon, and Z. Siddique, "Personalized Engineering Education for the Twenty-First Century," in *Curriculum Models for the 21st Century: Using Learning Technologies in Higher Education*, M. Gosper and D. Ifenthaler, Eds. New York, NY: Springer New York, 2014, pp. 91-111.
- [25] K. Pederson, R. Bailey, F. Mistree, and J. Emblemavag, "Validating Design Methods & Research: The Validation Square," presented at the ASME Design Engineering Technical Conferences, Baltimore, Maryland September 10-14, 2000.
- [26] D. A. Pierce, K. Bertrand, and C. Cretiu-Vasiliu, "Water Recycling Helps with Sustainability," presented at the Asia Pacific Oil & Gas Conference and Exhibition, Brisbane, Queensland, Australia, 18-20 October, 2010.
- [27] K. Rucke. (2014, March 27). *Radioactive Waste from Bakken Oil Field Raises Concerns About Local Water Contamination*. Available: <https://www.ecowatch.com/radioactive-waste-from-bakken-oil-fields-raises-concerns-about-local-w-1881874036.html>
- [28] J. D. Arthur, S. L. Dutnell, and D. B. Cornue, "Siting and Permitting of Class II Brine Disposal Wells Associated With Development of the Marcellus Shale," presented at the Eastern Regional Meeting, Charleston, West Virginia, 23-25 September, 2009.
- [29] D. V. S. Gupta and B. T. Hlidek, "Frac Fluid Recycling and Water Conservation: A Case History," presented at the SPE Production and Operations, 2009. Available: <https://www.onepetro.org/journal-paper/SPE-119478-PA>
- [30] I. Urbina, "Regulation Lax as Gas Wells' Tainted Water Hits Rivers," in *The New York Times*, ed. New York City: New York Times, 2011.
- [31] S. Whitfield, "Unconventional Resources: New Facilities Find Solutions to Limited Water Sources," *Oil and Gas Facilities*, vol. 3, no. 06, pp. 11-20, 2014.
- [32] L. M. Krieger. (2014, February 15) What the West's Ancient Droughts Say About Its Future. *National Geographic*.
- [33] A. Bjerga. (2015, March 27). *The Great Plains' Looming Water Crisis*. Available: <https://www.bloomberg.com/news/articles/2015-07-02/great-plains-water-crisis-aquifer-s-depletion-threatens-farmland>
- [34] SPE. (2017, March 27). *Challenges in Reusing Produced Water*. Available: <http://www.spe.org/industry/challenges-in-reusing-produced-water.php>
- [35] Aqwaterc. (2017, August 3). *Produced Water Treatment and Beneficial Use Information Center- About Produced Water*. Available: [http://aqwaterc.mines.edu/produced\\_water/](http://aqwaterc.mines.edu/produced_water/)

