

DISSERTATION

OPTIMIZING WATER MANAGEMENT IN HYDRAULIC FRACTURING

Submitted by

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ABSTRACT

OPTIMIZING WATER MANAGEMENT IN HYDRAULIC FRACTURING

Horizontal drilling and multi stage fracking have led to a boom in oil and natural gas production in the United States by allowing extraction of abundant unconventional oil and gas resources from tight gas, shale gas, and shale oil plays. Oil and gas development in Colorado has been around for decades, but due to recent advances in drilling technologies including hydraulic fracturing and horizontal drilling, development has increased significantly over the last few years. Most of the increased activity is occurring in the northeast part of the state particularly in Weld County where agriculture has been integral to the community for over a century. Oil and gas development using hydraulic fracturing requires large volumes of water and generates significant quantities of wastewater. Currently, more than 90% of oilfield wastewater in the USA is disposed of by deep well injection, essentially removing the water from the hydrologic cycle. Due to the complex nature of the shale oil and gas extraction process and the water requirements of hydraulic fracturing, the risk of environmental impacts is higher than with conventional energy development. The water management system or efficient use of water in oil and gas operations has been a key indicator of an operating company's success in the industry. Development of water management techniques well enough to tackle the problems with hydraulic fracturing, without hindering production and overall cost is a constant challenge.

This dissertation focuses on a portfolio of water management practices in Colorado, USA, consisting of different water strategies that could result in the value of oil and gas operations in

the face of consumption and environmental challenges while concurrently assuring communities and environmental activists that freshwater resources are secure. This water management portfolio for hydraulic fracturing is comprised of: (1) treatment of produced and flowback water, (2) optimization of treatment based on the solubility of target salts, reuse and recycling of produced and flowback water, and (3) developing a frac fluid which is more tolerable to brackish water containing organic matter content and dissolved salts. Treatment, recycling, and reuse of produced and flowback water is a smart water management strategy which substantially reduces the societal and environmental externalities of produced water disposal as well as reducing disposal costs and the transport logistics associated with obtaining freshwater and produced water disposal.

Conventional wastewater treatment processes include removal of suspended solids, oil, and some dissolved ions such as iron. Chemical coagulation, physical solid-liquid separation, and filtration are among the current treatment methods applied in the oil and gas industry. Conventional treatment, in particular chemical coagulation, has been neither successful nor cost effective in treating flowback and produced water because of spatial and temporal variability in water quality and high organic matter content. The cost of primary treatment, including removal of suspended solids and oil emulsion is mainly derived by chemical consumption including coagulants, acid and bases. Physicochemical treatment process such as electrocoagulation and softening treatments are one of the common wastewater treatment processes used in USA. In Chapter 4.1 the influence of pH sequencing on electrocoagulation (EC) treatment of flowback and produced water to remove divalent cations, boron, total organic matter (TOC), total dissolved solids (TDS), and turbidity was evaluated. While the results show in most cases softening (raising pH) in front of EC was more effective, no difference in turbidity removal was observed between the two treatment sequences. Although both treatment sequences were more effective in treating produced water samples than

flowback samples, the sequence of raising pH before EC was superior in removing the targeted constituents. Optimization of these treatment methods was studied in the following section (4.2) of Chapter 4. Softening before EC was also a better economic option due to the lower pH that reduces chemical consumption during this sequence of treatment. Modeling software (OLI systems) was used to simulate aqueous-based chemical systems and to determine the solubility constants for a variety of salts dissociated in water.

After examination of treatability of produced water and flowback water, the research was directed to assessing the feasibility of reuse of produced and flowback water in hydraulic fracturing. With the increased risks involved with deep well injection, this is an attractive alternative due to inherent reduction of transport of both freshwater and produced water therefore improving production economics and reducing environmental impacts. However, the high content of TOC and TDS associated with flowback and produced water and their impacts on frac fluid stability are largely unknown. A series of laboratory experiments were conducted on high pH zirconium crosslinked guar based polymer and low pH zirconium crosslinked carboxyl methyl cellulose (CMC) based polymer to determine the effects of salt species on the prepared polymer and the range of acceptable salts contents (Chapter 4.3). For this purpose, 80 frac fluid samples were analyzed and the maximum and minimum values of all the contents were determined to investigate the impact factor of each component. Among all the studied cations and ions, calcium, magnesium, sodium, potassium, iron, and phosphorous showed the strongest effect on the frac fluid stability. This effect becomes more pronounced as the ionic strength of the solution increases. Trivalent cations exhibit this behavior, possibly due to their increased ionic strength. They more easily compete with the typically quadrivalent crosslinker, resulting in less available crosslinking sites. A first of the kind water quality standard was developed based on the type of polymer in the frac fluid as a result of

this study. Section 4 in Chapter 4 investigates the organic matter influence on the CMC and guar based frac fluids. The organic matter content of flowback water was linked to polymers and surfactants formulated in frac fluid. According to the results of this study, TOC has a negative impact on the stability of both frac fluids. The TOC impact suggests that the residual organic matter crosslinks with the available crosslinker ions and form unstable and weaker polymer chains that generate less viscous and unstable fracking fluids. The chemical composition of the CMC based fluid was optimized at two levels of high and low TDS values and are presented in the last two sections of Chapter 4. A set of unique apparent viscosity contour maps was generated at different gel loadings between 25 and 55 pounds per thousand gallons of water. pH and crosslinker doses varied from 5 to 6 and 1 to 3 gallons per thousand gallon of water, respectively. These 3-dimensional maps will not only help oil and gas operators to minimize the quantity of downhole chemical injection and hence the cost of fracking, but also will reduce the difficulties regarding the flowback water treatment and diminish the environmental impacts associated with the injection of high loads of chemicals.

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DEDICATIONS

This dissertation is lovingly dedicated to my parents. Their support, encouragement, and constant love have sustained me throughout my life.

TABLE OF CONTENTS

ABSTRACT	II
ACKNOWLEDGMENTS.....	VI
DEDICATIONS	VIII
LIST OF TABLES.....	XI
CHAPTER 1 : INTRODUCTION	1
CHAPTER 2 : LITERATURE REVIEW	4
2.1 UNCONVENTIONAL OIL AND GAS	4
2.2 HYDRAULIC FRACTURING.....	7
2.2.1 Gelled frac fluid systems.....	11
2.2.2 Hydraulic fracturing wastewater.....	16
2.2.3 Water use	18
2.3 WATER DISPOSAL	20
2.3.1 Induced seismic activity.....	21
2.3.2 Trucking produced water.....	23
2.4 RECYCLING AND REUSE METHODS.....	23
2.4.1 Reuse in hydraulic fracturing	26
CHAPTER 3 : RESEARCH HYPOTHESES AND OBJECTIVES.....	35
3.1 RESEARCH HYPOTHESES	35
3.2 RESEARCH PLANS AND OBJECTIVES	37
CHAPTER 4 : RESULTS (JOURNAL ARTICLES).....	41
4.1 INFLUENCE OF SOFTENING SEQUENCING ON ELECTROCOAGULATION TREATMENT OF PRODUCED WATER.....	41
4.1.1 Introduction	41
4.1.2 Materials and Methods.....	43
4.1.3 Results and Discussion	48
4.1.4 Conclusions	61
4.2 OPTIMIZING METAL-REMOVAL PROCESSES FOR PRODUCED WATER WITH ELECTROCOAGULATION	62
4.2.1 Introduction	62
4.2.2 Methods	64
4.2.3 Results/discussion.....	67
4.2.4 Conclusion.....	79
4.3 INFLUENCE OF INORGANIC IONS IN RECYCLED PRODUCED WATER ON GEL-BASED HYDRAULIC FRACTURING FLUID VISCOSITY.....	81
4.3.1 Introduction	81

4.3.2 <i>Materials and Methods</i>	83
4.3.3 <i>Results and Discussion</i>	88
4.3.4 <i>Conclusion</i>	103
4.4 RECYCLING FRAC FLOWBACK WATER FOR USE IN HYDRAULIC FRACTURING: INFLUENCE OF ORGANIC MATTER ON STABILITY OF CMC BASED FRAC FLUIDS	105
4.4.1 <i>Introduction</i>	105
4.4.2 <i>Materials/Methods</i>	108
4.4.3 <i>Results and Discussion</i>	114
4.4.4 <i>Conclusion</i>	129
4.5 OPTIMIZATION OF CARBOXYL METHYL CELLULOSE FRAC FLUID PART I: INFLUENCE OF pH AND CROSSLINKER CONCENTRATIONS IN HIGH SALINITY WATER SOURCES	129
4.5.1 <i>Introduction</i>	130
4.5.2 <i>Material/Method</i>	133
4.5.3 <i>Results and Discussion</i>	137
4.5.4 <i>Conclusion</i>	146
4.6 OPTIMIZATION OF CARBOXYL METHYL CELLULOSE FRAC FLUID PART II: INFLUENCE OF pH AND CROSSLINKER CONCENTRATIONS IN LOW SALINITY WATER SOURCES	148
4.6.1 <i>Introduction</i>	148
4.6.2 <i>Material/Method</i>	150
4.6.3 <i>Results and Discussion</i>	154
4.6.4 <i>Conclusions</i>	167
CHAPTER 5 : CONCLUSION	168
5.1 SUMMARY	168
CHAPTER 6 REFERENCES	172
CHAPTER 7 APPENDIX	193

LIST OF TABLES

<i>Table 1- Water quality of produced water and flow back in Colorado (Collected data)</i>	17
<i>Table 2-TDS ranges for livestock water^{93,32}</i>	24
<i>Table 3- Characteristics of several treatment processes (^{188,189})</i>	31
<i>Table 4- Raw water quality for produced water samples</i>	49
<i>Table 5-Solubility products and solubility of possible compounds at 20° C and standard conditions¹²¹</i>	54
<i>Table 6-Water quality characteristics for Case I and Case II</i>	67
<i>Table 7-Classification of existent compounds in different pH</i>	68
<i>Table 8-Range of water quality for different water source</i>	83
<i>Table 9-List of added mineral compounds</i>	84
<i>Table 10- Frac fluid composition</i>	85
<i>Table 11- Viscosity ranges for acceptable run</i>	89
<i>Table 12- Weighted error for some ions in CMC and guar based fluids</i>	100
<i>Table 13- Summary of ions' effect based on spiked concentrations.</i>	102
<i>Table 14- Water quality measurements for different waters tested.</i>	108
<i>Table 15- Water sample descriptions</i>	110
<i>Table 16-Calculated p-value for model and recycle water samples</i>	119
<i>Table 17-Calculated p-value for PW and ETFB water samples, peak viscosity</i>	124
<i>Table 18- Water quality composition for model water</i>	134
<i>Table 19- Water quality composition for model water</i>	150

LIST OF FIGURES

<i>Figure 1- Unconventional and conventional gas reservoirs (Source EIA)</i>	4
<i>Figure 2- Oil and gas shale reservoirs in U.S. with the estimated reserves (Modified from Schlumberger, 2005)</i>	5
<i>Figure-3 Natural gas production forecast for U.S. ⁸ (Source EIA)</i>	7
<i>Figure 4-Oil and natural gas production trends in Colorado, 2000-2012 ¹⁵ (Source EIA and COGCC)</i>	8
<i>Figure 5- A schematic for Hydraulic fracturing (http://www.cleancoalsyngas.com/index.php/what-is-ucg/ucg-comparisons)</i>	9
<i>Figure 6- Structure of guar gum polymer ¹⁶³</i>	12
<i>Figure 7- The formulation of CMHPG from Guar ¹⁶³</i>	13
<i>Figure 8- Structure of sodium carboxymethyl cellulose ¹⁶⁵</i>	14
<i>Figure 9-Broken CMC and guar based fluids¹⁶⁶</i>	15
<i>Figure 10-Crosslinking Mechanism of transitional metal onto Guar¹⁶³</i>	16
<i>Figure 11- a) The average annual precipitation for United States ⁵⁵; b) Estimated use of water in the United States in 2010 ⁵⁴</i>	19
<i>Figure 12- Water management in hydraulic fracturing</i>	28
<i>Figure 13-Classification of membrane filtration as a function of molecular weight cut off and pore size ¹⁸⁷</i>	31
<i>Figure 14-Electrocoagulation unit and electrode configuration</i>	44
<i>Figure 15-Average water production rate of 86 horizontal wells in Weld County ⁹⁷</i>	45

Figure 16-A schematic diagram of experimental plan and line diagram of experimental set up for EC-Soft	47
Figure 17-Mg ²⁺ , Ca ²⁺ and hardness concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.	51
Figure 18-Raw water TOC value as a function of time (well age).	53
Figure 19-Ba and Sr concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.	55
Figure 20-Boron concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.	57
Figure 21-TOC and turbidity concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.	58
Figure 22- Al and Fe concentrations as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.	60
Figure 23-A typical water production curve ⁹⁶ .	64
Figure 24-A schematic of the sampling plan: (1) EC-Soft, (2) Soft-EC.	65
Figure 25-Precipitation and removal of divalent cations versus pH (assumes 100% solid-liquid separation following precipitation).	69
Figure 26-(A) Calcium and (B) strontium removal in different pH over time. Sr and Ca removal at different pH values were based on OLI model (left axes), Sr, Ca and Carbonate concentrations in the raw water samples (right axes)	70
Figure 27-Bicarbonate concentration in raw water samples	71
Figure 28-(A) Magnesium removal in different pH values over time; (B) magnesium concentration in the raw water samples and threshold concentration.	73

Figure 29-Barium removal rates at different pH values (left axis); barium and sulfate concentrations in the raw water samples (right axis) over time	74
Figure 30-Sulfate concentration in raw water samples over time and threshold concentration	75
Figure 31-Comparison between the experimental and modelled ion concentrations in the effluent at pH of 9.5 and 10.2: (A) Calcium; (B) Strontium	76
Figure 32-Comparison between the experimental and modeled magnesium concentration in the effluent at pH of 9.5 and 10.2	77
Figure 33-Comparison between the experimental and modeled Barium concentration in the effluent	78
Figure 34-Acid and base consumption	79
Figure 35- Viscosity profile of base fluid; a) CMC based fluid and b) Guar based fluid	87
Figure 36- The impact of sodium and potassium on viscosity, a) CMC based fluid and b) guar based fluid	91
Figure 37- Viscosity profile for divalent cations, calcium and magnesium, a) CMC based fluid, and b) guar based fluid	92
Figure 38- Aluminum and iron results a) CMC based fluid and b) Guar based fluid	94
Figure 39- Viscosity profile in presence of phosphorus ion, a) CMC based fluid and b) guar based fluid.	95
Figure 41-TOC quantity corresponding to TDS for different water samples	112
Figure 42-Low residue Carboxyl methyl cellulose (CMC): Model water with TDS ranging from 3000 to 9000.	114
Figure 43- Recycle versus model water at five different TDS values: 5000, 7000, 9000, 11000 and 13000 mg/l.	116

<i>Figure 44-TDS concentration and salting out phenomena</i>	118
<i>Figure 45-Peak viscosity versus TDS for model and recycled water</i>	118
<i>Figure 46-Δ Viscosity/ Δ TDS versus different times: 2.5, 7.5, 15, 20, 30 and 45 minutes</i>	120
<i>Figure 47-PW versus ETFB impacts on viscosity</i>	122
<i>Figure 48-Speculated mechanisms of cross linking in presence of organic matter</i>	123
<i>Figure 49-Comparing viscosity of recycled water and non-recycled water</i>	125
<i>Figure 50-Viscosity profile for different water samples at TDS of 7000, 9000, 11000 and 13000mg/l.</i>	127
<i>Figure 51-Low residue polysaccharide: Model water</i>	137
<i>Figure 52-Viscosity map at gel loading of 45ppt</i>	139
<i>Figure 53-Viscosity map at gel loading of 50ppt</i>	141
<i>Figure 54-Viscosity map at gel loading of 55ppt</i>	142
<i>Figure 55-Statistical analysis, a) Pareto graph; b) main effects</i>	145
<i>Figure 56-Low residue polysaccharide: Model water</i>	154
<i>Figure 57- Apparent viscosity at gel loading of 45ppt</i>	156
<i>Figure 58- Viscosity map for gel loading at 40ppt</i>	157
<i>Figure 59- Contour map of apparent peak viscosity at gel loading of 35ppt</i>	158
<i>Figure 60- Contour map of viscosity at gel loading of 30ppt</i>	160
<i>Figure 61- Contour map of viscosity at gel loading of 25ppt</i>	162
<i>Figure 62- Pareto chart and Normal plot of the effects</i>	164
<i>Figure 63- Interaction and individual effects for all three factors, gel, pH and crosslinker concentration</i>	165

Chapter 1 : Introduction

Recent technological advances, such as hydraulic fracturing have led to a boom in domestic oil and natural gas production through unconventional sources, leading to a low price, large supply with decreased greenhouse gas intensity as natural gas replaces coal as the primary fuel for generating electricity. As a consequence, many different sectors throughout the industry have shown significant interest resulting in significant financial investments. However, unconventional development of oil and gas has become controversial due to environmental challenges with respect to land, air and water pollution generated by development processes.

Unconventional oil and gas resource development, in particular shale gas, are fundamentally altering the profile of U.S. energy generation. Since 2009 the United States has been the world's leading producer of natural gas with production growing by more than seven percent in 2011^{1,2,3}. The proportion of shale gas production in U.S. has also increased during this time. In the decade 2000 to 2010, U.S. shale gas production increased 14-times and accounted for approximately 34 percent of total U.S. production in 2011^{1,2,4}. In 2007 and 2008 alone U.S. shale gas production increased by 71 percent³. Shale gas production is estimated to increase almost four fold between 2009 and 2035, when it is forecast to make up 47 percent of total U.S. production³.

Throughout history, the United States has undergone several energy transitions in which a main energy source has been replaced by another. The country appears to be going through another transition as the country seeks lower-carbon, more affordable, domestically sourced fuel options to meet a variety of market, policy, and environmental objectives. Prior energy transitions took place in times of lower populations without significant consideration of environmental impacts.

However, current times demand careful management utilizing technology to achieve both economic and environmental goals while satisfying inevitable regulatory and policy structures. Hydraulic fracturing imposes a significant environmental impact with respect to water usage and disposal. Water and energy are intrinsically interconnected, primarily because of water properties that make it a large component of chemicals needed to extract energy and also energy required to treat the water and make it suitable for human activities. With more than 69% of natural gas production coming from Texas, Pennsylvania, Wyoming, Colorado, Louisiana, Oklahoma and New Mexico⁵, where aquifers are depleted, water scarcity and water intensity are big challenges. Water has emerged to be a leading environmental concern associated with conventional and unconventional oil and natural gas resources particularly in the semi-arid West.

Management of the sourcing and disposal of this water has the potential to be economically and logistically advantageous to gas producers while simultaneously being environmentally beneficial satisfying regulators and the public. To establish water management and reuse strategies a good knowledge of water quality, water quantity, and spatial distribution are important. Water reuse and water management in developing unconventional oil and gas resources are required to address a strong temporal and spatial variation in water quality and quantity. Moreover the location of services for water collection, water treatment, water reuse/recycle and demand of fresh water for drilling is constantly changing in such developments.

A lack of water data regarding the water quality and quantity has been politically challenging. Most of the oil and gas service companies and operators hesitate to disclose their proprietary process and chemicals. Therefore knowledge of water quality and frac fluid composition has been sparse and not readily available in the literature. A better understanding of water requirements,

wastewater volumes, and water reuse potential is required to minimize the environmental, public health, and community impacts while developing unconventional shale gas.

In this document, a review of literature with an emphasis on water management associated with unconventional oil and gas development is provided in Chapter 2. Research hypotheses are presented in Chapter 3 along with objectives, tasks, and research progress. The results are divided into six peer-reviewed journal articles in Chapter 4 including treatment study of produced water (published in Journal of Hazardous Materials), optimization of metal removal in produced water treatment (published in Oil and gas facilities, Journal of Society of Petroleum Engineers), study of influence of inorganic dissolved ions on frac fluid stability (published in Journal of petroleum science and engineering), and reuse of produced water in hydraulic fracking (published in Journal of Society of Petroleum Engineers), finally optimization of chemical composition of CMC frac fluid at low and high TDS waters (both papers submitted to Journal of Society of Petroleum Engineers). The dissertation is summarized with conclusions in Chapter 6.

Chapter 2 : Literature Review

2.1 Unconventional oil and gas

Unconventional oil and gas resources have garnered tremendous attention in North America over the past decade, natural gas in particular due to its cleaner combustion and reduction in global green gas emissions. The term “unconventional resources” refers to wide range of oil and gas resources in which simulation is generally a necessary process in oil and gas production. Tight shale formation, Tight-Gas Sandstones, Gas Hydrates, Oil Shale formations, and Heavy Oil Sandstones, among others, are typically included in this category. These unconventional resources largely contain, shale, clay, quartz, and lime with ultra-low permeability, making the oil and gas production economically challenging. While conventional oil and gas are laid in shallower formations with higher permeability where production consists of drilling a well into the oil reservoir with no needs for simulation, resulting in at least some flowrates of oil immediately.

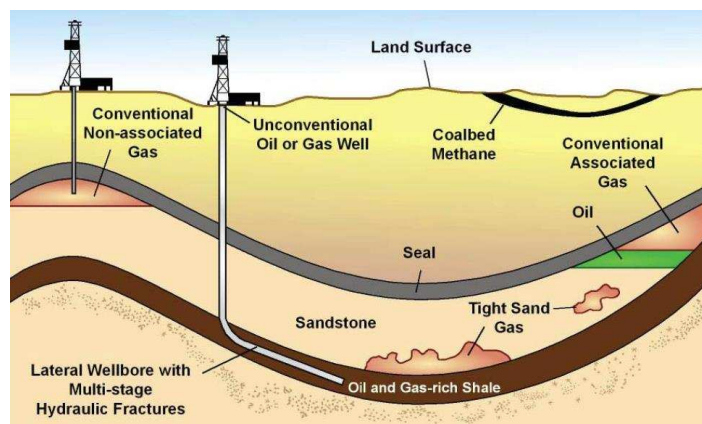


Figure 1- Unconventional and conventional gas reservoirs (Source EIA)

Shale represents a vast variety of formation rocks that are created by accumulation and compaction of sediments and extremely small grained particles, normally less than 4 microns in

diameter, but may contain various amounts of silt-size particles, formed under very high pressure and temperature centuries ago ¹. Drilling can liberate large amounts of oil and natural gas from the reservoir rock, but much of it remains trapped within the shale or adsorbed onto clay mineral particles that make-up the shale.

Production from tight shale formation known as Shale gas is one of the most rapidly increasing trends in on shore domestic exploration and production in United States⁴. The United States Energy Information administration (EIA) estimates that US has 2,119 trillion cubic feet of recoverable natural gas, about 60% of which is unconventional gas stored in low permeability formations such as Shale, coalbed and tight sands.²

Advanced technologies have brought shale gas exploration and production to the areas of nation which had not seen much oil and gas activity, for instance in Texas, Barnett play, urban and suburban has undergone of shale development Figure 2 shows the known shale plays across the United States ⁹.