- [36] K. Fennessey, W. Staudt, and J. Dell, "Water Management: Concept to Implementation," presented at the SPE International Conference of Health, Safety, and Environment, Long Beach, California, USA, 17-19 March, 2014. Available: <http://dx.doi.org/10.2118/168474-MS>
- [37] A. Bailey. (2008, March 27). *Appalachia to the Rescue*. Available: <http://www.petroleumnews.com/pntruncate/246893563.shtml>
- [38] A. S. Behrman, *Water is Everybody's Business; the Chemistry of Water Purification*, first ed. New York City, New York: Doubleday, 1968.
- [39] B. D. Lutz, "Generation, Transport, and Disposal of Wastewater Associated with Marcellus Shale Gas Development," *Water Resources Research*, vol. 49, no. 2, pp. 647-656, 8 February 2013.
- [40] E. Raber, R. E. Thompson, and F. H. Smith, "Improving the Injectability of High Salinity Brines for Disposal or Waterflooding Operations," presented at the ATCE, Dallas, Texas, 5-7 October, 1981.
- [41] F. v. d. Ham, G. J. Witkamp, J. d. Graauw, and G. M. v. Rosmalen, "Eutectic Freeze Crystallization: Application to Process Streams and Waste Water Purification," *Chemical Engineering and Processing: Process Intensification*, vol. 37, no. 2, pp. 207-213, 1998.
- [42] J. Thompson, "Fracking has a Big Water Footprint, but That's Not the Whole Story," in *High Country News*, ed: High Country News, 2015.
- [43] X. Lu, "Novel Applications of Eutectic Freeze Crystallization," Master of Science, Delft University of Technology, 2014.
- [44] M. J. Fernández-Torres, D. G. Randall, R. Melamu, and H. v. Blottnitz, "A Comparative Life Cycle Assessment of Eutectic Freeze Crystallisation and Evaporative Crystallisation for the Treatment of Saline Wastewater," *Desalination*, vol. 306, no. 1, pp. 17-23, 2012.
- [45] J. A. Veil, "Thermal Distillation Technology for Management of Produced Water and Frac Flowback Water," Argonne National Laboratory Water Technology Brief #2008-1, May 13 2008.
- [46] J. Minier-Matar, A. Hussain, A. Janson, and S. Adham, "Treatment of Produced Water from Unconventional Resources by Membrane Distillation," presented at the International Petroleum Technology Conference, Doha, Qatar, January 20-22, 2014.
- [47] D. Murtaugh. (2014, March 27). *Crumbling Roads in Oil Fields Slowing U.S. Energy Boom*. Available: <https://www.bloomberg.com/news/articles/2014-07-10/crumbling-roads-in-oil-fields-slowing-u-s-energy-boom>
- [48] A. Hussain, J. Minier-Matar, S. Gharfeh, A. Janson, and S. Adham, "Advanced Technologies for Produced Water Treatment," presented at the Offshore Technology Conference, Kuala Lumpur, Malaysia, 25-28 March, 2014.
- [49] S. Muraleedaraan, X. Li, L. Li, and R. Lee, "Is Reverse Osmosis Effective for Produced Water Purification? Viability and Economic Analysis," presented at the SPE Western Regional Meeting, San Jose, California, 24-26 March, 2009. Available: <http://dx.doi.org/10.2118/115952-MS>
- [50] G. F. Doran, F. H. Carini, D. A. Fruth, J. A. Drago, and L. Y. C. Leong, "Evaluation of Technologies to Treat Oil Field Produced Water to Drinking Water or Reuse Quality," presented at the SPE ATCE, San Antonio, Texas, 1997.
- [51] Siemens. (2016, March 27). *API Separators - The Workhorse of Refinery Wastewater*. Available: [https://w3.siemens.com/.../en/.../api-oil-water.../API\\_Separators\\_article\\_Solutions.doc](https://w3.siemens.com/.../en/.../api-oil-water.../API_Separators_article_Solutions.doc)

- [52] M. Tir and N. Moulai-Mostefa, "Optimization of Oil Removal from Oily Wastewater by Electrocoagulation Using Response Surface Method," *Journal of Hazardous Materials*, vol. 158, no. 1, pp. 107-115, 2008/10/01/ 2008.
- [53] V. Rao, "Earthquakes: Should We Be Worried?," *Journal of Petroleum Technology*, vol. 66, no. 09, 2014.
- [54] D. Kujawski. (2009, March 27). *New Trends in Oil Refinery Wastewater Reclamation*. Available: <http://www.waterworld.com/articles/2009/04/new-trends-in-oil-refinery-wastewater-reclamation.html>
- [55] A. Haddaway. (2017, March 27). *Desalination Trends in the Oil and Gas Industry*. Available: <http://www.waterworld.com/articles/iww/print/volume-15/issue-2/features/desalination-trends-in-the-oil-and-gas-industry.html>
- [56] H. Krishna, "Introduction to Desalination Technologies," Texas Water Development Board, Austin, Texas 2004.
- [57] *Recommendation 2001/1 Reporting Obligation for Produced Water*, 2001.
- [58] M. M. Chaves, J. Flexas, and C. Pinheiro, "Photosynthesis Under Drought and Salt Stress: Regulation Mechanisms from Whole Plant to Cell," *Annals of Botany*, vol. 103, no. 4, pp. 551-560, 2009.
- [59] WaterTectonics. (2017, March 4). *What is ElectroCoagulation*. Available: <http://www.watertectonics.com/electrocoagulation/>
- [60] P. V. S. Sistla, G. Venkatesan, P. Jalihal, and S. Kathioli, "Low Temperature Thermal Desalination Plants," presented at the Eighth ISOPE Ocean Mining Symposium, Chennai, India, 20-24 September, 2009.
- [61] T. Dunnahoe. (2013). *Understanding the Science Behind Induced Seismicity*. Available: <https://www.ogj.com/articles/uogr/print/volume-1/issue-3/understanding-the-science-behind-induced-seismicity.html>
- [62] N. Jacobs. (2017) What You Need to Know About Fracking and Sismicity in Pennsylvania *Energy in Depth*. Available: <https://www.energyindepth.org/what-you-need-to-know-about-fracking-earthquakes-pennsylvania/>
- [63] D. Mueller. (2015). *Recycling Wastewater from Oil and Gas Wells Poses Challenges*. Available: <http://blogs.edf.org/energyexchange/2015/11/11/recycling-wastewater-from-oil-and-gas-wells-poses-challenges-2/>
- [64] L. Boerner. (2013, March 27). *Sewage Plants Struggle to Treat Wastewater Produced by Fracking Operations*. Available: <https://cen.acs.org/articles/91/web/2013/03/Sewage-Plants-Struggle-Treat-Wastewater.html>
- [65] K. Schaefer. (2012, March 27). *Fracking and Water: A New Way to Profit from the Industry's Biggest Problem*. Available: <https://oilprice.com/Energy/Energy-General/Fracking-and-Water-A-New-Way-To-Profit-from-the-Industrys-Biggest-Problem.html>
- [66] OLI-Systems-Inc., *OLI Stream Analyzer, Version 9.5.0*. Morris Plains, New Jersey, USA, 2016.
- [67] A. V. Plyasunov and E. L. Shock, "Correlation Strategy for Determining the Parameters of the Revised Helgeson-Kirkham-Flowers Model for Aqueous Nonelectrolytes," *Geochimica et Cosmochimica Acta*, vol. 65, no. 21, pp. 3879-3900, 11/1/ 2001.
- [68] (2012, March 27). *Solving the Scale Problem*. Available: <http://mie.esab.upc.es/ms/formacio/An%20E0lisi%20Qu%20EDmica/Pr%20E0ctiques/precipitacions%20en%20aigua.pdf>