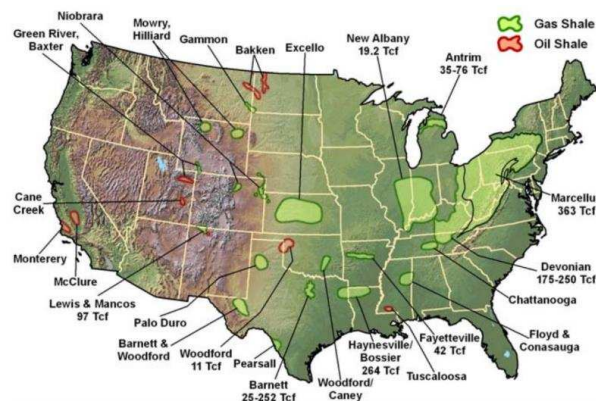


Figure 2- Oil and gas shale reservoirs in U.S. with the estimated reserves (Modified from Schlumberger, 2005)

Large scale production of shale gas has become economically available due to development of advanced technological drilling, hydraulic fracturing or fracking^{4,6}. Such advances have

dramatically amplified the natural gas production in several basins throughout the nation. These basins include Barnett, Haynesville, Fayetteville, Woodford, Utica, and Marcellus shale formations⁹ (Figure 2). In 2009, 2224.83 billion cubic feet of natural gas was produced from shale gas and doubled to 4866.4 billion cubic feet in 2010⁸. United States shale gas produced an average of 25.7 billion cubic feet per day (Bcf/d) in 2012, with a total of 65.7 Bcf/d. In other words, 27% of gas production was produced from shale gas in 2010 and EIA projects that by 2040, 50%, of U.S. natural gas production will be supplied from Shale gas⁸. As the consequence of these unconventional oil and gas developments, U.S. total natural gas import dropped from 30% of total energy consumption in 2005 to 13% in 2013. Figure 3 clearly displays the steep upward trend in gas production seen in the US over the last decade, corresponding to the start of the shale boom in 2005, with total production now 27% higher than production in 1990. The high natural gas production in 1973 was due to development in conventional resources and over time these conventional sources depleted and gas production followed a downward trend in the mid-1980s. It is clear that not only natural gas production in U.S. will supply the nation's domestic energy demand but also U.S. will be a natural gas exporters to other countries.

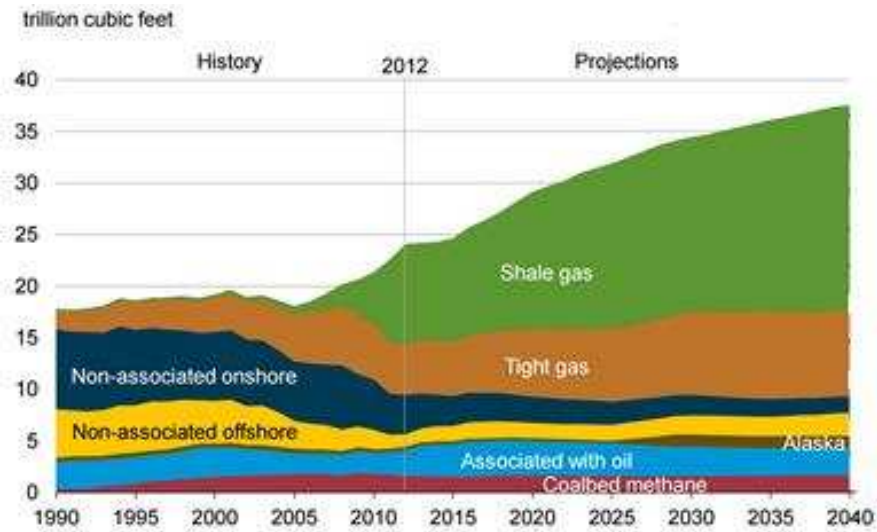


Figure-3 Natural gas production forecast for U.S. ⁸ (Source EIA)

2.2 Hydraulic fracturing

Shale gas basins have been sources of natural gas in small, but continuous flow volumes since the earliest developments. Although shale gas has been produced in the United State for many decades, it was not considered to be a significant resource until the last decade when new horizontal drilling and hydraulic fracturing technology facilitated economic production. Shale gas exploration was begun in the early 1800s^{9, 10}. With the first shale gas well completed in 1825 in Devonian-aged shale, New York.¹⁰

The Wattenberg basin in Colorado has been one of the largest exploration and production targets since 1970.¹¹ Today, advanced technological hydraulic fracturing including multi staged horizontal drilling have been applied to liberate the ultra-low permeable shale gas deep beneath the ground. Oil and gas production from this play has been increasing since 2000.

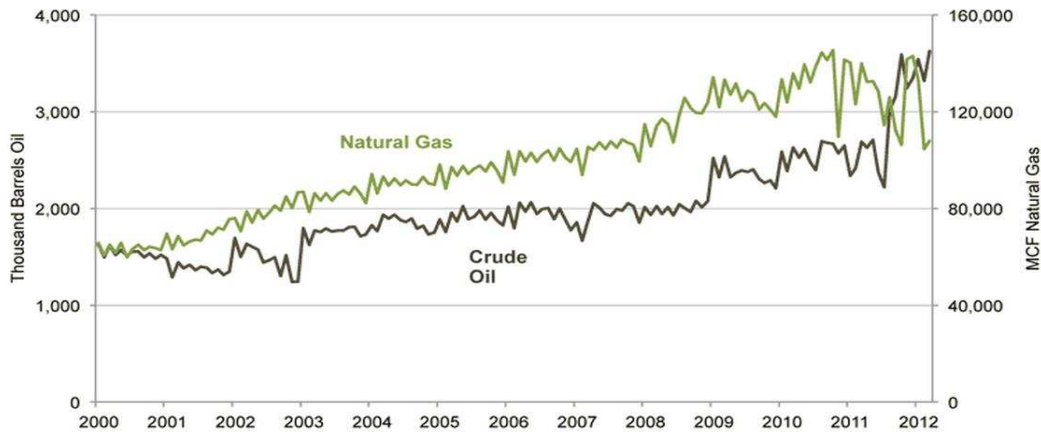


Figure 4-Oil and natural gas production trends in Colorado, 2000-2012 ¹⁵ (Source EIA and COGCC)

Although hydraulic fracking and horizontal drilling technology have attracted significant attention from environmental activists and regulators, they are not new tools. The first hydraulic fracking was conducted by Halliburton in 1947 in Houston and Oklahoma.¹⁴

One way to increase the flow rate and permeability of a formation to have higher production rates is to create fractures in the rock formation. Simulation of formation by hydraulic fracturing is a way to facilitate oil and gas mitigation from downhole to the surface ¹⁵. Thousands of gallons of water are injected downhole under high pressure to create fractures or expand the existing natural fracture sand to increase the formation permeability. In order to keep the fractures open, proppant is pumped with the water. Proppants are sand or any fined grained material which are pumped with the fluids to maintain the induced fractures open for the oil and gas to flow to the surface ¹⁴.

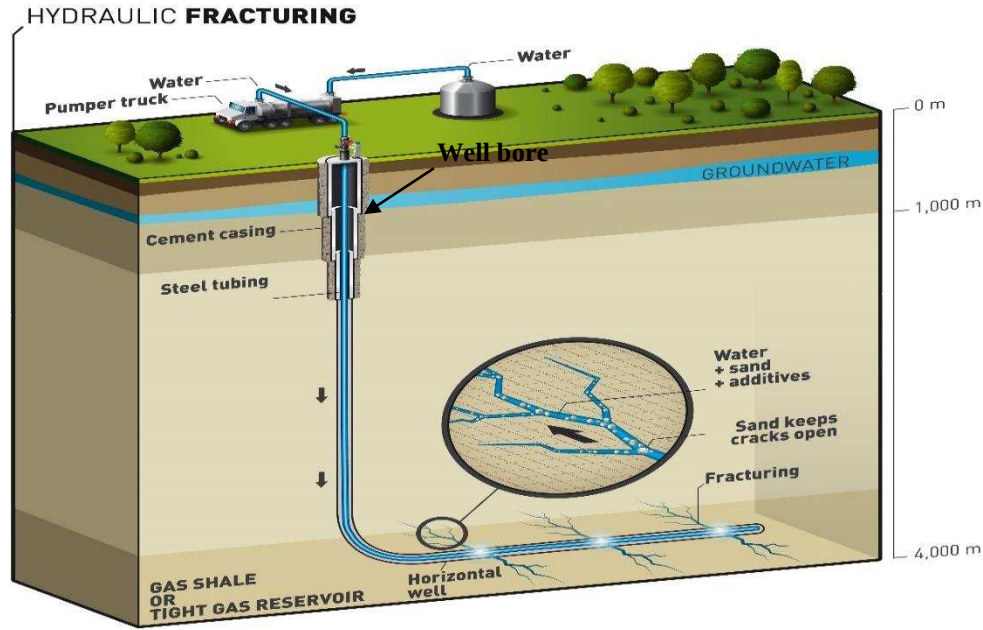


Figure 5- A schematic for Hydraulic fracturing (<http://www.cleancoalsyngas.com/index.php/what-is-ucg/ucg-comparisons>)

The fractures are created at the horizontal layer in the target formation (Figure 4). Once the rock is fractured, the oil and gas can flow in to the pipe and to the wellbore. Shale is usually fractured in multi stages and each stage is typically a few hundred feet.¹³

A typical conventional natural gas well is drilled vertically to 5900-6600 feet underground to get to more permeable layers and easier oil and gas resources. Ground water aquifers are usually laid far on top of shale gas in 200-1200 feet underground depending on geographic and climate of the location. To get to shale gas, a vertical well first is drilled to 5000-20000ft down, then using a directional drilling machines, the well is horizontally drilled. At this point horizontal drilling starts¹⁶. The length of horizontal drilling typically is several thousand feet.¹⁶ During the vertical drilling, several steel casings are inserted and cemented down the well to prevent any chemical migration and potential contamination of water aquifers.

There are several methods of fracking and all of them require some sort of liquid, typically water. Frac fluid selection greatly influences how the formation rock is fractured and consequently gas production. There are several types of frac fluids and each frac fluid has a different chemical composition depending on the fracking job. Formation rock, its thickness, and type of resources typically determines the type of fluid to be applied for fracking.^{20, 21} Various type of frac fluid used in U.S. include: Slick water, Water-base polymer solutions of Natural guar gum (guar), Hydroxypropyl guar (HPG), Hydroxyethyl cellulose (HEC), Carboxymethyl hydroxyethyl cellulose (CMHEC)*and Polymer water-in-oil emulsions of hydrocarbon plus water-base polymer and gas phase such as CO₂ among the others.¹³

A good frac fluid is capable of carrying the suspended proppant far enough into downhole and create well networked fractures¹². Frac fluid also helps to flow back the residue of proppant and other suspended solids created due to drilling.¹² Some desirable characteristics of a good fluid include: (1) low fluid loss to obtain the desired penetration with minimum fluid volumes; (2) Necessary effective viscosity to create the desired fracture width, (3) transport and distribute the proppant in the fracture as required; (4) good temperature stability for the particular formation being treated; (5) Good shear stability; (6) minimal damaging effects on formation permeability; (7) Low friction- loss behavior in the pipe; (8) Good post-treatment breaking characteristics; (9) good post-treatment cleanup and flowback behavior; and (10) Low cost.^{3,13, 12, 18,19}

Comprehensive details on all the fluids and their design information are not usually fully disclosed, however most of frac fluids are comprised of: water, bacteria control agents, breakers for reducing viscosity, buffers, clay stabilizing agents, crosslinking or chelating agents (activators), demulsifying agents, emulsifying agents, fluid-loss control agents, foaming agents, friction reducing agents, scale inhibitors, pH control agents, surfactants, temperature stabilizing agents.¹³

^{21, 22, 23, 24, 25} Water comprises more than 99% of frac fluid and it is the largest component used in individual frac fluids. Typically proppant is the second large component of frac fluid while additives could be less than 1% of total volume of a frac fluid^{14, 26, 27}.

2.2.1 Gelled frac fluid systems

Slick water and polymer (gel) based frac fluids are the two main frac fluid systems used in unconventional oil and gas resources. While slick water fracking, which mostly uses water to place the proppant for stimulation, is most common in gas formations, water based viscous polymeric frac fluids play a significant role in shale oil reservoir simulation techniques, where viscosity is the primary characteristic of these fluids. They can be applied in many conditions such as different formations, depth, temperature, and pressure. They can also be crosslinked for expanded viscosity in higher temperature formations¹³. CMC and guar based fluids, usually called gelled frac fluids, are the most common water based polymer systems.

In general polymer solutions exhibit a non- Newtonian pseudo plastic behavior meaning that the viscosity varies with shear rate, it decreases with increasing shear rate and vice versa. In Newtonian fluids such as water, viscosity is only dependent on temperature. At 68.4°F, pure water has a viscosity of 1 cP¹⁶⁴. Viscosity is a precisely defined and calculated by the ratio of shear stress S_s to shear rate S_r (Eq. 1) and is expressed in units of centipoise (cP) ¹⁶⁴.

$$\mu = \frac{S_s}{S_r} \dots\dots\dots \text{EQ. 1}$$

Shear stress is the force per unit cross-sectional area applied to the polymer solution. Shear rate has the units of reciprocal seconds and is the ratio of the displacement of the polymer solution divided by the height of the solution affected by the shear stress.

Guar based frac fluids

Guar gum is derived from seeds of guar plants and is composed of mannose and galactose sugar molecules. The structure of a molecule of guar gum is illustrated in Figure 6. Guar gum and its derivatives are the most common gelling agent used in hydraulic fracturing ¹⁶³.

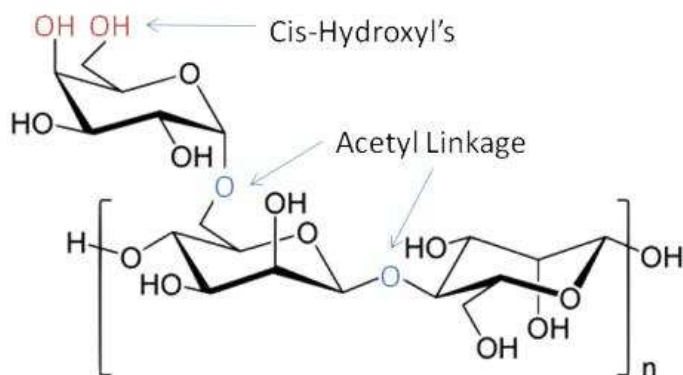


Figure 6- Structure of guar gum polymer ¹⁶³

Up to 6–10% by weight insoluble residue is expected from guar¹⁶⁵. This initial insoluble residue causes damage to the proppant pack. In addition to the residue made during the preparation, the breakers also generate additional residues. To reduce the insolubility of guar, its derivatized polymers are mostly used in shale oil. Sequential treatment of guar with propylene oxide, and chloroacetic acid in an alkaline medium can result in “double-derivatized” polymers such as anionic carboxymethyl hydroxypropyl guar (CMHPG) ^{163, 164}. Broken hydroxypropyl guar gels contain no more than 2% insoluble residue¹⁶⁴. CMHPG is reportedly more stable and soluble than guar at temperatures up to 375 °F, but it is more sensitive in brine and electrolyte solutions¹⁶⁴. This process is shown in Figure 7.

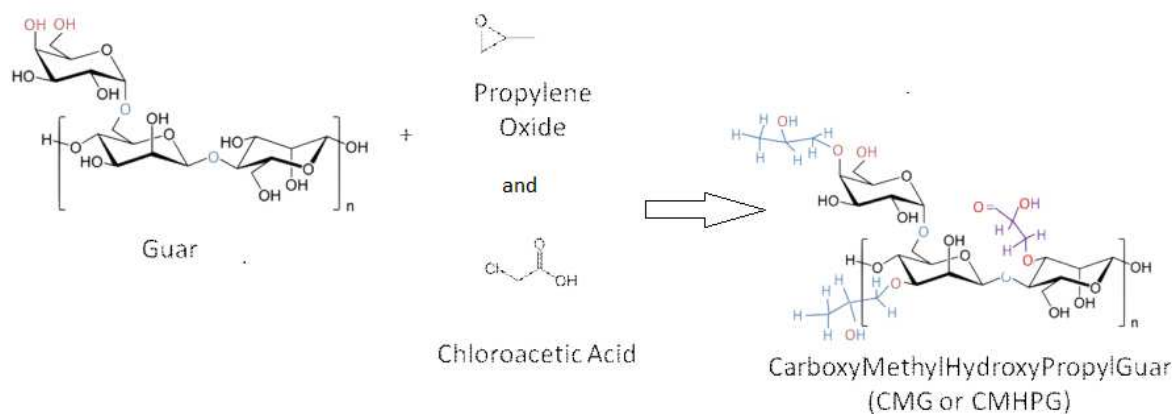


Figure 7- The formulation of CMHPG from Guar ¹⁶³

CMC based frac fluids

Cellulose is the most abundant of all the natural polymers and probably comprises at least a third of all vegetable matter in the world. Generally dry wood contains 40 to 50% cellulose¹⁶⁴. Cellulose is a linear molecule formed by the polymerization of a simple sugar glucose. Due to very strong intermolecular and intramolecular hydrogen bonding, cellulose is insoluble in water. Thus, water-soluble cellulose derivatives are superior for oilfield applications. To prepare water-soluble cellulose derivatives, cellulose is treated with an aqueous solution of a strong base, usually sodium hydroxide. This results in separation and swelling of polymer particles¹⁶⁴. The larger space between polymer chains allows penetration of chemical reagents¹⁶⁴. Sodium carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups (-CH₂-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbones and it is prepared by the reaction of cellulose with chloroacetic acid in the presence of sodium hydroxide^{163, 164}. The structure of the cellulose molecule is shown in Figure 8.

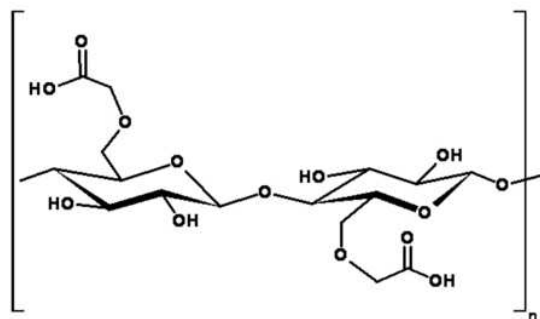


Figure 8- Structure of sodium carboxymethyl cellulose ¹⁶⁵

Service companies and oil and gas operators have been challenged by enormous price swings and shortages of guar in the past few years. CMC was recently introduced in applications requiring efficient gelling while leaving no residues and less damage to the formation. It is also more compatible with salts of monovalent metals such as sodium chloride and potassium chloride. Tolerance for divalent metal salts including calcium chloride and magnesium chloride is dependent on the number of substituted hydroxyl groups (DS), pH of solution, and the salt concentration¹⁶⁴. Maximum viscosity and best stability of CMC based frac fluid system occur at a pH of 7 to 9 in fresh water.¹⁶⁴

The main advantage of CMC is its cleanup properties due to the substantial lack of insoluble residue. Some benefits of CMC based fluids over guar frac fluid system are summarized as below¹⁶⁶:

- Clean fluid system provides high regained proppant pack permeability
- Contains none of the residue typical of guar-based fluid systems: CMC Polymer <1% compare to guar: 8-15%.
- Results in cleaner fluids and less formation and proppant pack damage

- Provides better proppant transport
- Improves well cleanup resulting in greater effective frac length
- Tolerates salt– up to 7% KCl or NaCl

Figure 9 illustrates the broken form of two fluids of CMC and Guar based.



Figure 9-Broken CMC and guar based fluids¹⁶⁶

Crosslinkers

In general linear gels that can be applied at ambient surface temperatures are incompatible with the operations at bottomhole temperatures and carry large quantity of proppant¹⁶⁷. Therefore crosslinkers are used to increase the molecular weight of the polymer by forming a three dimensional structure consisting of transitional metals and carboxylate ligand on the polymer backbone. As a result the viscosity of a crosslinked gel significantly increases up to 5000 cP or more compared to 50cP with only linear polymers¹⁶³. Several transitional polyvalent metal ions are commonly used in hydraulic fracturing such as cadmium, aluminum, and zirconium. However, cadmium application has been diminished due the concerns of its toxicity^{167,163}. Typically

bottomhole temperature, pH, and the designed viscosity of frac fluid govern type of crosslinking agents used in hydraulic fracturing¹⁶⁸.

CMHPG may be crosslinked by treatment with transition metal ions including titanium and zirconium under basic conditions to form a highly viscous gel¹⁶⁴, which is enabled by a robust covalent bond of polyvalent cations and the carboxyl group pairs on the polymer backbone and forming longer and more complex polymer chains (Figure 10). Consequently, the rheological properties of the polymers including elasticity and proppant transport ability are improved¹⁶³.

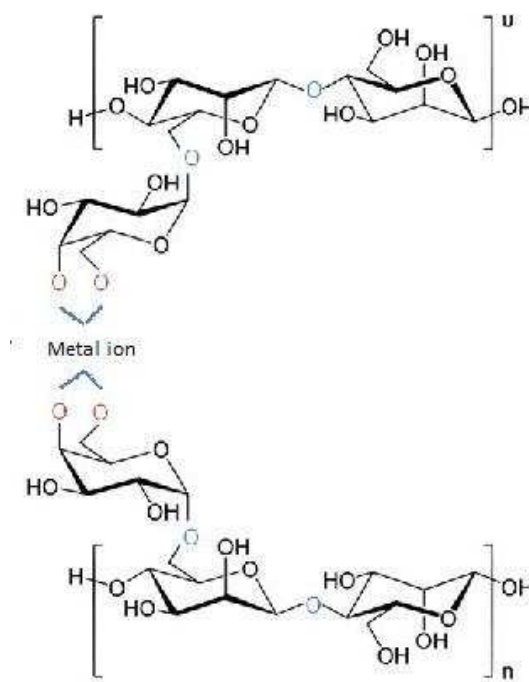


Figure 10-Crosslinking Mechanism of transitional metal onto Guar¹⁶³

2.2.2 Hydraulic fracturing wastewater

A significant amount of frac fluid along with formation water flows back with oil and gas to the surface during the first month of a well production. This water called “flowback”, accounts for

approximately 25%-30% of total volume of water which flows to the surface over the lifetime of a well^{28, 29, 30, 31}.

“Produced water” then refers to the fluid that continues to be produced with the oil and gas once the well is placed into production and may be present over the lifetime of the well. These water typically have high concentration of salts, organic matter and suspended solids. The salinity and total dissolved solids (TDS) of the water increases over time while organic content decreases. Meaning that flowback water usually has a high organic load and lower TDS which has some of frac fluid characteristics comparing to produce water which represents the formation water^{32, 33, 34, 35}. High organic content of flow back water has been an obstacle for treatment and recycling these waters. Moreover spatial and temporal variability in water quality of flowback and produced water are the other major characteristics that must be considered in water management in hydraulic fracturing^{33, 35, 36, 37, 38}. Typical water quality of produced water and flow back water is shown in table 1.