- [69] D. G. Randall and J. Nathoo, "A Succinct Review of the Treatment of Reverse Osmosis Brines Using Freeze Crystallization," *Journal of Water Process Engineering*, vol. 8, pp. 186-194, 2015.
- [70] Anonymous, "Final Environmental Impact Statement: Keterson Program," U.S. Bureau of Reclamation, Sacramento, CA1986, vol. 1.
- [71] R. Vaessen, M. Seckler, and G. J. Witkamp, "Eutectic Freeze Crystallization with an Aqueous KNO<sub>3</sub>-HNO<sub>3</sub> Solution in a 100-L Cooled-Disk Column Crystallizer," *Industrial & Engineering Chemistry Research*, vol. 42, no. 20, pp. 4874-4880, 2003/10/01 2003.
- [72] P. M. Williams, M. Ahmad, and B. S. Connolly, "Freeze Desalination: An Assessment of an Ice Maker Machine for Desalting Brines," *Desalination*, vol. 308, pp. 219-224, 1/2/ 2013.
- [73] AOGHS, "The Petroleum Age," vol. 1, ed. Washington, D.C. : American Oil and Gas Historical Society, 2017.
- [74] M. S. Rahman and M. Al-Khusaibi, "Freezing-Melting Desalination Process," in *Desalination: John Wiley & Sons, Inc.*, 2014, pp. 473-501.
- [75] W. E. Johnson, "State-of-the-Art of Freezing Processes, Their Potential and Future," *Desalination*, vol. 19, pp. 349-358, 1976.
- [76] G. L. Stepakoff, D. Siegelman, R. Johnson, and W. Gibson, "Development of a Eutectic Freezing Process for Brine Disposal," *Desalination*, vol. 15, no. 1, pp. 25-38, 8// 1974.
- [77] C. Murray-Gulde, J. E. Heatley, T. Karanfil, J. H. Rodgers, and J. E. Myers, "Performance of a Hybrid Reverse Osmosis-Constructed Wetland Treatment System for Brackish Oil Field Produced Water," *Water Research*, vol. 37, no. 3, pp. 705-713, 2003.
- [78] P. Boschee, "Handling Produced Water from Hydraulic Fracturing," *Oil and Gas Facilities*, vol. 1, no. 1, 2014.
- [79] J. Easton. (2012, March 27). *Fracking Wastewater Management*. Available: <http://www.waterworld.com/articles/wwi/print/volume-28/issue-5/regional-spotlight-us-caribbean/fracking-wastewater-management.html>
- [80] A. E. Williams-Jones and I. M. Samson, "Theoretical Estimation of Halite Solubility in the System NaCl-CaCl<sub>2</sub>; Applications to Fluid Inclusions," *The Canadian Mineralogist*, vol. 28, no. 2, pp. 299-304, 1990.
- [81] Adam T. Bourgoynne, Martin E. Chanevert, Keith K. Millhelm, and F. S. Young, *Applied Drilling Engineering*, Second ed. Society of Petroleum Engineers, 1991.
- [82] K. S. Sorbie and N. Laing, "How Scale Inhibitors Work: Mechanisms of Selected Barium Sulphate Scale inhibitors Across a Wide Temperature Range," presented at the SPE International Symposium on Oilfield Scale, Aberdeen, United Kingdom, 2004/1/1/, 2004.
- [83] S. T. Reddy, A. E. Lewis, G. J. Witkamp, H. J. M. Kramer, and J. van Spronsen, "Recovery of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O from a Reverse Osmosis Retentate by Eutectic Freeze Crystallisation Technology," *Chemical Engineering Research and Design*, vol. 88, no. 9, pp. 1153-1157, 9// 2010.
- [84] S. Adham, A. Hussain, J. Minier-Matar, R. Dores, and A. Janson, "Application of Membrane Distillation for Desalting Brines from Thermal Desalination Plants," *Desalination*, vol. 314, pp. 101-108, 4/2/ 2013.
- [85] S. Adham, "Desalination Needs and Opportunities in the Oil and Gas Industry," presented at the International Conference on Emerging Water Desalination Technologies in Municipal and Industrial Applications, San Diego, California,

- [86] M. L. V. Ramires, C. A. Nieto de Castro, J. M. N. A. Fareleira, and W. A. Wakeham, "Thermal Conductivity of Aqueous Sodium Chloride Solutions," *Journal of Chemical & Engineering Data*, vol. 39, no. 1, pp. 186-190, 1994/01/01 1994.
- [87] J. W. Meewisse and C. A. Infante Ferreira, 1, Ed. *Freezing Point Depression of Various Ice Slurries*. Delft University of Technology: Delft University of Technology, 2001.
- [88] A. Esmon. (2014, March 27). *The Physics of Ice: It All Begins with Nucleation*. Available: <https://www.thermofisher.com/blog/biobanking/the-physics-of-ice-it-all-begins-with-nucleation/>
- [89] G. M. Graham, L. Boak, and K. S. Sorbie, *The Influence of Formation Calcium and Magnesium on the Effectiveness of Generically Different Barium Sulphate Oilfield Scale Inhibitors*. 2003, pp. 28-44.
- [90] M. Adewumi, "The Hydrate Problem," Lecture, 2015.
- [91] Q. Zhang, Q. Wu, and H. Zhang, "Effect of Propane and NaCl-SDS Solution on Nucleation Process of Mine Gas Hydrate," *Journal of Chemistry*, vol. 2017, p. 12, 2017, Art. no. 1059109.
- [92] G. González, M. A. Sousa, and E. F. Lucas, "Asphaltenes Precipitation from Crude Oil and Hydrocarbon Media," *Energy & Fuels*, vol. 20, no. 6, pp. 2544-2551, 2006/11/01 2006.
- [93] J. Fink, *Petroleum Engineer's Guide to Oil Field Chemicals and Fluids*, 2nd ed. Waltham, MA: Gulf Professional Publishing, 2015.
- [94] J. J. Wylde and J. L. Slayer, "Halite Scale Formation Mechanisms, Removal and Control: A Global Overview of Mechanical, Process, and Chemical Strategies," presented at the SPE International Symposium on Oilfield Chemistry, the Woodlands, Texas, USA, 2013. Available: <https://www.onepetro.org/conference-paper/SPE-164081-MS>
- [95] N. E. R. Zimmermann, B. Vorselaars, D. Quigley, and B. Peters, "Nucleation of NaCl from Aqueous Solution: Critical Sizes, Ion-Attachment Kinetics, and Rates," *Journal of the American Chemical Society*, vol. 137, no. 41, pp. 13352-13361, 2015/10/21 2015.
- [96] M. J. Qazi, R. W. Lieferrink, S. J. Schlegel, E. H. G. Backus, D. Bonn, and N. Shahidzadeh, "Influence of Surfactants on Sodium Chloride Crystallization in Confinement," *Langmuir*, vol. 33, no. 17, pp. 4260-4268, 2017.
- [97] J. Ireland, "Corrosion Monitoring Of Produced Waters," presented at the Technical Meeting / Petroleum Conference of The South Saskatchewan Section, Regina, September 15 - 17, 1985.
- [98] L. Torres, O. P. Yadav, and E. Khan, "Perceived Risks of Produced Water Management and Naturally Occurring Radioactive Material Content in North Dakota," *Journal of Environmental Management*, vol. 196, pp. 56-62, 2017/07/01/ 2017.
- [99] A. E. Pillay, F. M. Salih, and M. I. Maleek, "Radioactivity in Oily Sludge and Produced Waste Water from Oil: Environmental Concerns and Potential Remedial Measures," *Sustainability*, vol. 2, no. 4, p. 890, 2010.
- [100] "Naturally Occurring Radioactive Materials (NORM) in Produced Water and Oil-Field Equipment-An Issue for the Energy Industry," in "Fact Sheet," Report 142-99, 1999, Available: <http://pubs.er.usgs.gov/publication/fs14299>.
- [101] D. Nichols. (2015, January 22). *Radioactive Marcellus Shale Results in Radioactive Produced Water*. Available: <http://www.frackcheckwv.net/2015/12/27/radioactive-marcellus-shale-results-in-radioactive-produced-water/>
- [102] M. Resnikoff, "Radioactivity in Marcellus Shale: Challenge for Regulators and Water Treatment Plants."