Table 1- Water quality of produced water and flow back in Colorado (Collected data)

Water quality parameter	Flowback water	Produced water
Aluminum(mg/l)	1.27	1.10
Boron(mg/l)	12.50	20.40
Barium(mg/l)	2.88	30.50
Calcium(mg/l)	94.70	294
Chloride(mg/l)	6840	20647
COD(mg/l)	919	480
Iron(mg/l)	11	160
Magnesium(mg/l)	15.00	48.80
Strontium(mg/l)	12.40	51.40
TDS	13174	34359
TOC(mg/l)	2184.33	843
Turbidity(NTU)	679	3440

2.2.3 Water use

Energy and water have a strong relationship and are interconnected. This energy water nexus is even more intense in shale gas exploration because of large quantity of water required for horizontal drilling. This water is used in drilling and completion of wells to maintain the downhole hydrostatic pressure, cool the drill-head and remove mud and drill cuttings²⁵. Most studies on environmental impacts of hydraulic fracturing have focused on water source contamination^{39, 40} and water quality while a few have addressed the influence of fracking on quantity of water resources.^{41, 42, 43, 44, 45}

Water usage in hydraulic fracturing varies throughout the nation and depends on the frac fluid system, formation, stages of drilling and length of each stages. Operators reported that an average of between two and five million gallons of fresh water is required for drilling a horizontal well^{46, 47, 48}. Typically the oil and gas water is acquired from the surface water or ground water (fresh water) in the region.²⁵ The water quality associated with fresh water is normally good with TDS of lower 1000mg/l.⁴⁹ Limited fresh water resources in Mid-West U.S. and semi-arid areas such as Texas, Colorado, California and New Mexico, has put lots of pressure on oil and gas operators and will eventually limit the shale gas production if alternatives for water source do not considered^{25, 49}. Although water use in hydraulic fracturing appears to be relatively high in volume, oil and gas industry is not the largest water consumer of fresh water. Cooling water for power plants accounts for approximately 40% of the total volume of fresh water use in the U.S, while mining and oil gas industry's share is only 1%.^{49, 50, 51} In Colorado the total industrial water use reported for 2012 accounts for 0.8 percent of the total water withdrawn⁵². Because the oil and gas industry is a subsector in this category, the total water used by hydraulic fracturing is even less than that. However, in arid or semi-arid climate, Colorado and Texas, where there is high pressure on water

aquifers, relying on ground water as the main water source for hydraulic fracturing could result in local water shortages.⁴⁹ In fact, shale gas production overlaps with depleted and stressed ground water aquifers. Nearly half of unconventional oil and gas activities in U.S. have been developed at areas, Colorado, Texas and New Mexico, where water shortages are also growing⁵³.

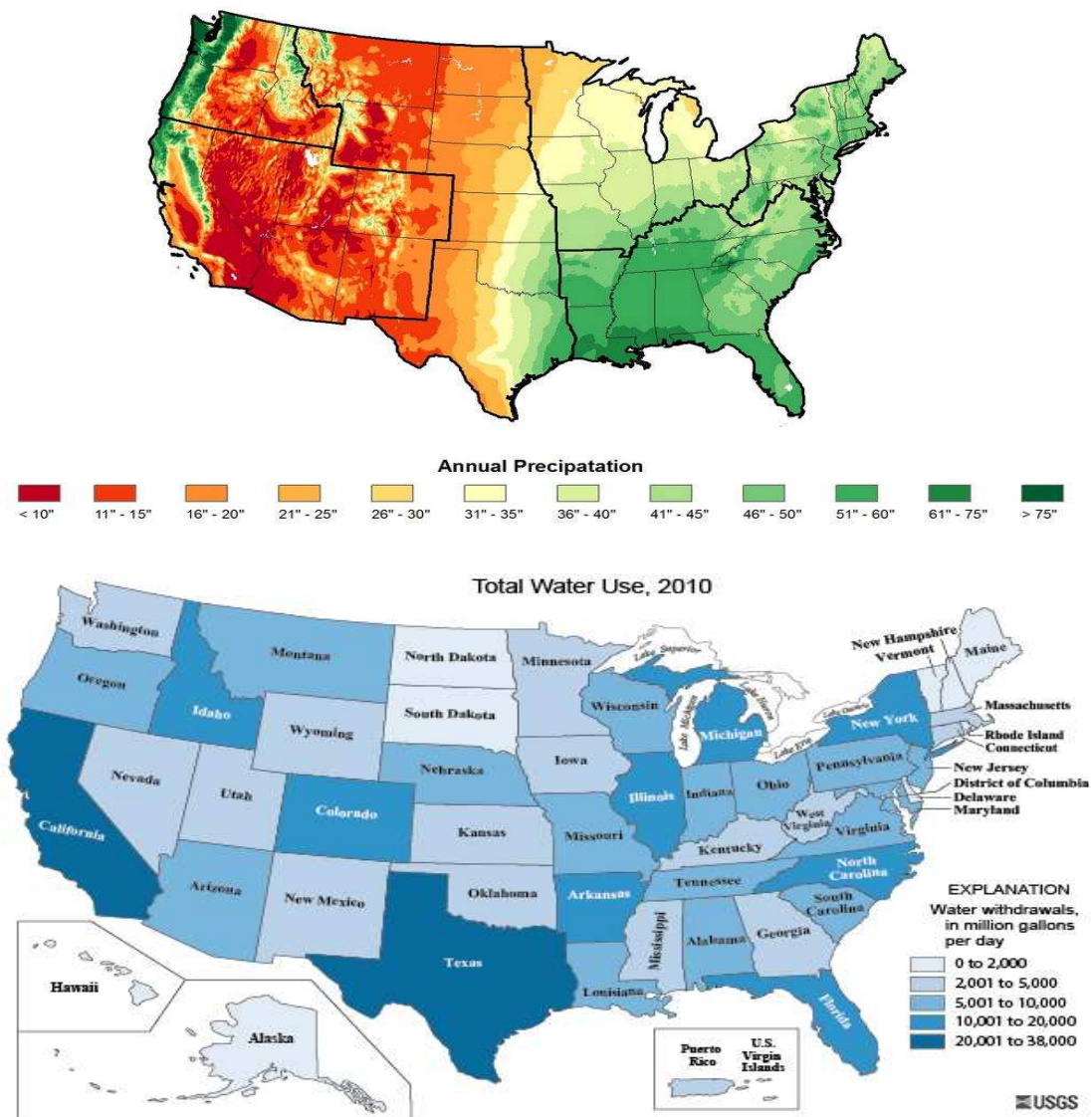


Figure 11- a) The average annual precipitation for United States⁵⁵; b) Estimated use of water in the United States in 2010⁵⁴

The average annual precipitation during 1981-2010 for the contiguous United States and water usage in 2010 are shown in Figure 6a and 6b, respectively. It is clear that despite high water consumption in the Mid-West of the country, not much precipitation occurs in those regions. Therefore, alternative water sources such as recycling produced water, brackish water, desalination of sea water and treated municipalities wastewaters should be considered as potential water sources for oil and gas drilling. While future shale gas production growth will increase water demand, produced water the byproduct of oil and gas development could serve as the primary water resource²⁵.

2.3 Water disposal

Temporal and spatial variability in produced water and flowback characteristics along with high salinity are the two primary obstacle for discharging untreated produced water to surface water. Produced water quality varies throughout a well life, high TOC and lower TDS levels associate with frac flowback while, lower TOC and higher salinity levels are associated with produced water. The total dissolved salts (TDS) content of produced water ranges from below seawater, 20,000 mg/L, to significantly higher than seawater (250,000mg/l), depending on the shale formation.^{25, 56}

Public concern regarding high content and variability of organic matter and TDS in water quality has made produced and flowback water management a sensitive issue. High TDS and organic content originate either from chemical additives in frac fluid composition or formation rock^{33,34}.

In United States, several strategies have been deployed to manage produced water. Produced water has been disposed by deep well injection technique, discharged to surface water after treatment

and meeting the standard water quality or recycled^{57,58}. The treatment strategy includes discharging to public municipalities, or industrial treatment plants. In addition to these techniques, some states including Colorado allows the operators to treat road surfaces for dust suppression^{57,58}. More than 90% of produced water and flowback is disposed by deep well injection in the U.S as well as Colorado, making it the most common disposal practice.³⁸ Operators utilize EPA Class II disposal underground wells ⁶² for produced water disposal. Today, there are approximately 144,000 operational disposal wells (Class II) in the U.S. ⁶³, with 350 locating in Colorado. More than two billion gallons of brine associated with oil and gas operations are injected every day. Most of these wells are located in Texas, California, Oklahoma, and Kansas have located most of these class II wells.

2.3.1 Induced seismic activity

The potential association between deep well injection and induced seismic activities has raised considerably high attentions⁶⁴. The total earthquakes with magnitude scale of 3 and higher has significantly raised in central U.S., from an average of 29 per year between 1970 and 2000 to over 100 per year in the past decade⁶⁷. Some states, Arkansas, Colorado, Texas, New Mexico, Ohio, Oklahoma, and Virginia,⁶⁸ have experienced higher seismic activity compared to historic seismic activities. The increase in seismic activities in some of these states has coincided with the increase in deep well injections because of higher oil and gas production and hydraulic fracturing growth⁶⁸. Colorado has about 350 disposal wells and two or three sets of small earthquakes in the state have been linked to injection wells.⁶⁵

The central Arkansas and Ohio earthquakes in 2011 have also been linked to deep well injection activities⁶⁶. Ohio has undergone over than 109 small earthquakes between 2011 and 2012, despite

the fact that no seismic activity had been recorded previously.⁶⁵ The earthquakes were in close proximity to disposal wells.⁶⁵ The Barnett Shale in north central Texas which has been under lots of oil and gas developments, has also experienced notable levels of seismicity⁶⁹. Compared to the past 25 years, when there was no seismicity, nine earthquakes have been recorded since the beginning the exploration and operations in 1998.⁶⁹ Investigations confirmed that disposal wells associated with oil and gas operations caused seismic activities in the Dallas-Fort Worth area during 2008-2009⁷⁰. While not all scientist agree that disposal wells are associated with earthquakes in Oklahoma⁷¹. For all the recent seismic activities, epicenters were located within 1.9 miles of high rate disposal wells⁷². This suggests a high probability that earthquakes are induced by deep well injection are influenced by volume and rate of injected fluids.

In 2011, Colorado Oil and Gas Conservation Commission, COGCC, addressed environmental concerns by regulating the injection pressure and volume of injected wastewater pumped down the wells⁶⁵.

In the case of produced water deep well injection, the danger of even small earthquakes should be pointed because in the event of occurrence, contamination of local ground water, soil and upward migration of produced water could happen⁷³. Besides the environmental concerns, insufficient number of Class II wells, complexity of the process, and a high capital cost associated with construction of disposal wells⁷⁴, necessitates other strategies for flowback and produced water management.

2.3.2 Trucking produced water

Ground transportation by trucks of fresh water and produced water, is the primary water transport practice method used in the U.S oil and gas operations. In most cases long haul trucking is used because fresh water resources may be insufficient and geology may not be conducive for disposal wells. Due to the large volume of water and produced water associated with hydraulic fracturing, many trucks are required for water transportation during fracking. Spills, traffic, noise, and carbon emission are another environmental concerns regarding water trucking. Public concerns about the impacts and risks of trucking water long distances has increased with the dramatic increase of oil and gas developments in Colorado ^{160,161} .

Water hauling and transportation is the primary cost in water acquisition and disposal. Fresh water usually costs about \$0.5-1 while transportation costs between \$2/bbl and \$4/bbl^{33,75}, depending on the hauling distance, wait time and trucking charges. Trucking is also used for produced water transportation to disposal wells. Costs for deep well injection ranges from \$0.50/bbl to \$1.75/bbl⁷⁵. Overall, transportation costs represent from 56% to 84% of the total water-handling costs, thus justifying an assessment of the economic potential of flowback and produced water recycling and reuse⁷⁵. Additional non-economic benefits such as reducing environmental, noise and health impacts from trucking can also be mitigated through recycling and reuse management strategies.

2.4 Recycling and reuse methods

Recycling and reuse of produced water has raised interest among oil and gas operators in recent years. The large volume of water required for fracking a horizontal well, 2-5million gallons, has created competition and scarcity among other fresh water withdrawal constituents including the

oil and gas industry. Produced water being the largest by product of oil and gas production, has a huge potential to serve as part of the fresh water needed for fracturing thereby reducing demand for freshwater.

Some example of future produced water management scenarios are: livestock, irrigation, stream flow augmentation, dust suppression, firefighting and reuse in hydraulic fracturing ^{93,94,32}. However there are very stringent water quality standards for non-industrial produced water applications well as public concerns about produced water.

Produced water could be a water source for livestock activities. Although animals are less sensitive to poor quality water, the water quality standards depend on the type of animal. Water quantity required also varies throughout the year, depending on temperature, type and size of animal^{93, 32}. The satisfactory TDS level varies among different animals and species, some animals are more sensitive than other animals (Table 2)^{93,32}.

Table 2-TDS ranges for livestock water^{93,32}

TDS Category	TDS Range	Description
Level 1	< 1,000	Satisfactory
Level 2	1,000 to 2,999	Satisfactory, slight temporary illness
Level 3	3,000 to 4,999	Satisfactory for livestock, increased poultry mortality
Level 4	5,000 to 6,999	Reasonable for livestock, unsafe for poultry

Level 5	7,000 to 10,000	Unfit for poultry and swine, acceptable short term for livestock
Level 6	> 10,000	Not recommended

Oil and gas activities are not always in remote areas. The Mid-West region of the country has experienced significant exploration and production. These areas are dust-prone which can raise environmental concerns in communities. Produced water can be locally applied for dust suppression on unpaved roads in hydraulic fracturing developments. To spray the produced water it should be controlled such that it does not percolate down the soil within a buffer zone around any water streams and buildings^{94,95,32}.

Wild fire is also a natural phenomenon which happens in semi-arid areas. Typically fresh water sources are used to fight fires, produced water is a potential water sources for firefighting. However in order to use a water source for firefighting, it must be in a large volume and easily accessible. Produced water could be stored in covered ponds so it could be transferred to the desired location when required. Water quality requirements for firefighting is not as stringent, meaning a comprehensive treatment is not necessary³².

Another potential water management strategy for produced water is application in cooling towers for power plants, as they need large volumes of water. However this option requires that power plants be located near oil and gas production fields⁹⁶.

2.4.1 Reuse in hydraulic fracturing

One of the most promising technologies for flow back and produced water management is reuse in hydraulic fracturing. Recycling of produced water for reuse in frac fluid could reduce the costs of acquisition and disposal as well as address public concerns related to water shortages and environmental impacts. In recent years operators have been more motivated to recycle flowback water since more than 30% of total volume of water comes back to the surface in the first month of a well life.⁹⁷ Re-using produced water would reduce trucking and its attendant risks as well. However water treatment needs are constantly varying as a field produced therefore a well-structured water management strategy should be implemented. Today, produced water has been reused either after dilution or pretreatment for subsequent fracking. This water management strategy is specially a great opportunity in areas where water resources has been depleted due to water scarcity. The reuse of produced water and flow back not only reduces environmental risks associated with deep well injection, community impacts and potential spills regarding to trucking but also enhances the economic and future of oil and gas industry.

Although reuse of produced water for oil and gas drillings and slickwater-based fracturing have been explored through dilution with fresh water in the Denver basin^{33, 34}, little has been done to use high-TDS produced water containing broken gelled and crosslinked-gel-based hydraulic fracturing fluids^{98, 99}. One Halliburton study claims water reuse with 285,000 mg/L of total dissolved solids is possible⁹⁹. Another recent study has alluded to high dissolved solids content improving production because of a similar composition to the formation, but high suspended solids impeded hydraulic fracturing fluid development¹⁰⁵.

Few studies have examined the influence of specific water quality parameters beyond the scope of solids and a few inorganic parameters. A limited number of reports have placed wide ranging water

quality limits on other inorganic parameters^{104, 103, 98, 100,101,102, 104}. Water quality impacts on hydraulic fracturing fluid rheology tests are incredibly sparse in literature and a consensus has not been reached.

Unusual characteristics of flowback and produced water including high TDS and organic content, requires fundamental and comprehensive understanding of the interaction of produced water constituents with frac fluid components. Understanding operational limits with respect to varying base water characteristics is key to the continued use of recycled water in practice^{102, 104}. The realization that fracturing does not require fresh water opens the door to new sources such cleaned-produced water.

Produced water treatment

While many treatment technologies can be applied to produced water, the economics of implementation and performance are the main factors to be considered for success. The main characteristic of produced water treatment is flexibility to accommodate the temporal and spatial variations in water quality and volume throughout well life. It is also of vital importance economically and practically to understand the treatment goals and final usage of cleaned-produced water so that only the required contamination is removed. High salinity of the water is an important parameter that needs to be fully considered since salt removal technologies have always been associated with high capital and maintenance costs.

Because of the large variation in produced water volume during well development, fixed treatment facilities are not always the best option. Mobile treatment plants designed for specific flow rates can be adjusted as the flow rates of the wells change. That is, a mobile plant designed for high

flow can be used during flowback and then moved to a new well that is being fracked, while a lower capacity plant can be used during the produced water phase, and so on. Mobile treatment plants have the potential to meet the immediate requirements of the wells and reduce pressure on operators because they can be readily mounted, dismounted, and transported between well sites. Mobile treatment plants would especially reduce trucking impacts particularly in Colorado where haul rates are substantial. Figure 12 illustrates the water management portfolio in hydraulic fracturing.

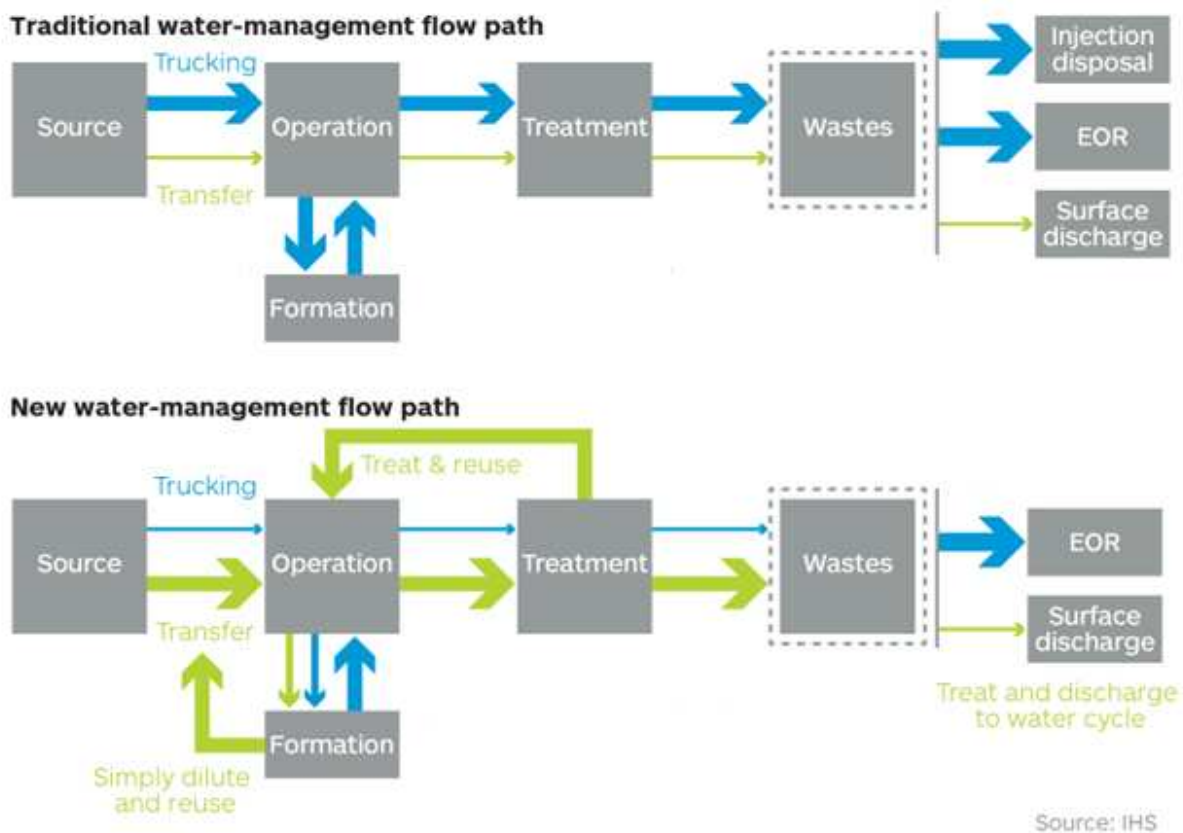


Figure 12- Water management in hydraulic fracturing

Treatment processes

Depending on the target water quality, several treatment processes could be deployed to treat produced and flowback water. The main contaminants that are necessary to address in produced water treatment, are suspended solids, organic compounds, and dissolved solids.

Primary treatment typically consists of physical removal of free oil and suspended solids. Dissolved air flotation, sedimentation are common in removing large particles and non-emulsified oil drops. However, oil water separation techniques are only required if the free oil content of water is high enough, i.e. early time flowback water.

Colloidal particles and stabilized suspended solids are responsible for the turbidity of water and don't settle in a reasonable timeframe. These particles are removed by chemical coagulation and electrocoagulation (EC). Destabilization and charge neutralization of these ultra-fine colloids occur by adding metallic coagulants, followed by flocculation in which destabilized fine flocs aggregates and form a large floc. Ferric chloride, alum, and polyaluminum chloride are among the most common coagulant and flocculants used in wastewater treatment. EC is an in-situ method of chemical coagulation whereby an electrical current induces sacrificial anode corrosion releasing trivalent iron and aluminum ions. As in chemical coagulation, the iron and aluminum ions hydrolyze to form coagulants and metal hydroxides that can charge neutralize and aggregate with solution particles to form settleable floc.

Softening is precipitation removal of the Mg and Ca ions via increasing water pH to 9.5-10.5. It is often less expensive than membrane processes, and it can achieve multiple objectives including more than 90% hardness removal^{130,131, 132,133}. Calcium and strontium carbonate and magnesium hydroxides and barium sulfate are can be removed with chemical precipitation. Ion exchange is

another process for dissolved ion removal used in water and wastewater treatment, in which the targeted ions in the water are exchanged for other ions fixed to the resins. Both softening and ion exchange techniques are used as a pretreatment to reverse osmosis (RO), where sodium and chloride are the primary target ions.

High organic content of these waters, which are residues of frac fluid chemicals particularly polymers and surfactants, can impact the efficacy of precipitation methods. Therefore higher coagulant dosage is required to overcome the large load of organic matter, increasing the cost of treatment associated with chemical consumption. Depending on the quantity and category of the organic compounds, activated carbon adsorption and chemical oxidations are among the organic matter removal methods in wastewater treatment processes. In recycling produced and flowback water, the quantity of these organic compounds are important due to interference with gelling agents and crosslinking phenomena in subsequent fracking operations, but has been neglected in industry.

Ultrafiltration can also be used as pretreatment or polishing step for RO, removing very fine but large molecular weight suspended solids that went through coagulation and flocculation units. A hydrostatic pressure is applied to push water against a semipermeable membrane with pore sizes in the range of 0.01 to 0.1 microns, equivalent to molecular weight of approximately 10,000 to 100,000 Daltons.

Reverse osmosis is the last step used in water treatment. The pore structure of RO membranes is much tighter than UF membranes, in fact RO membranes are capable of rejecting dissolved substances less than 100 Daltons molecular weight. Figure 13 shows a schematic of classification of membranes for different contaminants. The diffusion process is the fundamental mechanism of

RO membranes that is influenced by the gradient of chemical concentrations at the semipermeable membrane.

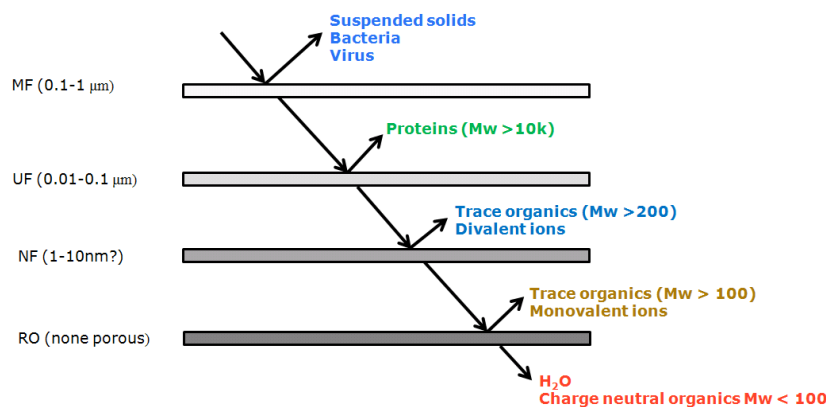


Figure 13-Classification of membrane filtration as a function of molecular weight cut off and pore size ¹⁸⁷

RO is mainly used to effectively eliminate monovalent ions (Figure 13) such as Na, B, K, Cl that are not removed during the previously mentioned processes. Due to the capital cost and complex operation and maintenance of these processes, pretreatments including precipitation, and ultrafiltration are necessary. Table 3 depicts the common treatments used to treat oil and gas waters, advantages, relative cost, and target water constituent.

Table 3- Characteristics of several treatment processes (^{188,189})

Treatment Type	Target Contaminant	Advantage	Disadvantage	Cost*
Dissolved air flotation/ Settling	suspended solid	Easy and simple operation/maintenance	Does not remove dissolved solids	Cheap

Chemical coagulation	suspended solid/ Ca, Mg	Easy and simple operation	Requires pH adjustment before/after Does not remove a broad range of dissolved ions Requires large coagulant dosage when treating flowback water Generates large quantity of solid waste	Relatively Expensive Chemicals including coagulants coagulant-aid are costly
Electrocoagulation	suspended solid/ Ca, Mg, Ba, Sr	Relatively easy operation and maintenance Generates relatively less solid waste Eliminates chemical transportation to field	Does not remove a broad range of dissolved ions Electrodes corrode after a while	Relatively cheap Electricity is the only cost
Ion exchange	Some dissolved ions	Removes dissolved inorganics effectively. Regenerable (service deionization). Relatively inexpensive initial capital investment	Does not effectively remove particles, pyrogens or bacteria. DI beds can generate resin particles and culture bacteria. High operating costs over long-term.	Relatively expensive
Activated carbon	Organic compounds	Removes dissolved organics and chlorine effectively. Long life (high capacity).	Can generate carbon fines	Relatively inexpensive
Ultrafiltration	Larger molecule organic compounds	Effectively removes most particles, pyrogens, microorganisms, and	It is pretreatment for RO Will not remove dissolved inorganics.	Cartridges are expensive

		colloids above their rated size. Produces highest quality water for least amount of energy. Re-generable.		
Reverse osmosis (RO)	All contaminant types	Effectively removes most of cations/anions and organic compounds	Complex operation and maintenance Require a complex pretreatment processes Flow rates are usually limited to a certain gallons/day rating Managing the brine solution is problematic	Huge capital costs Maintenance could also be costly depending on the level of damage to membrane

*Cost associated with each treatment is completely dependent on the specific inlet water quality, volume and effluent quality.

Electrocoagulation

Electrocoagulation (EC) is a common treatment practices that has been used in industry since the early 1900s⁷⁸. EC has also been one of the treatment methods used in oil and gas water treatment. EC uses electricity to oxidize and dissolve metal ions into solution and generate coagulants continuously in situ. It has been successfully applied to remove a variety of pollutants from

industrial wastewater such as hardness^{79,80,81}, chemical oxygen demand (COD)^{82,83,84,85} heavy metals, oil^{86,79,81} dye related organic compounds^{87,88} and other organic substances^{89,90}.

During the EC process, anode metal is oxidized to M^{n+} followed by hydrolysis to form aluminum or iron hydroxide which then acts to coagulate the negatively charged particles through one of following mechanisms⁹¹:

1. Destabilization of particles due to charge neutralization followed by flocculation.
2. Precipitation of a contaminant with either the cation or hydroxide ion; or
3. Formation of metal hydroxides that sweep through the water (sweep coagulation) incorporating particles into floc.

Recently, there has been renewed interest in EC for the treatment of industrial wastewater largely because of technological improvements that have led to lower electricity consumption and a higher quality output. While most studies focus on the treatment efficiency of wastewater or manipulating a specific parameter^{92,76}, there have been few studies focusing on the mechanisms of electrocoagulation or integration into an overall treatment process. Because EC is only part of a treatment train in oil and gas industry that will be designed to precipitate and remove solids, it is important to understand how EC interacts with compatible processes such as softening, flocculation and filtration.

3.1 Research hypotheses

Water resources are limited while water consumption is growing. Agricultural activity accounts for 85% of fresh water withdrawal in the US Midwest⁵² and, hence, is the largest consumer of freshwater in the US. Despite the history of oil and gas drilling in this region, modern technologies such as multi stage horizontal drilling with hydraulic fracturing has led to a dramatic growth in oil and gas operations and also increased the industry's water demand. In Colorado, with a semi-arid climate, the oil and gas industry has to compete with the primary historical water user, the agriculture sector, for water. Population growth is also a major and increasing burden on fresh water resources. Therefore, this newly evolved industry must adopt new strategies in order to maintain and grow their operations in this water scarce environment.

While working with oil and gas operators such as Noble Energy Inc. and service companies like Halliburton, a need for understanding the produced water treatment and fracking fluid was observed. Noble energy was the bellwether in recycling produced water in Colorado by recycling 11.8 million gallons of their water in 2012¹¹⁷. While operators in Southern Colorado recycled much of their waters, in Northern Colorado¹⁶², despite the heavy oil and gas operation, water recycling was not an attractive option. In Northern Colorado the cost of fresh water is low, disposal wells are scarce, and there is a lack of recycling infrastructure. Use of a gel frac system in fracking activities in the Front Range also makes flowback and produced water more challenging to treat.

There is a lack of fundamental and academic study of produced water quality and gelled frac fluids despite the importance of these subjects in recycling and reuse of produced water and flowback in hydraulic fracturing in Weld County, Colorado. The goal of this dissertation is to analyze and optimize two water management practices in hydraulic fracturing. In the first part the reuse and optimization of flowback and produced water treatment is studied. In the second part alternatives to freshwater resources are considered and the development of a frac fluid that is less sensitive to poor quality water is investigated. Since high organic content and dissolved solids associated with flowback and produced water have been insurmountable obstacles in the treatment and reuse of these waters, understanding the target contaminants, chemical interaction of organic matter and dissolved solids and gelled frac fluids, and the importance of economic of treatment process could lead to a more sustainable water management.

Five research hypothesis were developed to help to comprehend different produced water management techniques in oil and gas industry in Colorado.

- I. Divalent cations removal with EC can be optimized by consideration of sequencing pH values.
- II. The cost of treatment can be optimized by understanding the solubility of target salts and their pKa values.
- III. Recycling of flowback and produced water can be optimized by understanding minimum water quality targets for frac fluid formation.
- IV. Organic matter residuals in frac fluid and produced water could impact frac fluid development and stability by interfering with crosslinking mechanism.

- V. The water quality range that is compatible with acceptable frac fluid can be increased by optimizing pH, gel loading and cross linker concentration.

3.2 Research plans and objectives

The objectives and tasks associated with each hypothesis are outlined below:

- I. Hypothesis: Divalent cations removal with EC can be optimized by consideration of sequencing pH values.

Research Objective: Treat produced water using electrocoagulation and softening.

- i. Collect water at different ages, to include frac fluid and produced water, from Noble Energy, Inc. for wells drilled in the Wattenberg Field since 2012.
- ii. Run water quality analysis on each raw water samples.
- iii. Treat each samples at two sequence, EC before softening and Softening before EC.
- iv. Run same analysis on the treated samples.
- v. Determine if any trend exist for each target pollutant or water quality parameter.

II. Hypothesis: The cost of treatment can be optimized by understanding the solubility of target cations and their pKa values.

Research Objective: precipitation of calcium, magnesium, barium and strontium were examined experimentally by adding target ligands followed by solid separation with electrocoagulation.

- i. Collect experimental data for removal of Ca, Mg, Sr and Ba.
- ii. Find the pKa values and determine the solubility of possible salts associated with each cation
- iii. Model the water chemistry with OLI (commercially available chemical equilibrium software)
- iv. Compare the theoretical removal rates with experiment results at different pHs

III. Hypothesis: Recycling of flowback and produced water can be optimized by understanding minimum water quality targets for frac fluid formation.

Research Objective: Study the influence of individual cations and anions on frac fluid stability

- i. Study the water quality of fresh water sources for hydraulic fracturing.
- ii. Determine three conditions representing the typical concentration of targeted ions for study

- iii. Spike CSU tap water with associated salts to reach to target concentration
- iv. Make frac fluid using the spiked water
- v. Run viscosity test for 45 minute
- vi. Plot each viscosity and assess the profiles

IV. Hypothesis: Organic matter residuals in frac fluid and produced water could impact frac fluid development and stability by interfering with crosslinking mechanism.

Research Objective: Understand the possibility of reusing produced water in hydraulic fracturing.

- i. Collect treated produced water from a commercial treatment facility.
- ii. Run water quality analysis on the sample, TDS, TOC, ..
- iii. Build a synthetic (model)water based on the ionic TDS of treated water sample
- iv. Dilute both model and treated water to reach to lower TDS values, 13000 mg/l, 11000 mg/l, 9000 mg/l, 7000 mg/l, 5000 mg/l and 3000 mg/l
- v. Run viscosity test for 45 minute for each samples
- vi. Plot each viscosity and assess the profiles
- vii. Analyze the result

V. Hypothesis: The water quality range that is compatible with acceptable frac fluid can be increased by optimizing pH, gel loading and cross linker concentration.

Research Objective: Optimize CMC based frac fluid for using model water by changing pH, gel loading and crosslinker concentration.

- i. Discuss the frac fluid composition and understanding the main and base components of frac fluid with Halliburton
- ii. Find the proper range for each of pH, gel loading and crosslinker
- iii. Build model water and dilute it to TDS= 15,000 mg/l, representing extreme condition
- iv. Build model water and dilute it to TDS= 2,500 mg/l, representing relatively moderate condition
- v. Build different frac fluid samples using model water and run viscosity test
- vi. Plot viscosity versus time
- vii. Analyze the results
- viii. Validate or invalidate the hypothesis
- ix. Publish the results in two peer review journals

4.1 Influence of softening sequencing on electrocoagulation treatment of produced water

4.1.1 Introduction

Produced Water

Produced water is the largest waste byproduct generated by the oil and gas industry. Approximately 80 million barrels of oil are produced each day around the world yielding about 250 million barrels of produced water⁵⁸. However, the quantities and characteristics of produced water are not uniform and depend on multiple factors, including the type of hydrocarbon that is produced, the geology of the formation, and the method of extraction⁷². Produced water that contains a high amount of total dissolved solids (TDS) requires significant treatment in order to be used for irrigation, agriculture, or to be discharged into surface waters. The predominant practice for produced water disposal is deep well injection through a Class II injection well (according to EPA classification), which is popular due to lower costs and less required pretreatment. Currently, over 90% of produced water is disposed of by injection into deep wells in the United States⁵⁸; the remaining water is generally discharged into surface waters, reused for crop irrigation or for hydraulic fracturing.

Although a few new treatment methods have become available recently, producers still hesitate to consider new technologies due to high costs and the past experiences with unreliable treatment methods. Given the large amount of produced water, the growing demands on freshwater

resources, and consumption of the energy on water transportation and reinjection of produced water, there is a significant incentive to recycle and reuse as much produced water as possible. Since current regulations do not allow produced water to be released into surface waters directly, it is usually either injected into disposal wells or treated to a quality that can be reused or discharged. However, water shortages in many areas make it advantageous to reuse and recycle the produced water.

Electrocoagulation

One of the common treatment practices is electrocoagulation. Electrocoagulation (EC) has been one of the treatment methods used in oil and gas water treatment. EC was introduced in the early 1900s⁷⁷. EC uses electricity to oxidize and dissolve metal ions into solution and generate coagulants continuously in situ. It has been successfully applied to remove a variety of pollutants from industrial wastewater such as hardness^{78,79,80}, chemical oxygen demand (COD)^{81,82,83,84} heavy metals, oil^{85,78,80} dye related organic compounds^{86,87} and other organic substances^{88,89}. During the process of EC, anode metal is oxidized to M^{n+} followed by hydrolysis to form aluminum or iron hydroxide which then acts to coagulate the negatively charged particles following one of the three mechanisms⁹⁰:

4. Destabilization of particles due to charge neutralization followed by flocculation.
5. Precipitation of a contaminant with either the cation or hydroxide ion.
6. Formation of metal hydroxides that sweep through the water (sweep coagulation) incorporating particles into floc.

Recently, there has been renewed interest in EC for the treatment of industrial wastewater largely due to the technological improvements that have led to lower electricity consumption and a cleaner output. While most studies focus on the treatment efficiency of wastewater or manipulating a specific parameter^{91,76}, there have been few studies focusing on the mechanisms of electrocoagulation or the integration into an overall treatment process. Since EC is only part of a treatment train that will be designed to precipitate and remove solids, it is important to understand how EC interacts with compatible processes such as softening, flocculation and filtration.

4.1.2 Materials and Methods

Electrocoagulation Unit

A commercial EC package manufactured by WaterTectonics Company (Everett, WA) was used for this study (Figure 14a). The EC unit utilized in this study consisted of aluminum and iron round-plate electrodes in an even quantity. The apparatus was a 30 cm (height) by 12 cm (diameter), table-mounted cylindrical vessel that consisted of eight electrode-discs, 7.4 cm in diameter.

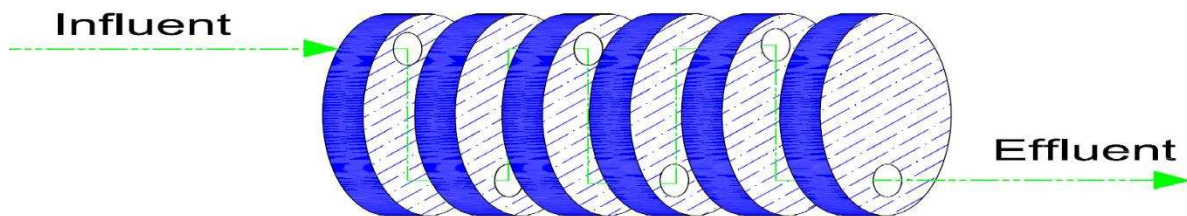


Figure 14-Electrocoagulation unit and electrode configuration

The gap between electrodes was 1 cm. Electrodes configuration is shown in Figure14b. The polarity of the electrodes was switched automatically by a control system every 90 seconds so that the iron and aluminum plates served as both anode and cathode depending on the polarity. It was also switched physically, swapping the cables and leads before each run for all runs. The polarity is reversed, switching anode/cathode sites, to ensure even wear on the cell plates and to double the life of the cell by minimizing mineral fouling.

A 92.4 ± 3.3 amp current with a voltage of 18 ± 4.5 volts was used. Four liters of samples were tested for each run and the flow rate was set at 6.8 liters per minute (0.11 l/s) with a run time of 35 seconds for all tests.

Produced Water Samples

The water samples were taken from oil and gas wells in the Wattenberg field of northeast Colorado shortly after flowback began (<2 days) for 160 days thus incorporating a wide range of water quality. All sampled wells were hydraulically fractured with either guar based, pH 10.2 fluid or cellulose based gel with a pH of 5.0. To have an adequate and comprehensive data coverage for different type of wells and produced water, it was decided to choose several different wells with different time of flow back, meaning that the samples were chosen based on the age of each well since the objective of the study was to run experiments at multiple points in the life cycle of production. Typical water production rates are shown in Figure 15. The average production bbl/d for 86 horizontal wells are shown in this plot.

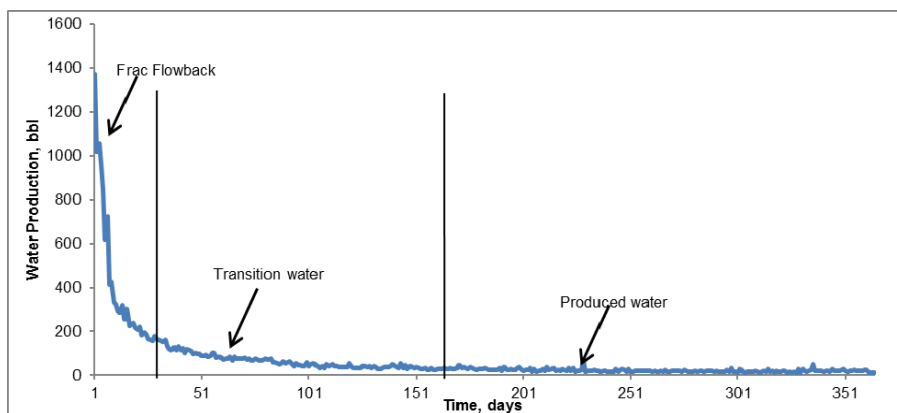


Figure 15-Average water production rate of 86 horizontal wells in Weld County⁹⁷

The ages of the eight samples collected after flowback began were: 1, 2, 30, 60, 90, 153, 161 and 183 days. Water samples were collected in 5-gallon containers, stored at room temperature and covered until treatment was performed within 5 days.

Experimental Plan

Two sets of experiments were run on each water sample. The objective was to investigate the effect of chemical softening on EC including understanding if particle formation (e.g. $\text{CaCO}_{3(s)}$) before electrocoagulation resulted in better overall removal of metal ions. Therefore, softening was performed both before and after running EC on each sample by raising the pH to 9.5 before and 10.2 after EC. The pH of 10.2 was chosen for softening after EC since it is the pH that is being used in the treatment process for the water being examined (the control condition in this study). The hypothesis was that softening could be done at a lower pH before EC resulting in lower chemical costs while still increasing removal efficacy. Suspended solids after softening and EC treatment processes were filtered through a 2.5 μm , Whatman 42 filter followed by pH adjustment of the final sample. A schematic diagram of the treatment, sampling and analysis process is shown in Figure 16. Softening after and before EC are shown as process 1 and 2, respectively. Three sets of samples were taken for each raw water sample including raw total and final samples for each process. Final sample was taken at the end of each process.

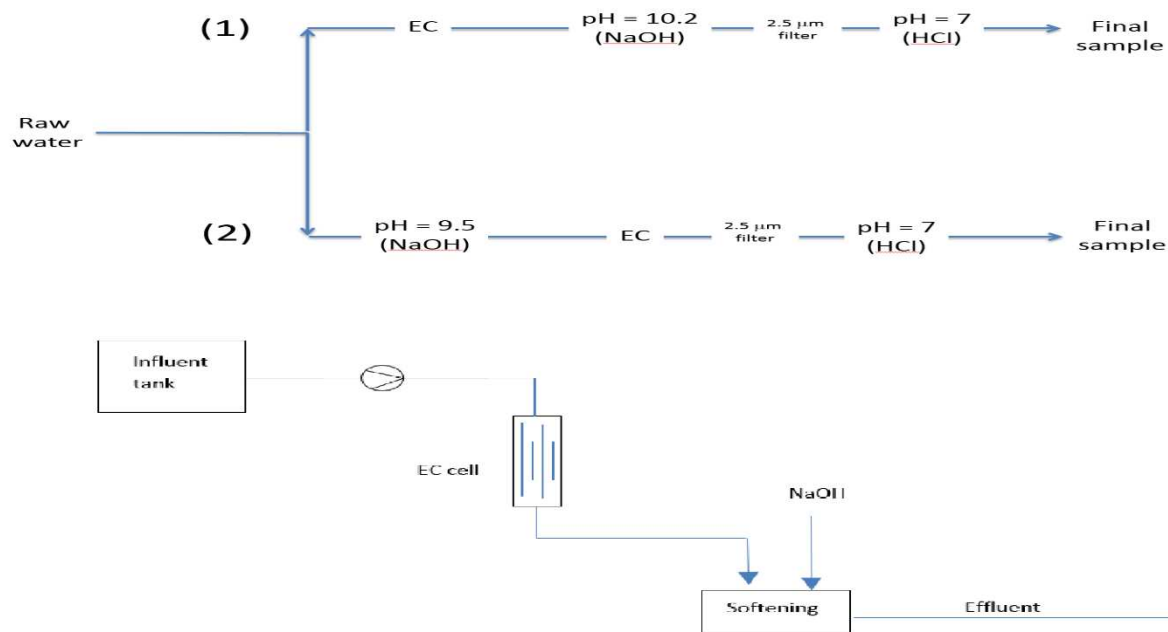


Figure 16-A schematic diagram of experimental plan and line diagram of experimental set up for EC-Soft

The stock solutions of 10N sodium hydroxide and 5N hydrochloric acid were used to raise the pH of samples and to lower the pH to 7 at the end of each process. The chemicals were obtained from VWR in Radnor, PA.

Water Quality Analyses

All water quality analyses were done using Standard Method procedures⁹². The chemical oxygen demand (COD), TOC, turbidity, pH and total suspended solids (TSS) analyses were conducted at the Colorado State University water quality laboratory. eAnalytics Laboratory (Loveland, CO) provided analysis of metals, cations and anions. Total dissolved solids (TDS) concentration was calculated by summing the anion and cation concentrations. pH was measured using a Hach (Hach, Loveland), HQ40d pH meter. TSS and TOC were measured based on Standard Methods 2540D and 5130B, respectively. COD and turbidity analyses were conducted using a Hach COD high

range kit with colorimeter, Hach DR400 U and Hach 2100 N Turbidimeter, respectively. Cations were measured based on EPA method 6010 C using a Varian ICP-AES, Liberty AX.

Theoretical Iron Generation Based on Faraday's Law

The mass (m) in grams of metal oxidized or reduced at a specific current (I , amps) and period of time (t , sec) can be calculated using the following expression of Faraday's law:

$$m = I \times t \times M / (Z \times F)$$

Where Z is the number of electrons transferred (eq/mol), M is the molecular weight (g/mol), and F is Faraday's constant (96,485 Coulombs/eq).

Using Faradays' law, aluminum and iron ions for both softening/EC and EC/softening runs were generated at a rate of 37.5 ± 2.2 mg/L and 116.8 ± 6.9 mg/l, respectively.