- [103] *The Impact of Low-Level Radioactive Waste Management Policy on Biomedical Research in the United States*. Washington, D.C. : National Academy Press, 2001.
- [104] L. K. McKay, "Pennsylvania and Ohio Regulatory Efforts Regarding NORM/TENORM in Oil and Gas Production Wastes," in *Lexology*, First ed, 2014.
- [105] "Radioactive-Waste Disposal: NORM Disposal," 2017, Available: <https://www.tceq.texas.gov/permitting/radmat/uranium/norm.html>.
- [106] IER, "Marcellus Shale Fact Sheet," Institute for Energy Research, Washington, D.C. 2012.
- [107] (2009). *How Much Natural Gas Can the Marcellus Shale Produce?* Available: <http://www.marcellus.psu.edu/news-events/docs-pdfs/day-gas-reserves-2009.pdf>
- [108] PDEP. ( 2016). *2016 Oil and Gas Annual Report*. Available: <http://www.depgis.state.pa.us/oilgasannualreport/index.html>
- [109] J. A. Veil, "U.S. Produced Water Volumes and Management Practices in 2012," Groundwater Protection Council 2015.
- [110] A. Berman. (2016, February 9). *Natural Gas Price Increase Inevitable in 2016*. Available: <https://www.forbes.com/sites/arthurberman/2016/02/21/natural-gas-price-increase-inevitable-in-2016/#75065f5d3473>
- [111] D. Lemery. (2018, February 8). *Pennsylvania Governor Proposes Controversial Natural Gas Severance Tax in Budget Address*. Available: [https://www.watchdog.org/pennsylvania/pennsylvania-governor-proposes-controversial-natural-gas-severance-tax-in-budget/article\\_569cdf84-0b81-11e8-ba83-578f671bc39c.html](https://www.watchdog.org/pennsylvania/pennsylvania-governor-proposes-controversial-natural-gas-severance-tax-in-budget/article_569cdf84-0b81-11e8-ba83-578f671bc39c.html)
- [112] ExxonMobil, "Global Energy Mix Shifts to Lower-Carbon Fuels," ed: ExxonMobil World Energy Outlook, 2016.
- [113] E. Corcoran and GRID--Arendal, *Sick Water?: The Central Role of Wastewater Management in Sustainable Development : A Rapid Response Assessment*. UNEP/GRID-Arendal, 2010.
- [114] C. Polsky, J. Allard, N. Currit, R. Crane, and B. Yarnal, "The Mid-Atlantic Region and its Climate: Past, Present, and Future," *Climate Research*, vol. 14, no. 3, pp. 161-173, 2000.
- [115] A. Krautmann, "Overview of Climate Change and Variability in the South Central Region," ed: Southern Climate Impacts Planning Program, 2010.
- [116] Maldon. (2018, February 23). *The Many Uses of Salt*. Available: <http://www.maldonsalt.co.uk/About-Salt-The-many-uses-of-Salt.html>
- [117] Cargill. (2018, February 23). *Industrial Salt Uses*. Available: <https://www.cargill.com/industrial/industrial-salts>
- [118] S. L. Earl and J. J. Nahm, "Use Of Chemical Salt Precipitation Inhibitors To Maintain Supersaturated Salt Muds For Drilling Salt Formations," presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 1981/1/1/, 1981.
- [119] Freedonia. (2016, February 13). *World Salt - Demand and Sales Forecasts, Market Share, Market Size, Market Leaders*. Available: <https://www.freedoniagroup.com/World-Salt.html>
- [120] (2010). *Salt Sellers*. Available: <https://www.economist.com/node/15276675>
- [121] R. Hankey, "Electric Power Monthly," Energy Information Administration, Washington, D.C. 2017.
- [122] SAMCO. (2017, February 5). *How Much Does an Industrial Water Treatment System Cost?* Available: <https://www.samcotech.com/how-much-does-an-industrial-water-treatment-system-cost/>