4.1.3 Results and Discussion

Raw Water Quality

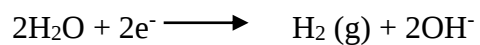
Raw water quality parameters of the collected produced water are shown in Table 4. As discussed previously, the produced water characteristics change over time and are not consistent, even for a specific well. The pH for the raw water samples was inconsistent and varied between 6 and 7 with the age of the wells. The other water quality parameters including TOC, monovalent and divalent cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc) and anions (Cl^- , CO_3^{2-} , etc) were also inconsistent and varied for each sampled well. This observation has been confirmed in the literature^{58,117}. As shown in Table 4, total dissolved solids (TDS) increased from 13,200 mg/l to over 30,000 mg/l, as the water

being produced is more indicative of formation equilibrium conditions. During this period, total organic carbon (TOC) decreases by half from over 2000 mg/l to less than 1000 mg/l. The decrease in TOC is likely due to the flushing out of the organic matter associated with the gels added to aid in the fracking process. As the well ages, a greater fraction of the water is influenced by formation water and less by the frac fluid originally injected.

Table 4- Raw water quality for produced water samples

Water quality parameter	Sample age(day)							
	1	2	30	60	90	153	161	183
Aluminum(mg/l)	1.27	1.19	1.29	1.50	0.40	1.37	1.60	1.10
Boron(mg/l)	12.50	12.90	17.50	23.50	21.00	23.00	13.30	20.40
Barium(mg/l)	2.88	3.85	6.57	11.80	23.10	15.00	30.60	30.50
Calcium(mg/l)	94.70	104	206	397	282	267	301	294
Chloride(mg/l)	6840	6720	11100	16815	14340	22209	21613	20647
COD(mg/l)	919	1100	840	1120	522	680	1163	480
Iron(mg/l)	11	15.10	52.40	102	154	63.80	189	160
Magnesium(mg/l)	15.00	17.70	30.60	53.30	45.70	47.40	54.80	48.80
Strontium(mg/l)	12.40	14.50	28.00	48.80	44.40	49.50	52.70	51.40
TDS	13174	12593	17368	16787	25457	36969	38174	34359
TOC(mg/l)	2184.33	2490.25	2027	1286	1760.50	512	806	843
Turbidity(NTU)	679	526	875	3944	1115	1591	3733	3440

The first set of experiments (designated EC-Soft) involved EC processing followed by chemical softening at pH=10.2 and size exclusion filtration. The second set of experiments (designated Soft-EC) included softening at pH=9.5 followed by EC and the same disc filtration. The pH increased for all samples after EC treatment, a result consistent with previous studies^{118, 119, 79}. This observation is thought to be due to cathodic OH⁻ production;



Magnesium and Calcium

Figure 17 shows magnesium and calcium concentrations and removal rates of the different treatment sequences. Ca^{2+} and Mg^{2+} concentrations in the raw water samples showed an increasing trend over time. The maximum hardness level ($4.12 \times \text{Mg}^{2+} \text{ mg/l} + 2.5 \times \text{Ca}^{2+} \text{ mg/l}$) concentrations, was 1214 mg/l as CaCO_3 , observed for the 2- month old sample and the minimum was 287 mg/l as CaCO_3 with the one-day sample.

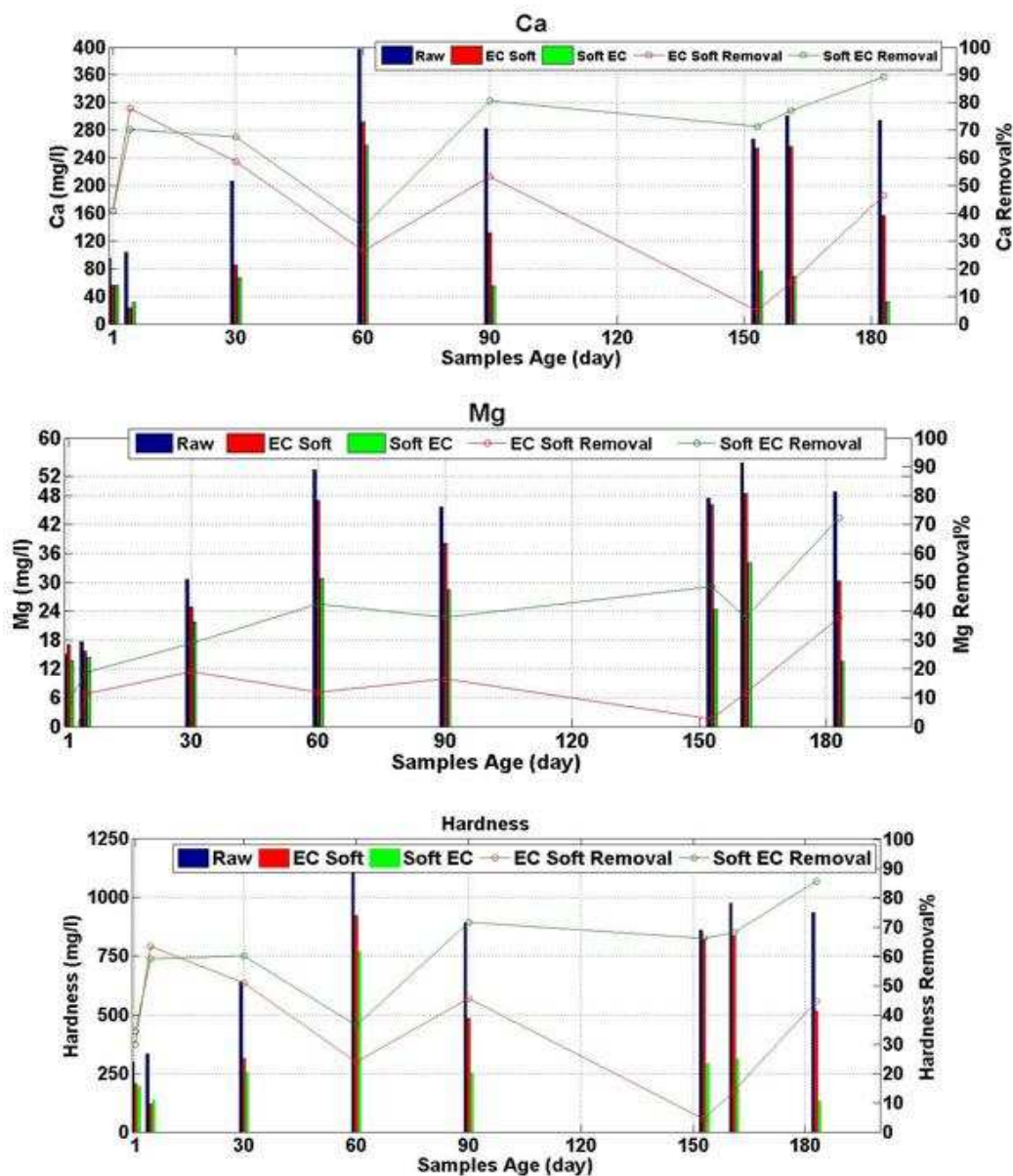


Figure 17- Mg^{2+} , Ca^{2+} and hardness concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.

The maximum removal rate of Ca^{2+} for Soft-EC was 90% and occurred with the 183-day sample (oldest sample tested). For EC-Soft the maximum removal rate occurred with the 2-day sample,

approximately 70%. However, the maximum removal rate for Mg^{2+} with both Soft-EC and EC-Soft occurred with the 183-day sample at approximately 70% and 40%, respectively. As seen in Figure 17, there is a flat and slightly up trend in removal efficacy of Soft-EC over time. Figure 17 shows the gap between Soft-EC and EC-Soft removal efficiencies increased over time. Also Soft-EC efficacy becomes significantly greater with water collected after 1 month as the raw water Ca^{2+} and Mg^{2+} concentrations get higher and solids removal becomes greater. Both magnesium and calcium concentrations in raw water increased by 70% from 30-day to 60-day. The hardness stayed constant at 895 ± 63 mg/l for the samples collected after 60 days. For hardness removal, Soft-EC had significantly higher removal efficiency than EC-Soft with samples older than 60 days. This could be explained by precipitation of calcium ions as calcium carbonate before the electrocoagulation treatment resulting in an increase of the effectiveness of solid-liquid separation. However with EC-Soft, softening at a pH of 10.2 after EC, solids removal did not appear to work as efficiently since calcium and magnesium solids are formed after the coagulation process. For the early samples, both methods' removal efficiency decreased and converges with the 2- day old sample. Also, the graphs show that the maximum hardness happened with the 2-month old sample. However, the minimum removal for both Soft-EC and EC-Soft happened with the 1-day sample, 8.7% and -13.3% for Mg^{2+} , and 35% and 4.9% for Ca^{2+} , respectively. These results could be due to the presence of high concentrations of organic matter in the early samples leading to re-stabilization of colloids and prevention of floc aggregation and subsequent settling. To support this hypothesis, TOC values were measured for all the samples. Figure 18 shows the TOC values for the raw water samples. The plot indicates that the TOC is significantly higher for samples younger than seven days and decreases over time confirming the hypothesis of high loads of organic matter can causes difficulty in treatment of early flow back water.

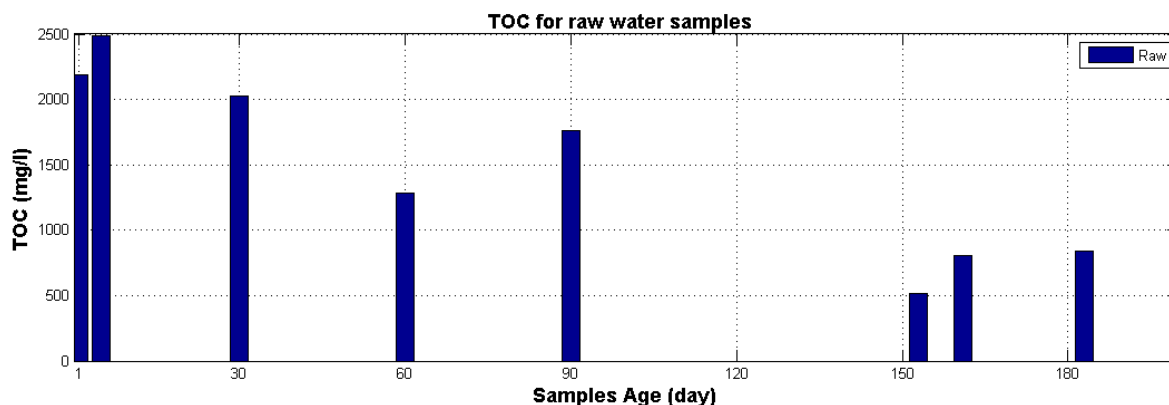


Figure 18-Raw water TOC value as a function of time (well age).

Another observation is that Ca^{2+} removal with both methods was higher than Mg^{2+} removal since magnesium precipitates as magnesium hydroxide at a higher pH than calcium carbonate requiring a pH greater than 11 to precipitates as hydroxide^{120,121}. In Table 5, the K_{sp} and molar solubility are shown for possible Ca, Mg, Ba and Sr compounds. Magnesium hydroxide requires a pH of 11.2 in order to precipitate¹²², which is higher than calcium carbonate's required pH of 9.4^{123,124}. Due to the fact that having an inert salt in a sparingly soluble salt increases the solubility of the sparingly soluble salt¹²⁵ the high salinity of the waters studied here impacts the removal of divalent cations.

Barium and Strontium

Barium and strontium are also targeted for removal from produced water. Barium and strontium are members of the alkaline earth group of elements and, as such, have similar chemical properties to calcium and magnesium^{126, 127}. The higher solubility of barium hydroxide compared to magnesium hydroxide indicates that its formation in a traditional lime softening process would not usually be a practical way to remove barium from a wastewater. Strontium hydroxide is fairly

soluble in water while the other Sr^{2+} complexes, in particular the carbonate, are relatively insoluble (Table 5).

Table 5-Solubility products and solubility of possible compounds at 20° C and standard conditions ¹²¹

Compound	K_{sp}	Solubility of salt (mol/L)	Compound	K_{sp}	Solubility of salt (mol/L)
SrSO_4	3.2×10^{-7}	5.7×10^{-4}	BaSO_4	1.1×10^{-10}	1.05×10^{-5}
SrCO_3	5.6×10^{-10}	2.4×10^{-5}	BaCO_3	5.1×10^{-9}	7.1×10^{-5}
Sr(OH)_2	6.4×10^{-3}	8×10^{-2}	Ba(OH)_2	5×10^{-3}	7.1×10^{-2}
Mg(OH)_2	5.6×10^{-12}	2.4×10^{-6}	MgCO_3	6.82×10^{-6}	2.6×10^{-3}
CaCO_3	3.36×10^{-9}	5.8×10^{-5}	CaSO_4	7.1×10^{-5}	8.43×10^{-3}
CaCl_2	1210	3.5×10			

The concentrations for both Ba^{2+} and Sr^{2+} are shown in Figure 93. Similar to Ca^{2+} and Mg^{2+} , Ba^{2+} and Sr^{2+} concentrations increased over time in raw water and the minimum concentration occurred at the 1-day old sample. Also the Sr^{2+} and Ba^{2+} concentrations in raw water tended to be constant at and after the 60-day sample staying at 49.4 ± 3.1 mg/l and 26.8 ± 7.8 mg/l, respectively. The same shift in raw water concentration with the 60-day old sample is also seen here. Barium (Ba) increased from 6.6 mg/l to 11.8 mg/l, showing an 80% increase and strontium increased from 28 mg/l to 48.8 mg/l (74% increase). These results confirm that the formation is significantly impacting the water quality beginning at less than 30 days.

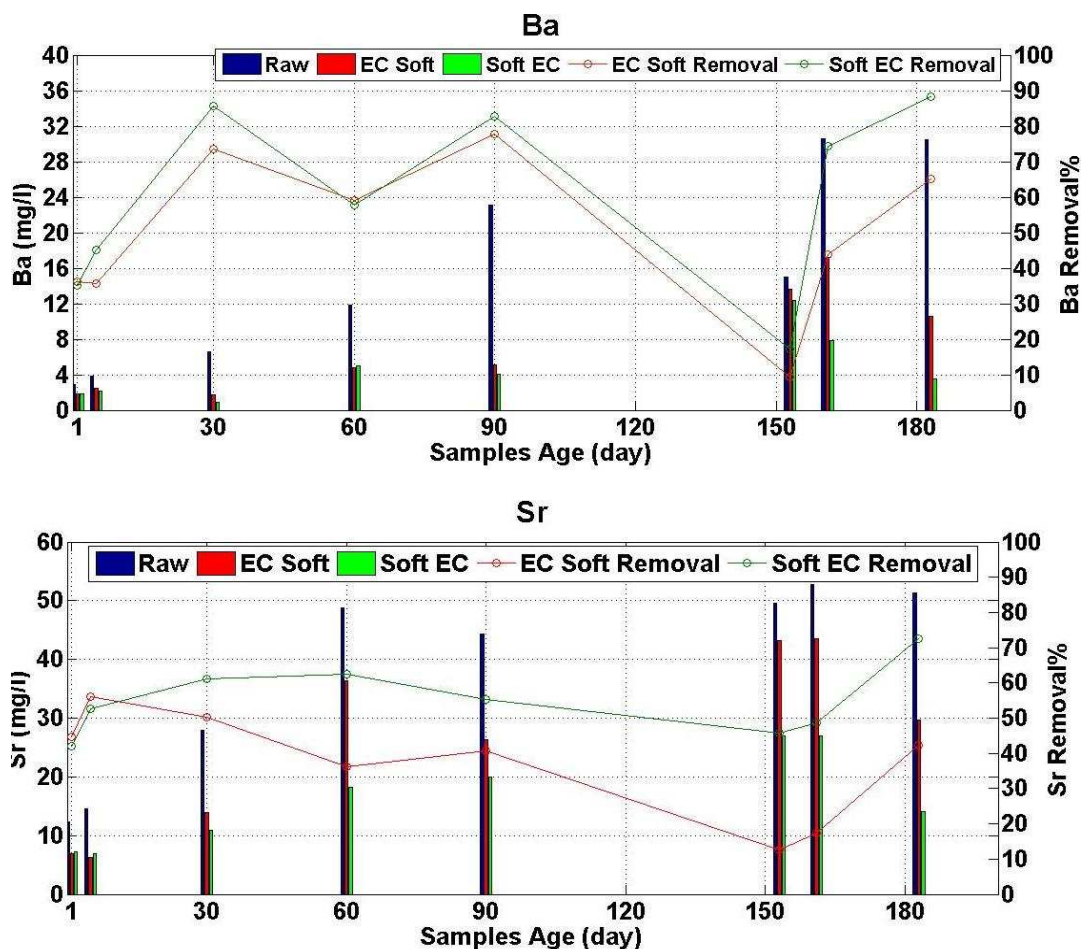


Figure 19-Ba and Sr concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.

Both treatments' removal efficiencies for Ba^{2+} and Sr^{2+} were similar to the hardness ions' removal. However, Sr^{2+} removal efficacy is significantly greater for Soft-EC (61.1%) than EC-Soft (50.4%), starting from the 1-month sample point. For Ba^{2+} removal however, this starts at the 161- day sample with 74.2% and 43.8% for Soft-EC and EC-Soft, respectively. Despite the concentrations increasing over time in raw water, the maximum removal efficiency occurred with the oldest sample and in contrast, the minimum efficiency occurred with the early stage samples. Soft-EC seems to be more efficient as concentrations get higher, particularly for Sr. The maximum removal

for both EC-Soft and Soft-EC occurred with the oldest sample and Soft-EC maximum removal rate was 88.4% and 72.6% for Ba and Sr, respectively.

Insight on this observation can be obtained by considering the solubility product constant, K_{sp} . Using K_{sp}^{119} , the solubility of each compound was determined for the dissociation of M_xA_y salt.



$$K_c = [M^{y+}]^x [A^{x-}]^y$$

K_{sp} and associated solubility of possible compounds are given in Table 2. A metal ion may be precipitated with a proper ligand so it will coagulate and settle out. In fact, a compound with a lower K_{sp} is more readily precipitated out of a solution¹²⁰. Considering the supersaturated conditions of the solution, solubility of these compounds, and the fact that the lower the value the more probable the precipitation of a salt, $BaSO_4$ will likely precipitate. Since $BaSO_4$ is less soluble than $SrCO_3$ it will precipitate to a greater extent, an observation supported by the higher Ba removal with both treatments.

Boron

Boron is also challenging to remove by softening¹²⁵ since it is typically present as borate ions $B(OH)_4^-$ ($pK_{a1}=9.2$) at pH greater than 9.2.

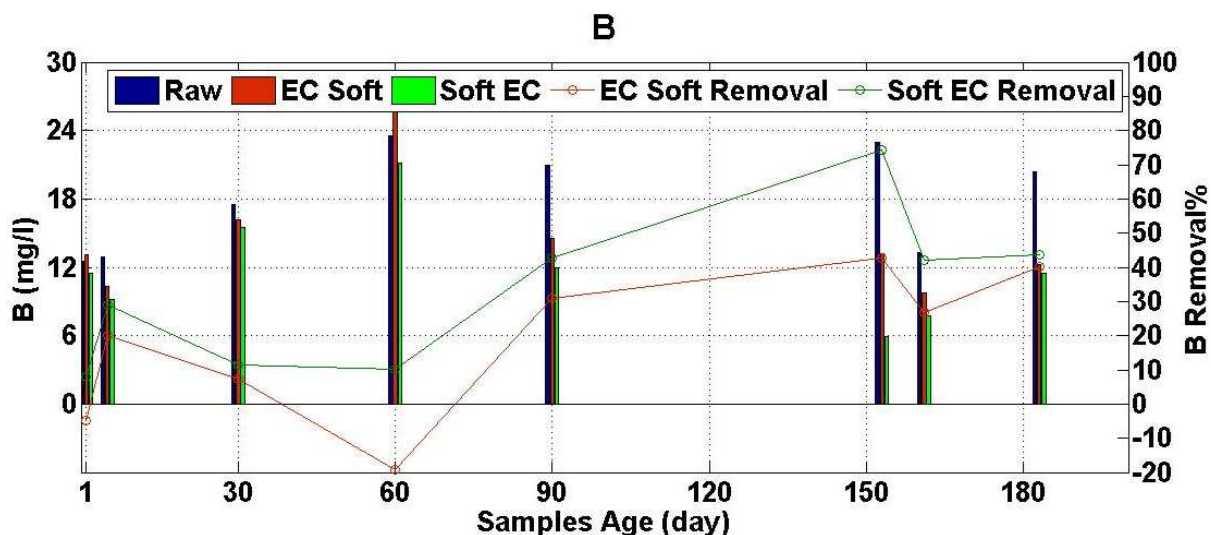


Figure 20-Boron concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.

As shown in Figure 20, boron's raw water concentration does not have a noticeable trend and treatment efficacy is also erratic. Raw water boron concentration ranged from approximately 12 to 24 mg/l and Soft-EC was more effective than EC-Soft with removals for the 1-month sample being over 250% higher. Although the maximum concentration in raw water occurred at the 2-month old sample at 23.5 mg/l, the minimum removal rate (similar to the rest of the ions) happened with the 1-day old sample (having the lowest concentration, 10 mg/l) with 8% for Soft-EC. However it should be noted that EC-Soft had a negative efficacy at the 1-day and 60-day old samples in contrast to Soft-EC. The maximum removal rate for both EC-Soft and Soft-EC was 43% and 74%, respectively, with the 153-day old sample.

TOC and Turbidity

TOC and turbidity concentrations and associated removal rates are shown in Figure 21.