[123] D. Keep. (2014, March 27). *Selected Chemicals and Their Properties*. Available: <http://www.tsnn.com/events/great-lakes-trade-exposition-glte-2018>

## Appendix A - Water Quality Report Data

This appendix includes the relevant water quality report information for the brines that are used in the simulation section for hypersaline multi-component brines in Chapter 3, Section 3.4 with ion concentration reported in ppm. These specific water quality reports are included as they were used in the analysis presented in Section 3.5. The data was provided courtesy of Baker Hughes Inc. and was solicited only for academic purposes.

**Table 7.1** has the water quality reports for the East Coast shale plays analyzed in this thesis. Similarly, **Table 7.2** includes the Permian Basin brine that was used in EFC simulation. The inclusion of wells from multiple plays was to validate EFC to test the sensitivity to changing concentrations of contaminants and ions. The average water quality for the Utica and Marcellus shale are included as they represent the best estimate for the water stream that would be sent for central treatment in the region. The average columns are a simple average of all the water quality reports provided by Baker Hughes. In an effort to better protect the privacy of BHI and their customers, the water quality report for every well has not been included. There was not an adequately large sample size of water quality reports from the Permian to merit the inclusion and simulation of EFC for that play. The unit of TDS is mg/L unless otherwise specified in Tables 7.1 and 7.2

Table 7.1 - Marcellus and Utica WQR

<b>Formation(s)</b>	<b>Marcellus 7</b>	<b>Marcellus 75</b>	<b>Marcellus Ave.</b>	<b>Utica Ave.</b>
<b>State</b>	PA	PA	PA	OH
<b>API #</b>	37-031-25508	37-019-22194	-	-
<b>Sample Point</b>	Separator	Separator	Separator	Separator
<b>pH</b>	6.6	5.9	6.05	6.11
<b>S.G.</b>	1.155	1.2	1.085	1.1608
<b>Temp. (F)</b>	70.5	67.8	75.2	76.8
<b>CO2 (ppm)</b>	202.4	410	286	380
<b>H2S (mg/L)</b>	0	0	0	0
<b>Bicarbs (mg/L)</b>	95.3	61	152.5	118.2
<b>TDS (mg/L)</b>	221451	310161	144552	257774
<b>Calcium (Ca++)</b>	28147.9	32871.9	13882.9	51120
<b>Magnesium (Mg++)</b>	2097.59	2074.1	1278.12	115.531
<b>Sodium (Na+)</b>	47869.3	67794.8	34141.6	17.254
<b>Iron (Fe++)</b>	104.046	127.1	133.961	3051.18
<b>Manganese (Mn++)</b>	17.169	12.6	4.71	109.018
<b>Strontium (Sr++)</b>	3861	5948	2467.95	118.2
<b>Barium (Ba++)</b>	931.524	8292.8	93.194	0
<b>Bicarb (HCO3-)</b>	95.3	61	152.5	168471
<b>Sulfate (SO4=)</b>	0	0	0	1.89
<b>Chloride (Cl-)</b>	137753	192526	91881	0
<b>Biocide</b>	-	-	-	-
<b>Scale Inhibitor</b>	-	-	-	-

Table 7.2 - Permian WQR

<b>Formation(s)</b>	<b>Permian</b>
<b>State</b>	TX
<b>API #</b>	-
<b>Al</b>	3.51
<b>B</b>	62
<b>Ba</b>	2.53
<b>Ca</b>	420
<b>Cu</b>	0
<b>Fe</b>	0.969
<b>K</b>	159
<b>Mg</b>	67.4
<b>Mn</b>	0.715
<b>Mo</b>	0
<b>Na</b>	12200
<b>P</b>	5.29
<b>SO4</b>	284
<b>Si</b>	20.4
<b>Sr</b>	143
<b>Zn</b>	0
<b>Gravity</b>	1.0219
<b>Cl</b>	21200
<b>pH</b>	7.71
<b>HCO3</b>	1315
<b>OH</b>	0
<b>CO3</b>	0
<b>Calc TDS</b>	35884
<b>TSS</b>	198
<b>Oil &amp; Grease</b>	98
<b>H2S</b>	NM
<b>Turbidity</b>	NM

## Appendix B - Definition of Terms

To facilitate understanding by many audiences, the below list of terms and associated definitions has been included. This list is not comprehensive of all terminology of the thesis nor are the presented definitions adopted by any industrial standards institution. These select definitions are included in this appendix as they include the most inclusive and obscure that might not be readily found online or could have ambiguous meaning in other publications.