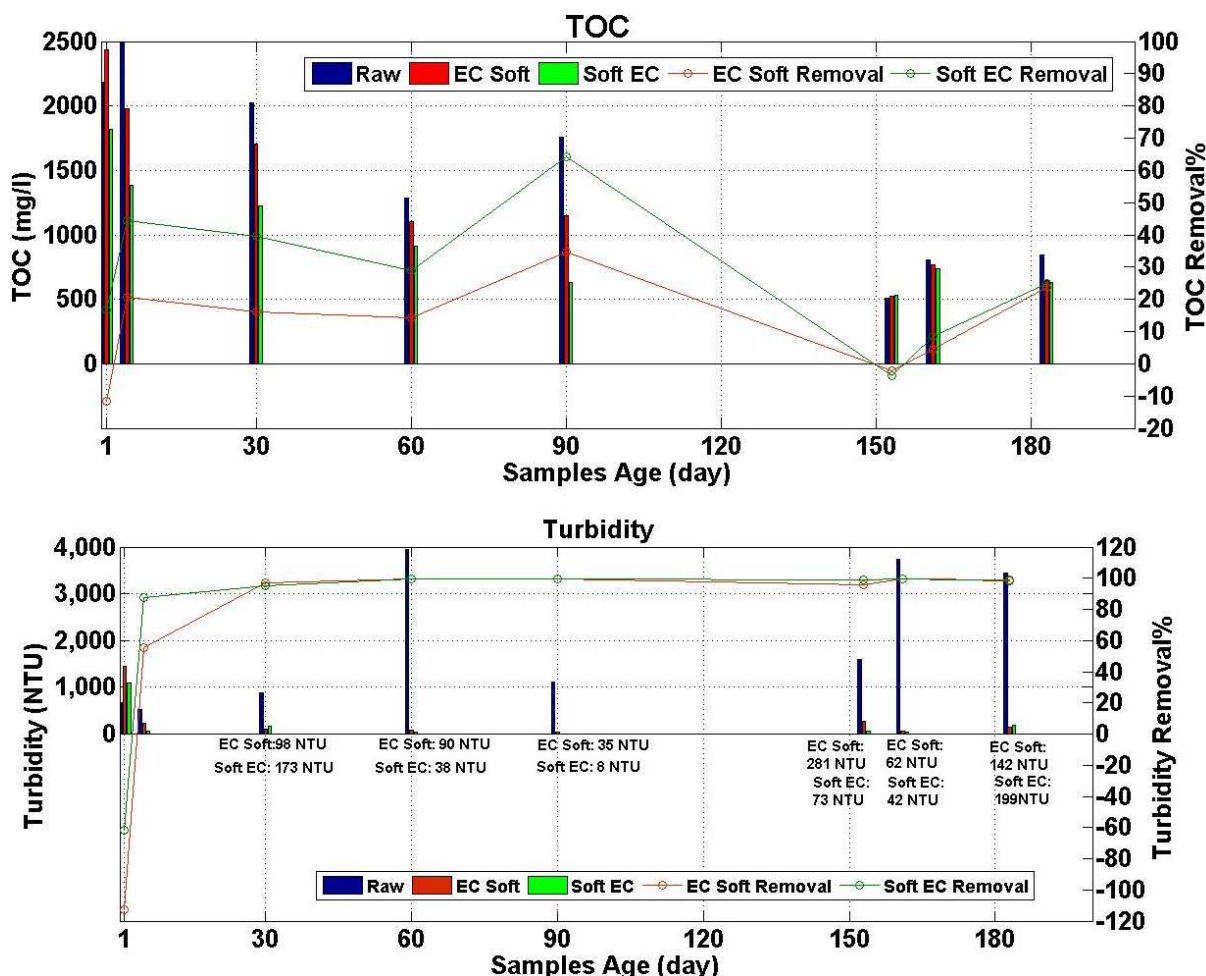


Figure 21-TOC and turbidity concentrations and removals as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.

Raw water TOC concentration is high initially (>2400 mg/L) due to the guar-based organic matter that is present in the frac fluid. The TOC concentration decreases with time as the flowback becomes diluted with formation water and is less under the influence of the frac fluid that was injected. The maximum TOC occurred with the 2-day sample at 2490 mg/L and the minimum was 512 mg/l with the oldest sample (153 days). TOC removal rates for both treatments were higher for early samples (flowback water) whereas cation removal rates were higher for later samples (produced water). Soft-EC was generally more effective than EC-Soft for TOC removal,

with a lower removal rate only with the 153 day sample. The maximum removal efficiency for both treatments occurred with the 3-month old sample at 64% (Soft-EC) and 35% (EC-Soft) removal.

As discussed above and illustrated in Figure 21, the highest organic matter concentration occurred in the early samples (1-day and 2-day samples), which could explain the treatment challenges in the early produced water stage. Turbidity with earliest samples (Day 1 and Day 2) were relatively low (<700 NTU) and the post-treatment values increased because the micro-floc, very fine flocs which were observed after treatment, that did form would not aggregate to a size that would settle or filter. As discussed earlier, it is postulated that the high concentrations of organic matter (including surfactants) could be stabilizing these micro-floc after formation preventing flocculation.

Both Soft-EC and EC-Soft had significantly greater removal efficacy, more than 95%, for samples older than 30 days. Although the raw water turbidity dropped by 23% with the 2-day sample from 679 NTU to 526 NTU, there was a 242% increase in removal efficiency of Soft-EC and 149% in EC-Soft removal efficiency. Another notable observation is that both treatments converge as the turbidity increased over time, an observation opposite of that seen for the metal ions (cations) and TOC. In these cases, as the concentrations increased, the removal rates diverged. In fact there was no major difference in solids removal (turbidity reduction) with the operation of EC-Soft and Soft-EC for water samples collected from wells that had been flowing back for a month or more. Both methods had a negative removal rate for early produced water (1-day and 2-day samples). The additional dissolved Al^{3+} and/or Fe^{3+} ions that were added with the treatment increased the

turbidity in the water samples since these metals were forming hydroxide complexes without subsequent effective coagulation and removal.

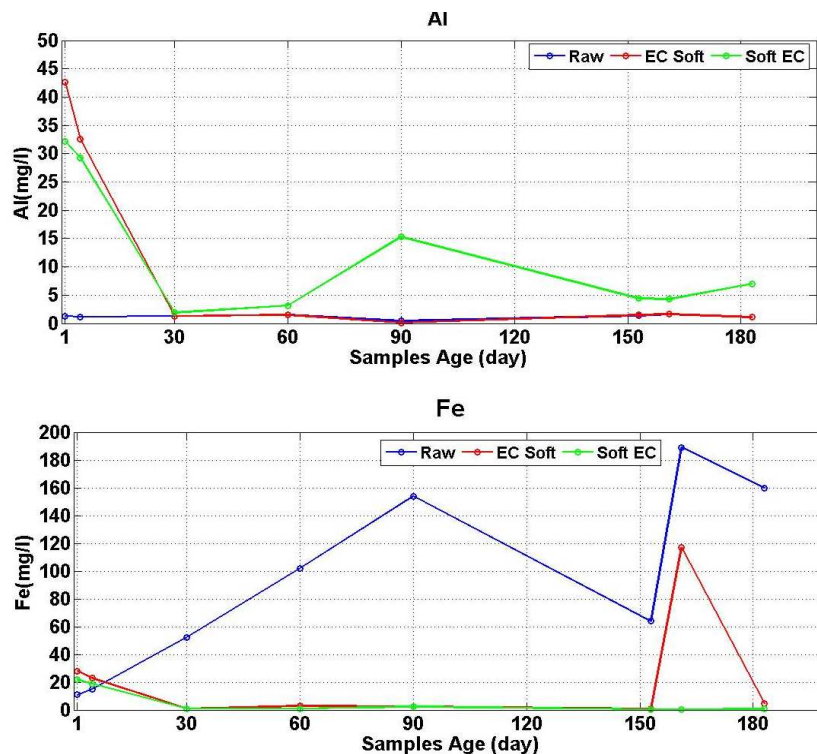


Figure 22- Al and Fe concentrations as a function of time. EC-Soft designates electrocoagulation followed by chemical softening, Soft-EC the reverse.

As observed in Figure 22, Al is negligible in the raw produced water unlike Fe that was present in concentrations that increased with well age. Al and Fe were added during electrocoagulation treatment by dissociation of the electrodes and during the early flowback period (Day 1, Day 2), these concentrations are higher in the treated water than in the raw water. This is likely due to the re-stabilization of colloids that occurs when charged organic matter adsorbs to the metal hydroxide surface. At the 30 day sample and older, Fe is mostly removed, a result that supports the solids removal efficacy shown in Figure 22. The Al results however, indicate a trend where the treated

concentration is higher than the raw water measurements. This is most likely due to Al dissolving from the electrodes as Al(OH)_4^- at the elevated pH, the primary issue with the Soft-EC process.

4.1.4 Conclusions

In this study, the impact of sequencing of softening with electrocoagulation treatment of produced water was examined. Overall, softening at a lower pH (9.5) before EC was more effective than softening after EC with a higher pH (10.2). In particular, Soft-EC removal efficiency was greater for Ba, B, Sr, Ca, Mg, Fe and TOC. Other observations include:

1. Both treatment sequences showed similar solids removal effectiveness (as measured by turbidity) after one month or more of flowback. This is likely due to the decrease in organic matter constituents that have not been identified.
2. However for the early flowback water (one and two day old samples), there was not a substantial difference in suspended solids removal efficiency between Soft-EC and EC-Soft. Both EC sequences were ineffective coagulating and flocculating colloids resulting in unacceptable treatment.
3. It appears that even though turbidity measurement could not resolve a difference in solids removal between the two process sequences, the increased removal of metals and TOC is a result of precipitating solids (e.g. $\text{CaCO}_{3(s)}$) before the EC process, leading to more effective subsequent solid-liquid separation.

4.2 Optimizing Metal-Removal Processes for Produced Water with Electrocoagulation

4.2.1 Introduction

Unconventional oil and gas development has been increasing rapidly throughout the United States, due largely to technical advancements in directional drilling and hydraulic fracturing techniques. Shale oil and gas production, one form of unconventional development, requires large volumes of water for hydraulic fracturing and much of this activity occurs in areas of the country that are prone to drought and water shortages¹¹⁷. The concurrence of large water requirements and water stressed regions has led to significant interest in reuse of the water that is returned during oil and gas production, commonly referred to as frac flowback and produced water¹²⁸. Historically, water co-produced with oil and gas (produced water) has been disposed of through evaporation or deep well injection, approaches that do not conserve the resource for beneficial reuse. Reuse of flowback and produced water currently varies significantly from region to region and even within the same oil and gas basin. For example, recycle of produced water is less than 10% of the total water used to drill and fracture in the Barnett, Fayetteville and Haynesville shale plays. However the fraction of water recycled is significantly higher in the Marcellus play, greater than 90% of the total water used¹²⁹.

Although treatment methods have been developed to recycle produced water for subsequent frac operations, wide spread adoption is often limited by costs. Important treatment aspects for frac water reuse include particle removal, reduction of scale forming metals, and disinfection. Removal of total dissolved solids (TDS) is expensive and therefore avoided if possible. Frac fluids have been developed that are compatible with high TDS concentrations but the other objectives (solids reduction, scale control and bactericide) almost always need to be satisfied. The focus of this study

was to examine the metal removal processes associated with reducing scaling potential using lab scale data and chemical equilibrium modeling with the goal of optimizing chemical use and minimizing cost.

Softening

Inorganic elements such as calcium, barium, magnesium and strontium either cause hardness/scaling issues or failure in frac fluid development. While there are proven methods for the removal of some of these contaminants, data on precipitate removal at high pH for produced water is lacking¹²⁶. Precipitative softening, one of the oldest and most common methods of divalent cation removal^{130,131, 132,133}, is often less expensive than membrane processes, and it can achieve multiple objectives including more than 90% hardness removal. Calcium and magnesium are removed from water as CaCO_3 , and $\text{Mg}(\text{OH})_2$, strontium and barium as the carbonate and sulfate, respectively.

Electrocoagulation

Electrocoagulation (EC) is an electrochemical method of treating polluted water whereby an electrical current induces sacrificial anode corrosion releasing trivalent iron and aluminum ions. As in chemical coagulation, the iron and aluminum ions hydrolyze to form metal hydroxides that can charge neutralize and aggregate with solution particles to form floc that can be removed with a range of solid-liquid separation processes. Accompanying electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode⁷⁷. Electrocoagulation has been successfully applied for more than three decades as a water treatment technology to remove an extensive range of pollutants^{78,79, 80,81,83,87, 85, 91}. Recently, there has been renewed interest in EC for the treatment of produced water largely due to the technological improvements that have led to lower electricity consumption and a cleaner output. According to Esmaeilirad et al. (2014)³³ using softening before

EC even at lower pH has higher removal efficiency than softening after EC at higher pH. However, since cost of treatment is a major factor when considering water management options, a full life-cycle analysis must be completed to adequately compare the alternatives.

4.2.2 Methods

Experimental

Produced water was collected from oil and gas wells in the Wattenberg field that is part of the Denver-Julesburg basin of northeast Colorado. The wells were hydraulically fractured and water sampling began immediately after flowback was started. Since the objective of the study was to run experiments on flow back and produced water (time period after which most frac fluid has flowed back), the sampled wells chosen had an age of 2-185 days. A typical production curve for the field is shown in Figure 23.

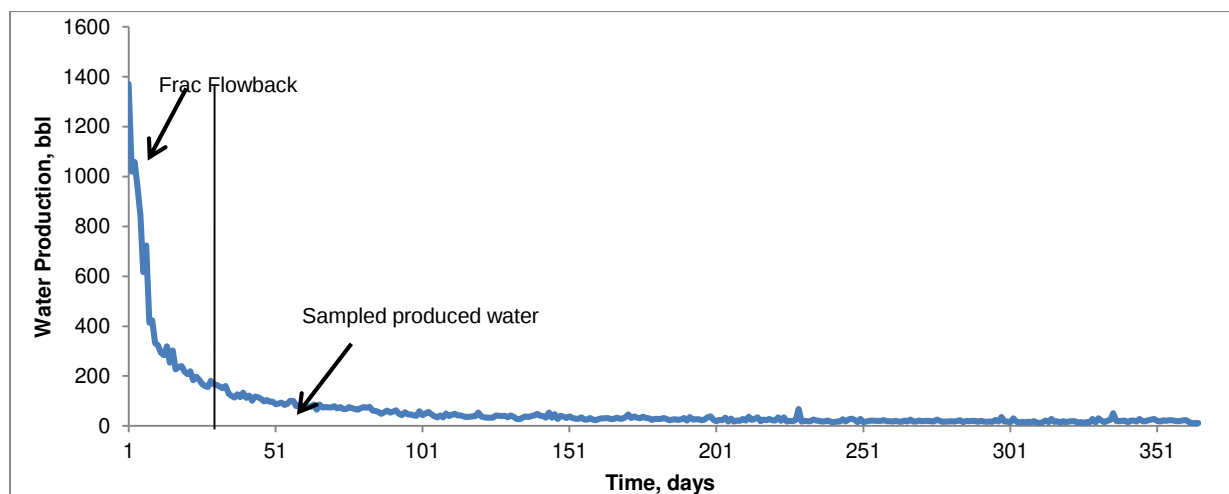


Figure 23-A typical water production curve⁹⁶.

Two sets of experiments were run on each water sample. The objective was to investigate the effect of chemical softening and pH on divalent cation removal during EC. Therefore, softening was

performed both before and after running EC on each sample by raising pH to 9.5 before and 10.2 after EC. The pH of 10.2 was chosen for softening after EC since it is the pH that is being used in the treatment process for the water being examined (the control condition in this study). The hypothesis was that softening at a lower pH before EC results in lower chemical costs while still increasing removal efficacy. Suspended solids after softening and EC treatment processes were filtered through a 2.5 μm (Whatman ashless #42) followed by pH adjustment of the final sample. A schematic diagram of the treatment, sampling and analysis process is shown in Figure 24. Softening after and before EC are shown as process 1 and 2, respectively. The final sample was taken at the end of each process.

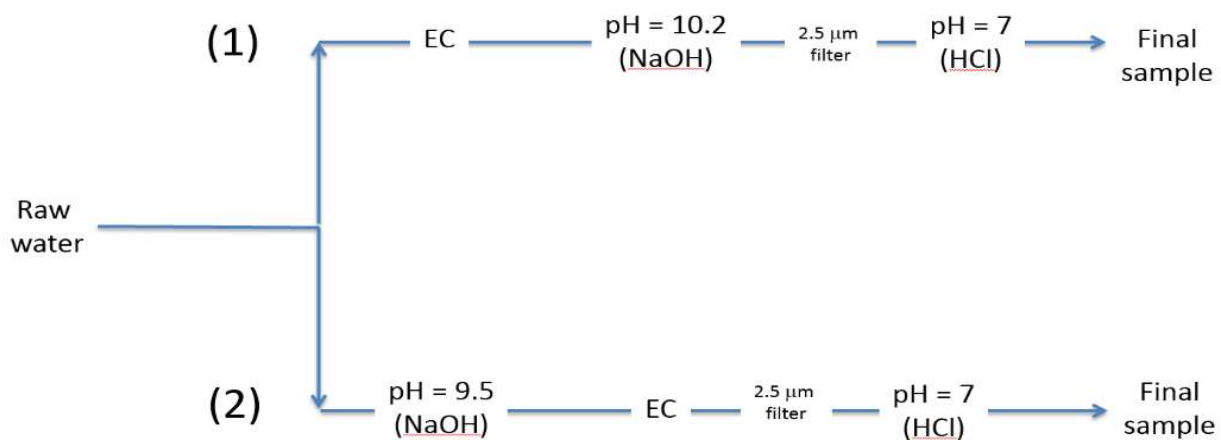


Figure 24-A schematic of the sampling plan: (1) EC-Soft, (2) Soft-EC.

Sodium hydroxide (50% w/w concentration, VWR, Radnor PA) was used to raise the pH of samples while hydrochloric acid (38% concentration, VWR, Radnor PA) was used to lower the pH to 7 at the end of each process. Water quality analysis of divalent cations such as Ca^{+2} , Mg^{+2} ,

Ba⁺² and Sr⁺² were measured using EPA 2007¹⁸⁵ method 6010C with a Varian ICP-AES, Liberty AX (Varian Inc., USA).

Equilibrium modeling

OLI Chemical Analyst is a software application used for simulating aqueous-based chemical systems. It is a graphical program developed by OLI Systems, Inc. (Morris Plains, NJ, USA) that utilizes a predictive thermodynamic framework for calculating the physical and chemical properties of multi-phase, aqueous-based systems¹³⁴. The software predicts reaction products, phase splits and complete speciation of all phases for a complex mixture of chemicals in water at a wide range of temperatures and pressures. Stream Analyzer can be used for computing bubble and dew point, pH and pH adjustments, precipitation point, acid/base/chelant titration curves and temperature, pressure and composition dependence of thermo physical properties¹³⁴. Prediction of metal salt precipitation and scaling tendencies for cations at a range of pH values using raw water quality as the input to the software was performed. The pH range was chosen to be 8.5 to 10.2 with intervals of 0.5. The software reconciled the pH, meaning pH was raised, using caustic and then was dropped to 7 for all the chosen values using hydrochloric acid. Standard temperature and pressure conditions were applied in the model (1atm and 25°C).

Chemical Use Analysis

An analysis of chemical requirements for different process scenarios was conducted by comparing two cases (Table 6). Case I water quality requirements include a “limiting concentration” of magnesium requiring significant removal of this ion. Concentrations of strontium and calcium are less limiting for this case and requirements should be met with any process that achieves magnesium targets. Magnesium requirements for Case II are not limiting since raw water

concentrations are less than this value. In this case, calcium and strontium removal define the pH conditions of the softening process. In both cases, barium is not important since softening pH will not influence the removal of this ion.

Table 6-Water quality characteristics for Case I and Case II

Parameters	Case I : Mg^{+2} limitation	Case II: Ca^{+2}, Sr^{+2} limitation
Ca^{+2}	300 mg/l	100 mg/l
Mg^{+2}	20 mg/l	100 mg/l
Sr^{+2}	5 mg/l	5 mg/l
Ba^{+2}	5 mg/l	5 mg/l

The assumption for the analysis is that a pH of 10.2 will be needed for the Case I precipitation process but a lower pH of 9.5 will be sufficient for Case II when magnesium removal is not required. These pH values were determined for this analysis based on the availability of experimental and modeled results for each. Both cases should be optimized for chemical use with an equilibrium model based on actual raw water concentrations and then verified with bench or pilot scale testing.

4.2.3Results/discussion

pH Effects

Raw water quality was used as input values for the OLI model and simulations were carried out to observe the efficacy of each treatment process. The OLI model was used to simulate an over-saturated condition (scaling tendency higher than 1) by allowing precipitation of solids at high pH values. The removal rates are based on the assumption of 100% solid-liquid separation. Stated

differently, divalent cations that are precipitated by reacting with the proper ligand (hydroxide, sulfate, and carbonate) are assumed completely removed with sedimentation or filtration.

Chemical compounds and scaling tendencies at different pH values, calculated using Pk_a values and actual concentrations, for one of the produced water samples are shown in Table 7. The higher the scaling tendency, the greater the driving force for precipitation and therefore dominant solids are expected to be calcium carbonate, strontium carbonate, magnesium hydroxide and barium sulfate. These compounds are colored in the table (calcium-blue, magnesium-green, strontium-yellow and barium-red).

Table 7-Classification of existent compounds in different pH

pH=8.5		pH=9		pH=9.5		pH=10		pH=10.2	
Solids	Tendency	Solids	Tendency	Solids	Tendency	Solids	Tendency	Solids	Tendency
Iron(III) hydroxide	28213.3	Iron(III) hydroxide	22951.9	Iron(III) hydroxide	14409.3	Iron(III) hydroxide	6598.79	Iron(III) hydroxide	4504.59
Sodium aluminum dihydroxide carbonate	578.532	Sodium aluminum dihydroxide carbonate	163.457	Strontium carbonate	150.837	Strontium carbonate	269.19	Strontium carbonate	311.235
Aluminum hydroxide	228.544	Aluminum hydroxide	72.641	Calcium carbonate (calcite)	91.941	Calcium carbonate (calcite)	107.464	Calcium carbonate (calcite)	110.693
Calcium carbonate (calcite)	32.8503	Strontium carbonate	64.173	Sodium aluminum dihydroxide	39.4661	Barium sulfate	14.8394	Barium sulfate	14.3703
Strontium carbonate	23.1803	Calcium carbonate (calcite)	63.7667	Aluminum hydroxide	22.9551	Sodium aluminum dihydroxide	7.27151	Aluminum hydroxide	4.55752
Barium sulfate	17.8622	Barium sulfate	17.347	Barium sulfate	16.2446	Aluminum hydroxide	7.23369	Sodium aluminum dihydroxide carbonate	3.38548
Strontium sulfate	0.054015	Barium carbonate	0.122853	Barium carbonate	0.276207	Barium carbonate	0.465083	Magnesium hydroxide	0.805599
Barium carbonate	0.045327	Strontium sulfate	0.053581	Strontium sulfate	0.052457	Magnesium hydroxide	0.335999	Barium carbonate	0.527179
Magnesium carbonate trihydrate	5.46E-03	Magnesium carbonate trihydrate	0.014468	Magnesium hydroxide	0.038422	Strontium sulfate	0.050789	Magnesium carbonate trihydrate	0.054734
Magnesium carbonate	5.18E-03	Magnesium carbonate	0.013715	Magnesium carbonate trihydrate	0.031029	Magnesium carbonate trihydrate	0.049271	Magnesium carbonate	0.051786
Sodium bicarbonate	4.53E-03	Magnesium hydroxide	4.26E-03	Magnesium carbonate	0.029394	Magnesium carbonate	0.046632	Strontium sulfate	0.050167
Calcium sulfate dihydrate	4.49E-03	Sodium bicarbonate	4.02E-03	Sodium bicarbonate	3.08E-03	Sodium iron(III) dioxide	3.70E-03	Sodium iron(III) dioxide	4.03E-03
Calcium sulfate	3.31E-03	Calcium sulfate dihydrate	3.12E-03	Sodium iron(III) dioxide	2.51E-03	Sodium bicarbonate	1.80E-03	Sodium bicarbonate	1.33E-03
Boric acid	1.02E-03	Calcium sulfate	2.30E-03	Calcium sulfate dihydrate	1.88E-03	Calcium sulfate dihydrate	1.19E-03	Calcium sulfate dihydrate	1.05E-03
Sodium iron(III) dioxide	4.78E-04	Sodium iron(III) dioxide	1.24E-03	Calcium sulfate	1.38E-03	Calcium sulfate	8.77E-04	Calcium sulfate	7.72E-04
Sodium chloride	4.69E-04	Boric acid	6.94E-04	Sodium chloride	4.80E-04	Sodium chloride	4.87E-04	Sodium chloride	4.89E-04
Magnesium hydroxide	4.47E-04	Sodium chloride	4.73E-04	Boric acid	3.46E-04	Boric acid	1.34E-04	Sodium carbonate decahydrate	1.52E-04
Strontium bicarbonate	1.96E-04	Strontium bicarbonate	1.51E-04			Sodium carbonate decahydrate	1.29E-04		

The effect of pH on precipitation of the four-targeted cations is shown in Figure 25. Calcium carbonate precipitation and therefore removal rate dramatically increases from 5% to 85% when pH was increased from 6.7 to 8.5. Above this pH, the equilibrium removal rate for calcium flattens out considerably but kinetics of reaction will also need to be considered when designing a treatment operation. Equilibrium chemical modeling predicts that removal of calcium at pH values as low as 9.0 can be greater than 97%.

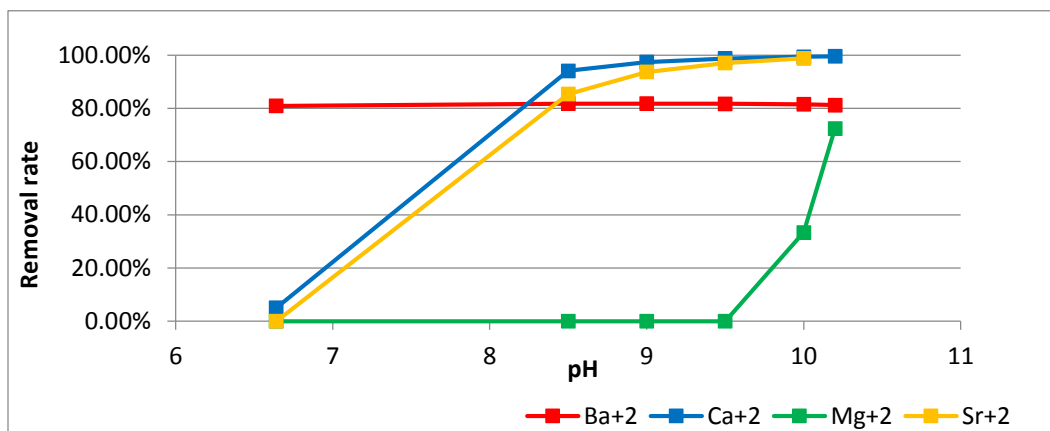


Figure 25-Precipitation and removal of divalent cations versus pH (assumes 100% solid-liquid separation following precipitation).

A similar trend was observed for the strontium ion since aqueous complexation with the same ligand (carbonate) is expected to form strontium carbonate solids. Removal jumped from less than 1% to 95% by increasing the pH from 6.7 to 9.0 before leveling off. Minimal magnesium precipitation is predicted until the pH is raised to 10, a significantly higher value than the other cations examined. Magnesium precipitates most effectively as the hydroxide achieving a relatively modest removal of 72% at pH of 10.2. As discussed, barium solubility is lowest when precipitating

solid barium sulfate and since this ligand is not acid-base active at the expected water quality conditions, the removal of the compound is not affected by pH.

In summary, if treatment processes are being designed to reduce the concentration of divalent cations for either scaling index control or specific ion interactions with frac fluids, process optimization should be considered by using the approach shown in Figure 25. For example, the sensitivity of frac fluid stability and scaling tendency of magnesium should be quantified to determine if acid and base chemical use can be reduced by operating at a lower pH.

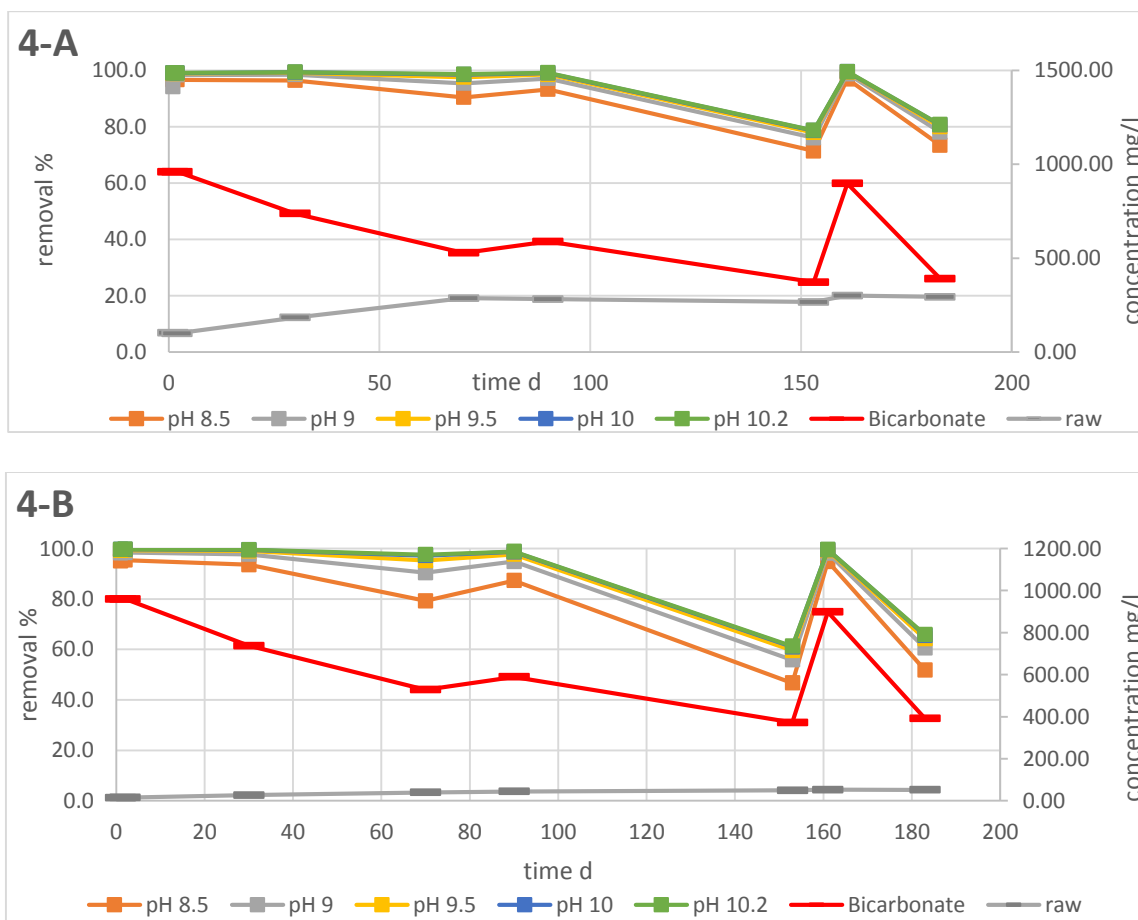


Figure 26-(A) Calcium and (B) strontium removal in different pH over time. Sr and Ca removal at different pH values were based on OLI model (left axes), Sr, Ca and Carbonate concentrations in the raw water samples (right axes)

Removal rates (left axis) for calcium and strontium at different pH values, ranging from 8.5 to 10.2 are shown in Figures 26A and 26B. Since calcium and strontium both precipitate as a carbonate complex, they have similar sensitivity to pH as removal rates level out above a pH value of approximately 9. Also the removal for both ions, Ca and Sr, was relatively constant except a sudden drop at the 153- day sample (Figure 26). This decline in removal rate could be due to a reduction in the ligand concentration in the raw water. As shown in Figure 27, the bicarbonate concentration varies in the raw water and can limit the precipitation of Ca and Sr if it drops below a threshold value. The lowest bicarbonate concentration happened with the 153-day sample at 372 mg/l corresponding to an average of 25% and 47% reduction in removal rate for calcium and strontium, respectively. There is another low point with the higher well-age sample (183 days) at 391 mg/L, corresponding to an average of 41% reduction in calcium and 23% in strontium removal rate.

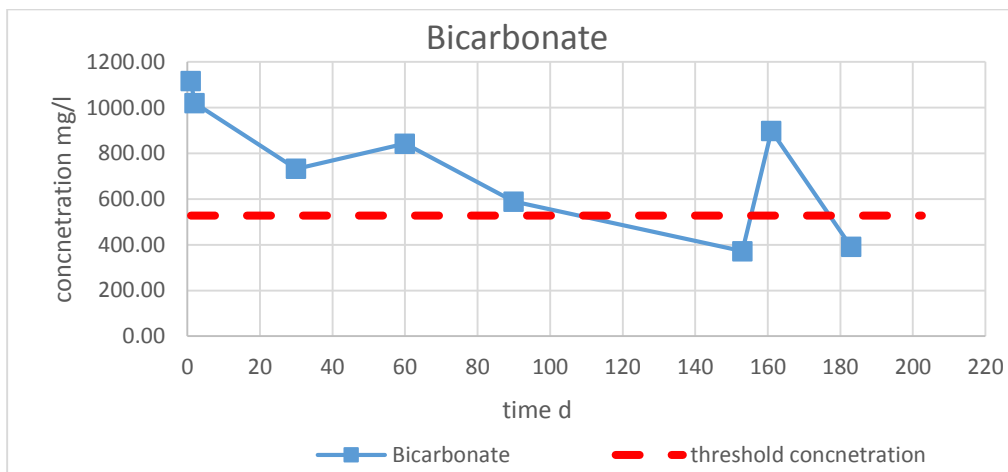


Figure 27-Bicarbonate concentration in raw water samples

Since the low-solubility ligand for both calcium and strontium is bicarbonate, the alkalinity of a produced water solution (an indicator of total carbonate concentration) can limit the removal of these metals. According to Figure 27, to reach a 90% removal of both calcium and strontium at all pH values (8.5, 9, 9.5, 10 and 10.2), a threshold carbonate concentration of 528 mg/l is required. In other words, based on the graph 26A and 26B, the minimum concentration of bicarbonate associating with 95% Ca and Sr removal was 528mg/l and when the concentration is lower than this, the removal rates for both Ca and Mg decreased. Below this threshold concentration, the system is carbonate deficient leading to a removal limitation that is not a function of pH. When designing a treatment process for calcium or strontium removal, the alkalinity of the influent water is an important process variable.

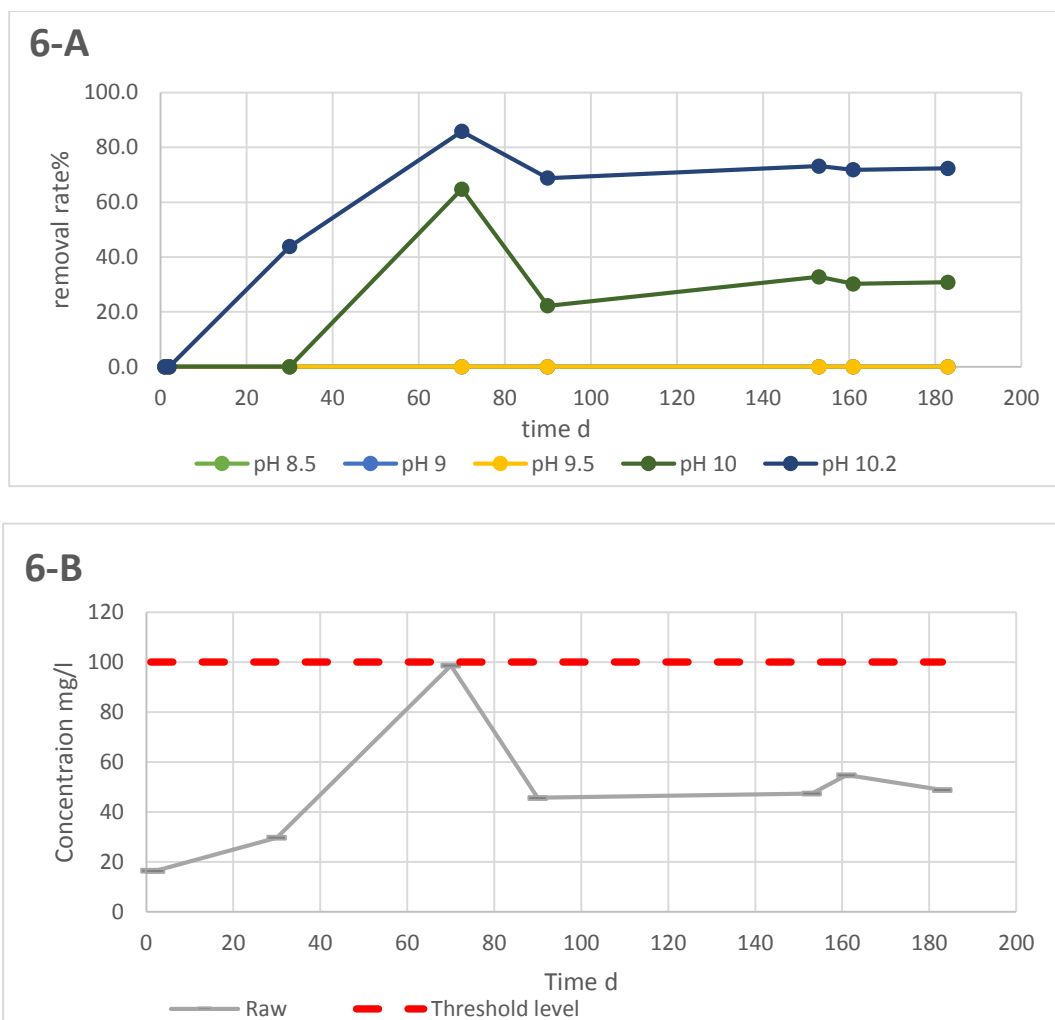


Figure 28-(A) Magnesium removal in different pH values over time; (B) magnesium concentration in the raw water samples and threshold concentration.

The magnesium removal rate and raw water magnesium concentrations are shown in Figure 28. As mentioned in the previous discussion, magnesium precipitates as a hydroxide after the pH is increased above 10. The plot shown in 28A indicates a sudden increase in magnesium removal at the pH of 10.2 for the water quality that was collected after 70 days (96%). This appears to be due to the increased raw water magnesium (98.7 mg/L at 70 days versus 29.7 mg/L for the 30 day sample that was collected immediately before). The predicted treated water concentrations of

magnesium were 29.7mg/l for the 30 day sample and 46.9mg/l for the 70 day sample, indicating similar equilibrium concentrations at the same pH. It was also seen that the removal rate is zero percent until pH was raised to 10 and higher. Also, the higher pH of 10.2 had a significantly greater efficacy than pH of 10 despite a 0.2 unit difference pH, equivalent to 1.6 mole/L more hydroxide ions.

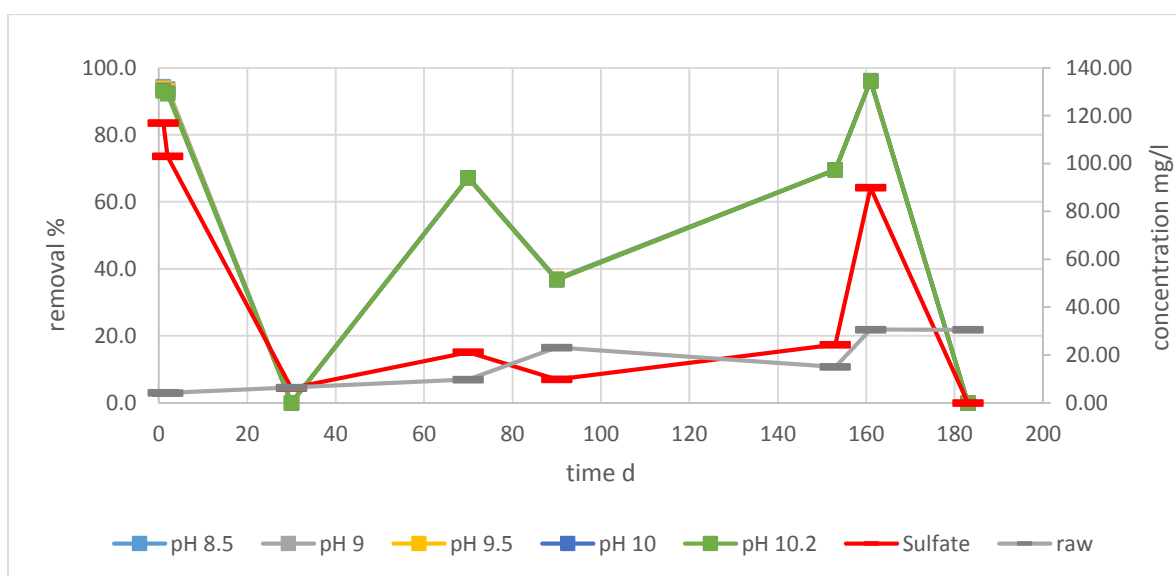


Figure 29-Barium removal rates at different pH values (left axis); barium and sulfate concentrations in the raw water samples (right axis) over time

Figure 29 shows barium removal over time at different pH values. As anticipated, pH did not influence barium removal rate and in the figure, all pH values are coincident with the pH=10.2 trend line. The modeled removal rate has a sudden decrease with the 30-day sample, due almost entirely to a decrease in the sulfate concentration. Barium sulfate is more soluble at higher temperatures^{135,136} and therefore supersaturated conditions that will lead to precipitation can occur when the solution cools during surface handling. Sulfate concentration and threshold concentration

is shown in Figure 30. Since the Ba concentration in the raw water samples was between 4 mg/l and 30.6 mg/l, it did not influence removal rates greatly and to achieve 70% Ba removal for the system, the sulfate concentration needs to be above the threshold concentration of 21mg/l (Figure 30). If additional barium needs to be removed, an excess concentration of sulfate will need to be added as a treatment chemical.

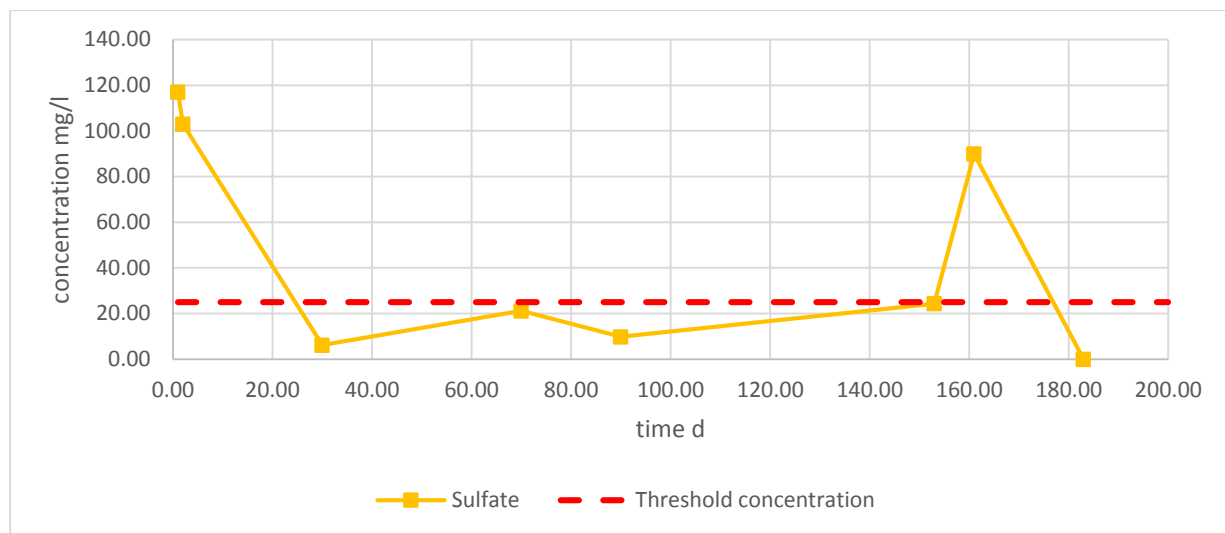


Figure 30-Sulfate concentration in raw water samples over time and threshold concentration

Comparison of experimental and modeled results

To determine if a treatment is working sufficiently, the target dissolved ion concentrations at the effluent were measured and plotted with the goal concentration in Figures 31-33.

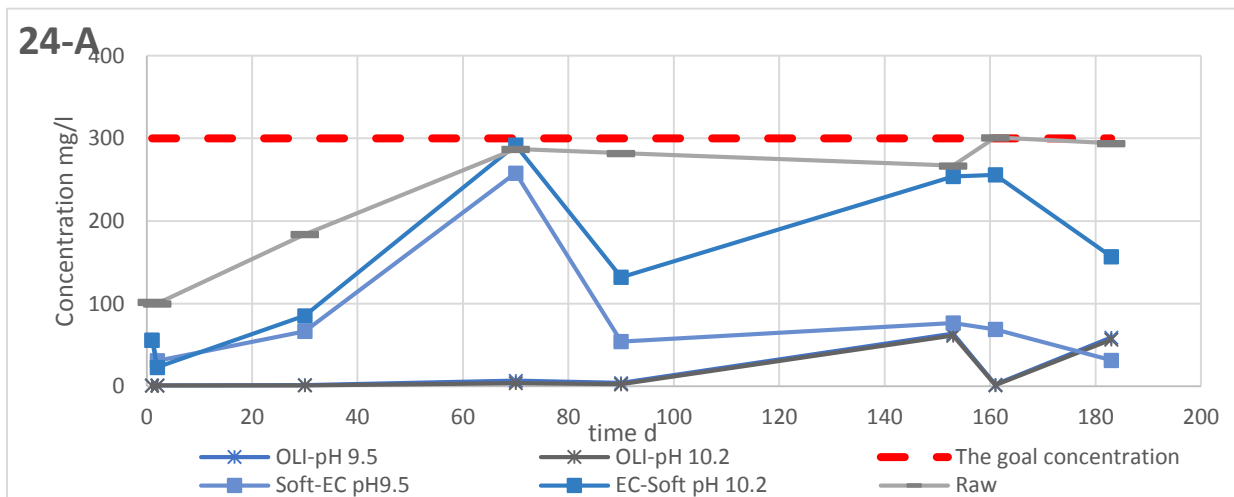
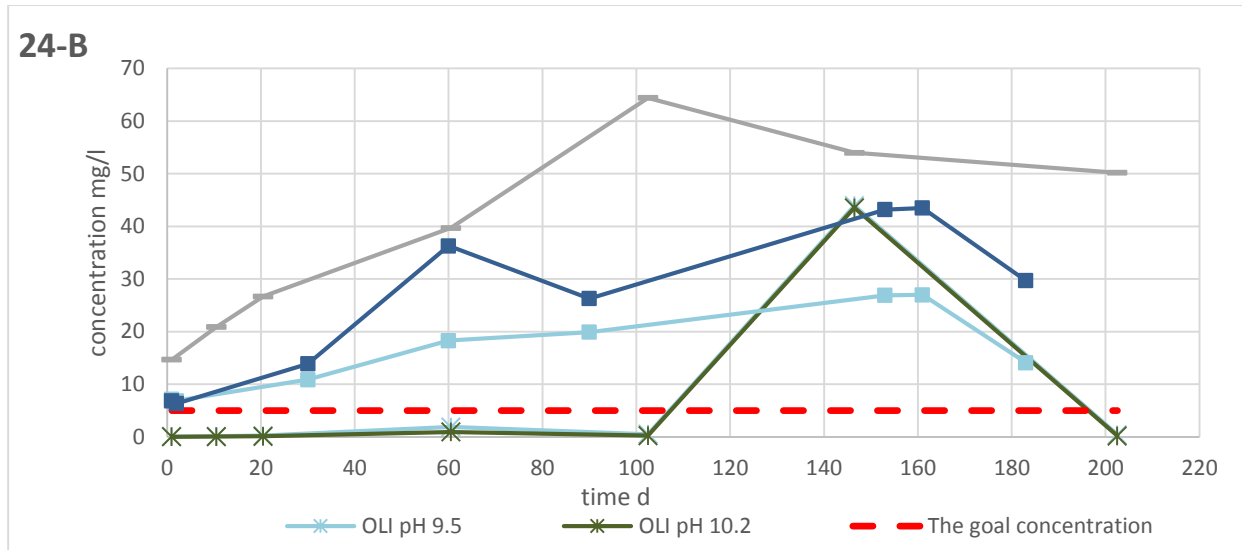


Figure 31-Comparison between the experimental and modelled ion concentrations in the effluent at pH of 9.5 and 10.2: (A) Calcium; (B) Strontium

Figure 31 shows the removal of calcium and strontium ions for both experimental and modeled trends and the raw water and goal concentration. It is shown that the experimental effluent has higher concentration than predicted with the OLI chemical equilibrium model. The experimental removal efficiencies are lower than the modeled data except for one data point (146-day sample), which could be due to the deficiency of solid-liquid separation (filtration using $2.5\mu\text{m}$) in the lab. Both experimental and modeled results follow a similar trend and the sudden rise in the

concentration as it is mentioned previously is because of a corresponding drop in the raw water carbonate concentration. Another major point is that pH value does not cause the difference between the two treatments because the modeled results show there is not any difference between the two pH values of 9.5 and 10.2. Hence the sequence of softening was the important factor in the increased effectiveness of the Soft-EC versus EC-Soft process in this study.