- 1)** Brine – A water saturated with salt, can include many salt ions and other contaminants such as suspended solids, entrained gases, and residual hydrocarbons.
- 2)** Hypersaline – A brine containing saline levels exceeding that of the ocean (3.5 wt% sodium chloride, i.e. 35 g/L or 35,000 ppm), used in this paper for oilfield brines that are exceedingly saline with sodium chloride content of 100,000 ppm (10 wt%).
- 3)** Species – A salt that is formed using only one cation and anion, this definition does not include double salts or complexes. A binary salt species would be a saturated brine that contains ions to form two unique salt species that are composed of only one cation and anion.
- 4)** Hydrohalite - a mineral that occurs in saturated halite brines at cold temperatures ( $-5\text{ }^{\circ}\text{C}$ ),  $\text{NaCl}\cdot 2\text{H}_2\text{O}$ .
- 5)** Eutectic Point - The point in a phase diagram indicating the chemical composition and temperature corresponding to the lowest melting point of a mixture of components. In Eutectic Freeze Crystallization, this is the point and which crystalline water and salt are coproduced.
- 6)** Eutectic Concentration – The concentration of a salt, in wt%, of a brine at the point that the mixture reaches its eutectic point.
- 7)** Eutectic Temperature – The temperature of a brine at the eutectic point necessary to cause supersaturation and concurrent crystallization of ice and salt.



**8) Potable Water** – Pure water. Colorless, odorless, and tasteless. Set by the U.S. EPA to have a maximum TDS of 500 mg/L. Local jurisdictions cover legal maximums of specific TDS contributors.

**9) Proppant** – A proppant is a solid material, typically sand, treated sand or man-made ceramic materials, designed to keep an induced hydraulic fracture open, during or following a fracturing treatment.

**10) Oleic** – Of or relating to the liquid portion of a hydrocarbon stream consisting of alkanes, alkenes and aromatics.

## Appendix C - Acronyms, Abbreviations, and Units

**API** – American Petroleum Institute

**BBL** – Unit of volume equal to 42 US Gallons

**CDCC** – Cooled Disc Column Crystallizer

**DEP** – Pennsylvania Department of Environmental Protection

**EFC** – Eutectic Freeze Crystallization

**EP** – Eutectic Point

**Gallon** – Unit of volume equal to 3785.4 milliliters

**GPD** – Gallons per Day

**MCF** – Thousand Standard Cubic Feet

**MD** – Membrane Desalination or Distillation

**MMSCF** – Million Standard Cubic Feet

**NORM** – Naturally Occurring Radioactive Material

**O&G** – Oil and Grease

**RO** – Reverse Osmosis

**SCF** – Standard Cubic Foot. Volume occupied by gas at STP (60°F and 1 atmosphere)

**SCWC** – Scraped Cooled Wall Crystallizer

**SI** – Scale Inhibitor

**SPE** – Society of Petroleum Engineers

**STP** – Standard Temperature and Pressure

**TCF** – Trillion Standard Cubic Feet

**TDS** – Total Dissolved Solids

**USGS** – United States Geological Survey

## Appendix D - Brine Crystallization using OLI Stream Analyzer

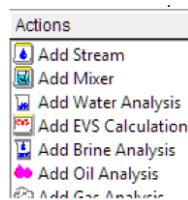
This is a prepared example showing how to use OLI Studio to model salt crystallization based on temperature and ion concentration. The case file contains one of the water surveys entered into the brine analysis object and then transferred to a stream where a temperature survey produces and simulates the ice. This information is provided for illustrative purposes only and is not indicative of work performed by the author.

Additional information and files can be found at

<http://downloads.aqsim.com/BrineCrystallizationExample.oad>

Here are the key instructions:

1. Use the Brine Analysis to enter the data



2. Change the Thermodynamic framework to MSE. The default is AQ

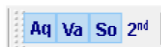


3. If a species is missing, type it in with the correct charge

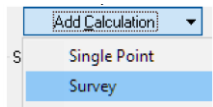


4. The elements B, P, and Si (for example) are MOSTLY present as  $B(OH)_3$ ,  $HPO_4^{-2}$  and  $SiO_2$  at the case file 77 pH. A user will need to convert the mass to these oxyanions.

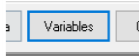
5. Add the pH and alkalinity in the Reconciliation tab grid and use pH-Alkalinity reconciliation (see key images)
6. Create the Process stream by right-mouse-clicking on the Brine Object in the navigation panel and then Add as Stream (see key images)
7. Turn on the So button (Solids) ON. They are off by defaults when creating a stream from a brine analysis.



8. Add a Survey Calculation using the Add Calculation button in the upper right



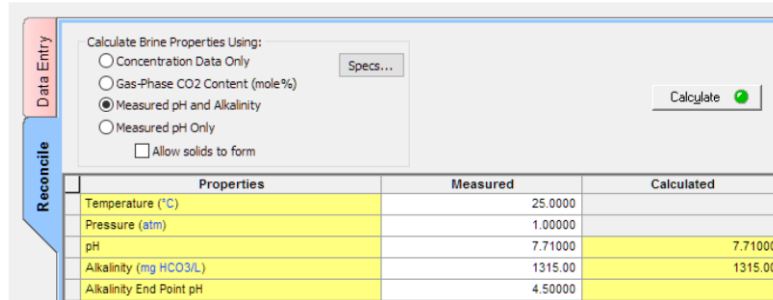
9. Modify the temperature survey using the Spec. button. Use 25°C (or ambient) to the lowest temperature needed (depends on EP, generally I use -30°C) by small increments

10. Plot the solids forming using the Variable  button to open the variables list. You should change the solids units for mg/l to mass since the liquid volume amount varies.

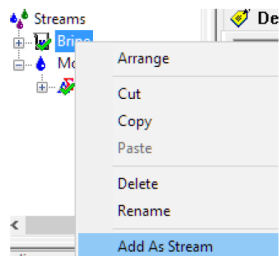


Key Images:

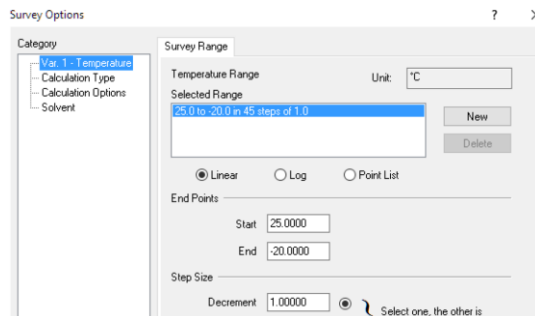
1. Reconcile tab for pH/Alkalinity calculation



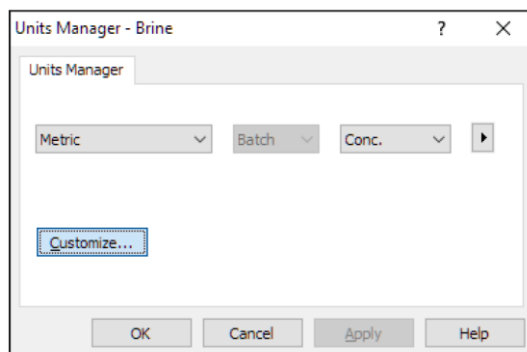
2. How to Add a Stream from the Brine Analysis – user right-mouse-clicks



3. Changing the Temperature survey range to crystallize ice



4. Modify Solids units by clicking the Customize button and then changing from concentration to mass



Edit Units - Survey ? X

Batch System  Flowing System

Composition Parameters Corrosion

Variable	Basis	Units
<b>Inflow variables</b>		
Stream Amount	Volume	L
Inflows	Concentration	mg/L
<b>Output variables</b>		
Aqueous Composition	Concentration	mg/L
Vapor Composition	Mass Fraction	mass %
Solid Composition	Mass	g
2nd Liquid Composition	Mass Fraction	mass %

## 5. Plotting the Solids variables

Select Data To Plot ? X

Curves

- Stream Parameters
- Calculation Results
- Inflows
- Additional Stream Parameters
- Phase Flow Properties
- Thermodynamic Properties
- Scaling Tendencies
- Pre-scaling Tendencies
- Liquid-1
- Vapor
- Solid
  - Dominant Solid
- Molecular Apparent - Liquid-2
- Molecular Totals

X Axis

Temperature

Y1 Axis

- SrSO4 (Celestine (celestite)) - Sol
- SrCO3 (Strontianite) - Sol
- SiO2 (Echatchelienite) - Sol
- NaAlCO3(OH)2 (Dawsonite) - Sol
- CaCO3 (Calcite) - Sol

Y2 Axis

H2O - Sol