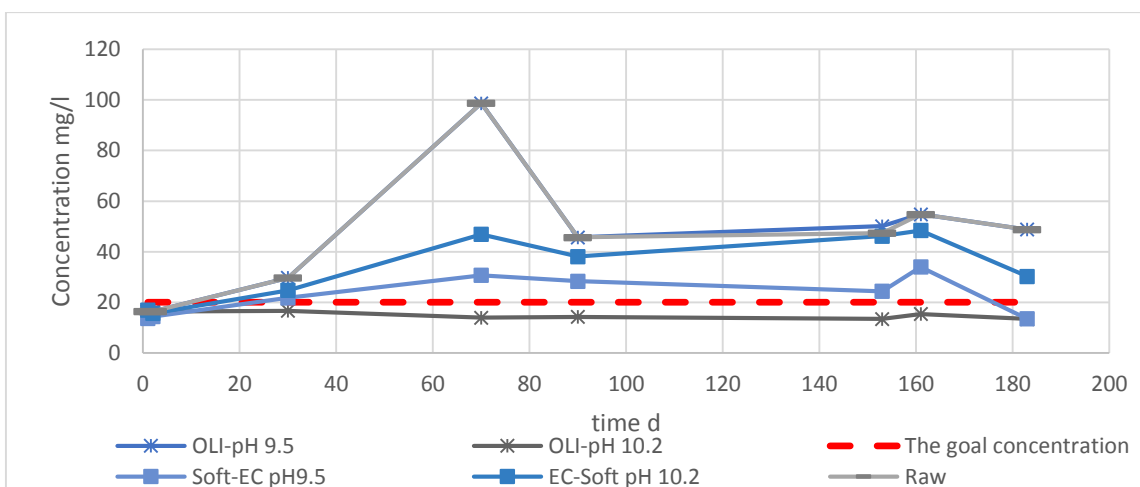


Figure 32-Comparison between the experimental and modeled magnesium concentration in the effluent at pH of 9.5 and 10.2

Magnesium, as discussed above and shown in Figure 32, was in the dissolved, divalent cationic form at the pH of 9.5 and by increasing pH to 10.2 there is a significant decrease in magnesium concentration in the OLI modeled result. However the same trend (higher efficiency in modeled result) was observed for magnesium as for calcium and strontium.

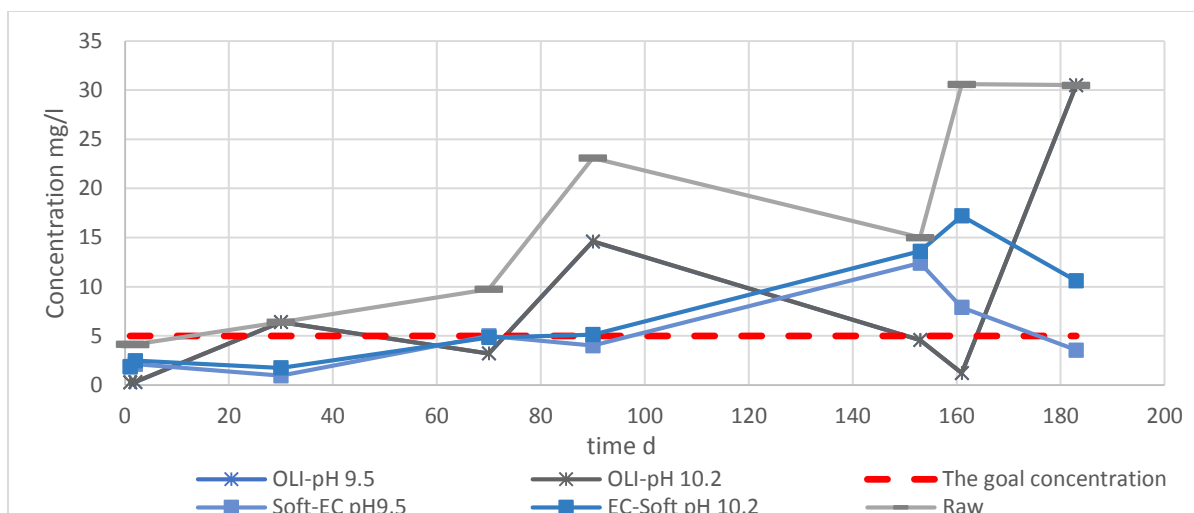


Figure 33-Comparison between the experimental and modeled Barium concentration in the effluent

Barium removal results, experimental and modeled, are shown in Figure 33. Initially, both treatments, EC-Soft and Soft-EC, had similar removal rates but the gap increased over time for samples from wells with an age greater than 160 days.

Chemical Use Analysis Observations

The required acid-base quantity for case studies (case I: Mg limited and case II Ca and Sr limited) based on OLI model results are shown in Figure 34. It was seen that there is a substantial difference in terms of chemical consumption between pH of 9.5 and pH of 10.2. Theoretically the required base (e.g. NaOH) at the pH of 10.2, base usage efficiency was 20% to 40% lower at pH of 9.5 compare to 10.2; likewise this amount was 21% and 48% for acid usage. The observed reduction for the experiments ranged from 10%-62% for base usage and 22%-73% for acid usage. Also it appears that there is a big difference between flowback water and produced water in terms of chemical usage. Much more chemical (acid and base) was used for the early flow back (water

samples earlier than one month) versus produced water (later water flows). This observation was much visible particularly for base consumption in first 30 days.

It is concluded that based on the target water quality, optimizing pH conditions could save substantial amounts of acid and base chemicals and therefore reduce the cost of treatment. Hence a comprehensive water analysis would be necessary in order to optimize the produced water treatment in terms of cost and chemical usage.

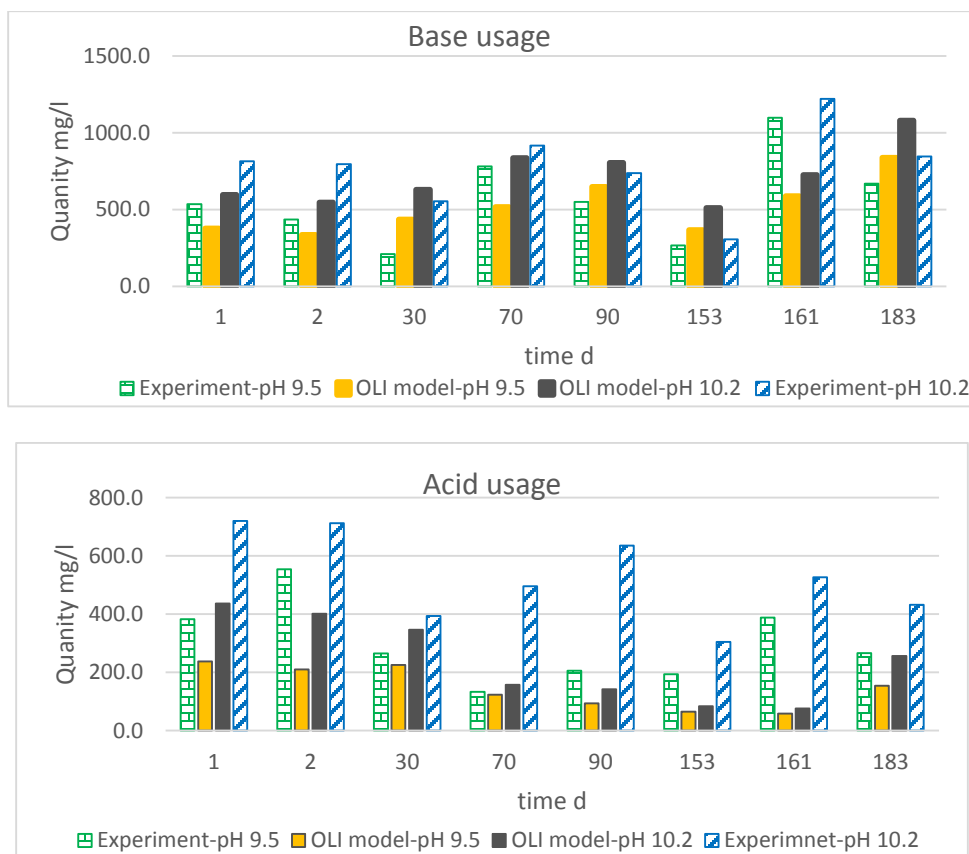


Figure 34-Acid and base consumption

4.2.4 Conclusion

- Magnesium removal targets will dictate the pH required for softening or metal precipitation processes.

- Equilibrium modeling results predict that removal efficacy of Ca and Sr will be minimally impacted by lowering pH from 10.2 to 9.5.
- The difference of removal rate for the modeled and experimental results for all of the metals may be due to a deficiency in the solid-liquid separation process. Coagulation with EC after precipitating the solids could result in a more effective solid-liquid separation process.
- Chemical consumption at pH values of 9.5 and 10.2 was significantly different. Chemical equilibrium modeling predicts that the average base usage was 30% lower at pH of 9.5 compare to 10.2 and 34% lower for acid usage. The reduction in use experimentally was 27% for base and 43% for acid.
- Broad knowledge of water chemistry and quality not only would save considerable amount of chemicals and the associated cost but also reduce sludge production and maybe lead to a more effective coagulation process.

4.3 Influence of Inorganic Ions in Recycled Produced Water on Gel-Based Hydraulic Fracturing Fluid Viscosity

4.3.1 Introduction

A better understanding of how treated produced water quality influences the stability of hydraulic fracturing fluids is essential for exploration and production companies to reduce their demand on local fresh water resources, while maintaining oil and gas production^{33,34,101}. Characterizing the spectrum of water qualities that are likely to occur when using produced water from several potential sources and is treated at varying fixed and mobile water treatment facilities, will allow oil and gas operators to optimize frac fluid formulations, water treatment operations and management strategies for produced water that achieves acceptable frac fluid stability, while minimizing cost of treatment and reducing the potential for screen outs. Water treatment technologies have been developed and refined for decades in a variety of other industrial applications that may provide assistance in optimizing frac fluid formulations and performance to achieve the operating objectives defined within this study.

Produced water treatment in the oil and gas industry has often focused on improving the water quality to fresh water standards, while service companies have been developing hydraulic fracturing fluids that are less sensitive to water quality, reducing treatment requirements and minimizing associated costs to the operator^{33,34,97}. By studying water quality and water treatment in conjunction with frac fluid formulation, water reuse can be maximized in a cost-effective and environmentally responsible manner. Furthermore, the temporal and spatial variability of recycled water^{33,34,100,101}, including Early Time Flow Back (ETFB) and Produced Water (PW), can be better

managed to meet an operator's water-related field development objectives, with fluid formulation optimization for preferred frac fluids.

The impact of using produced water with specific hydraulic fracturing fluids is not universally understood in the industry, nor documented effectively in the literature that is available. Some hydraulic fracturing fluids today are able to use water with total dissolved solids (TDS) values exceeding 270,000 mg/l¹⁴⁰ but tradeoffs may exist with these fluids when considering costs, scaling tendencies, collection of sufficient volumes of produced water to prepare for particular treatment events, etc. Even though a variety of TDS reduction methods are available to achieve any water quality desired, salt removal is expensive and is typically avoided if possible¹³⁹. Although the use of produced water for oil and gas drilling and slickwater-based fracturing have been explored in the Denver basin^{33,34}, little has been done to use the high-TDS produced water with linear-gel based and crosslinked-gel-based hydraulic fracturing fluids^{97,98}. A limited number of reports have placed wide ranging water quality limits on other inorganic parameters^{61,75,97,100,101,102}, but few studies have examined the influence of specific water quality parameters beyond the scope of solids and a few inorganic parameters.

Recycled flowback and produced water have been increasingly used in new gel fracs of oil and gas wells in the Denver-Julesburg Basin. With their increased use, higher ionic loadings have been placed on fracturing fluids, resulting in varied fluid stability. Understanding operational limits with respect to varying base water characteristics is key to the continued use of recycled water in practice^{61,101}. The objective of this paper was to evaluate the difficulties and complexity of reuse and recycling produced water in hydraulic fracturing.

4.3.2 Materials and Methods

Spiked Base Water Preparation

Table 8 outlines typical water quality concentrations seen in varying sources for fracturing base water in the DJ Basin which was examined in this study. These water qualities were then used to determine the maximum and minimum of an individual ion.

Table 8-Range of water quality for different water source

	Municipal Water		Surface Water		Ground Water		Treated Produced Water		Early Time Flowback Water	
Range (mg/l)	Low	High	Low	High	Low	High	Low	High	Low	High
Al							0.5	15	0.75	4
Fe	0	1	0	1	0	1	0.25	1.1	5	100
Ca	5	70	20	250	25	120	20	175	90	200
Mg	2	25	5	80	5	30	0	50	10	40
Ba							0.5	3	0.1	5.5
Sr							3	22	2	25
Cl	5	80	5	250	10	100	5000	10000	80	10000
HCO ₃	20	450	125	450	140	330	300	600	300	1400
SO ₄	3	150	150	800	5	300	25	125	30	1300
B							7	17	1	20
TDS	2	25	450	2200	300	1100	9000	18000	1000	18000

To study the effects of individual cation and anions on the viscosity of frac fluid, tap water from Colorado State University (CSU) was chosen as the base water for this study. Reagents were added to achieve varying ionic concentrations in the base tap water. Each sample contained only one specific ion at one specific concentration. Table 9 contains a list of all reagents used to spike the CSU tap water for the study. The concentration of each ions were chosen based on the typical water sources in Colorado, then extreme and minimum conditions were selected to represent a worse, normal and best water quality. The quantity of each compound was calculated based on the desired concentration of the individual ions. All the chemicals were supplied from Fisher and Sigma-Aldrich, (Missouri, USA) and were laboratory grade chemicals.

Table 9-List of added mineral compounds

Ion of Interest	Reagent Used	Formula
Aluminum	Aluminum Chlorohydrate Dihydrate	$\text{Al}_2\text{ClH}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$
Ammonium	Ammonium Chloride	NH_4Cl
Barium	Barium Chloride Dihydrate	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
Bicarbonate	Sodium Bicarbonate	NaHCO_3
Boron	Boric Acid	$\text{B}(\text{OH})_3$
Bromide	Sodium Bromide	NaBr
Calcium	Calcium Chloride Dihydrate	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
Chloride	Sodium Chloride	NaCl
Iron	Ferric Chloride	FeCl_3
Magnesium	Magnesium Chloride Hexahydrate	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Nitrate	Sodium Nitrate	NaNO_3
Phosphorous	Sodium Phosphate Dodecahydrate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$
Potassium	Potassium Chloride	KCl
Sodium	Sodium Chloride	NaCl

Strontium	Strontium Chloride Hexahydrate	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$
Sulfate	Sodium Sulfate	Na_2SO_4

Building frac fluid

Metal cross-linked carboxymethyl cellulose (CMC) based and double derivatized guar based polymers were selected as the base fluids. These fluid systems are commonly used in the DJ Basin of Colorado. The base components of these fluids are: cellulose based gel or guar based gel (Table 10).

Table 10- Frac fluid composition

Fluid	Gel	Cross linker #1	Cross linker#2	Notes
CMC based fluid	Polysaccharide based gel (CMC)	Zirconium Crosslinker	Metal Crosslinker	Low pH, pH<6
Guar based fluid	Guar based gel	Zirconium Crosslinker	Metal Crosslinker	High pH, pH>10

The following steps were conducted to prepare all frac fluid samples:

1. 1000 ml of desired water sample or salt water was placed in a 1000 ml blender to prepare the linear gel.
2. A blender was used at between 1300 to 1500 rpm circulating rate, which was needed to establish a vortex shape with no air bubbles trapped. The mixing rate was part of Halliburton Practice.
3. A suggested quantity of CMC/guar gel was added slowly from the shoulder of the created vortex to prepare the desired polymer loading rate. A timer was started at this time. Apparent viscosity

was measured at 3, 6 and 9 minutes of adding polymer to water sample to study the polymer hydration phenomena.

4. Finally, the first buffer was added, followed by the cross linker (based on the recommended table by the provider company) and second buffer to fix the pH, mixed for 10 s before loading into the viscometer.

5. To avoid and minimize the machines visibilities, three different machines were chosen for the study and rheology test was run on three samples, each $78\text{ml} \pm 1$, simultaneously.

To have the same test conditions for all prepared fluids, all viscosity measurements were conducted within couple minutes of the initial hydration time to avoid any viscosity changes due to polymer hydrolysis¹³⁸.

Concentrate Fluid Sample Preparation

In addition to the spiked water runs, an alternative sample preparation method was used to determine if operational changes could improve fracturing fluid stability. It was questioned whether tap water, a solvent with higher water quality, will improve the hydration of the gel or not. Therefore a hypothesis was made based on the gel hydration in tap water and introducing brine to the gel-water solution later. The method included hydration of the gel in 500ml of CSU tap water and then addition of spiked water, 500ml, to the solution making a total volume of 1000ml. The rest of the process was the same as the main method (Section 2.2). The only difference between concentrate fluid and normal fluid was the solvent, CSU tap water and spiked water, respectively. For this reason some samples were formulated using this methodology, however no difference in frac fluid stability was observed between these samples and the base frac fluid.

Rheological Testing

The viscometer used in this study was the Chandler Model 5500 HPHT Viscometer. A computer was directly connected to the viscometer and recorded viscosity and temperature. All the runs were conducted at 200 °F in 45 minutes.

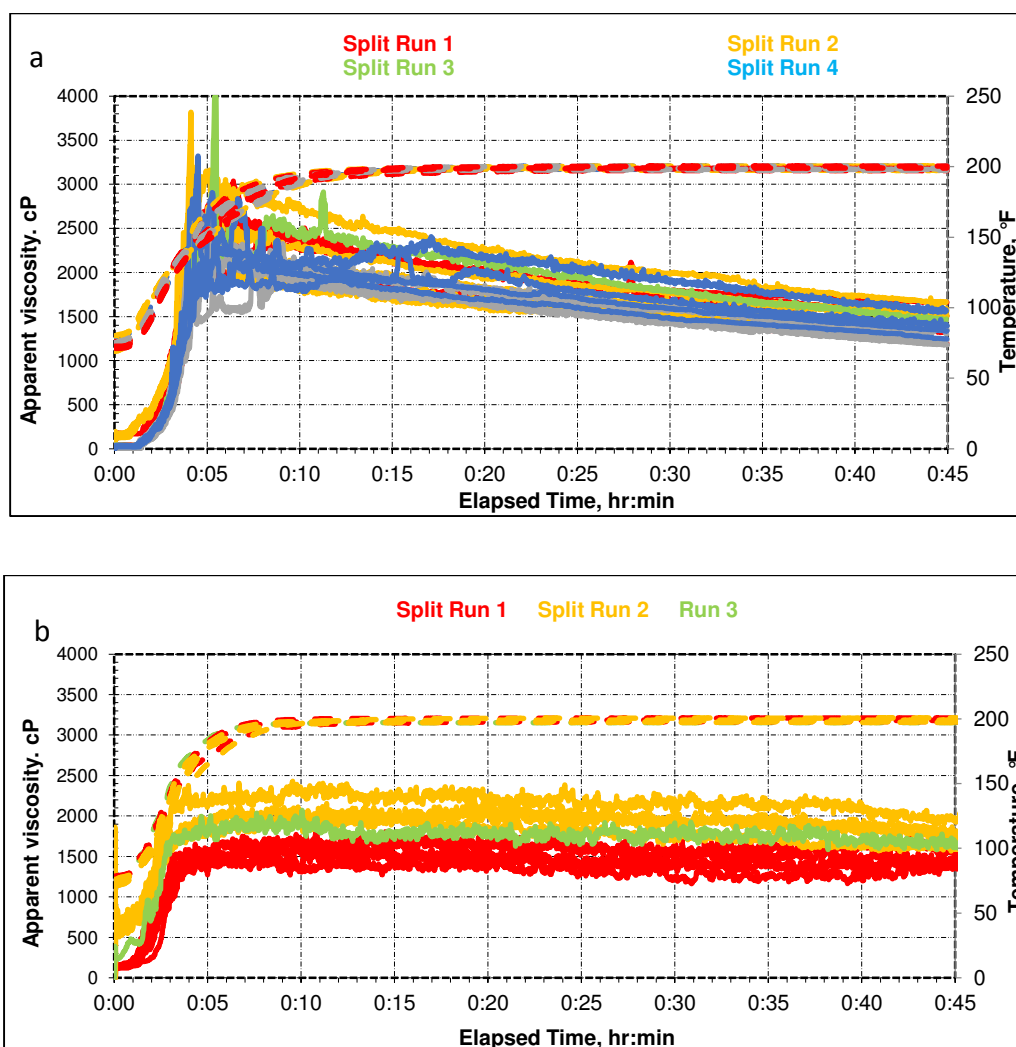


Figure 35- Viscosity profile of base fluid; a) CMC based fluid and b) Guar based fluid

The raw data of model water for CMC based gel is shown in Figure 35. The solid line represents the viscosity profile and dash line represents sample temperatures. The temperature was raised from 75°F to 200°F within 15 minutes and was kept constant at 200°F. Shear rate was set on 40s⁻¹

¹ for all the experiments in this paper. All the settings during the rheology experiments were part of Halliburton Practice.

Water quality analysis

All water quality analyses were done using Standard Method procedures¹¹⁶. Total organic carbon (TOC), gravimetric TDS and pH analyses were conducted at the Colorado State University water quality laboratory. e-Analytics Laboratory (Loveland, CO) provided analysis of cations and anions. Gravimetric TDS was measure based on Standard Methods of Water and Wastewater (AWWA, 2012). The ionic TDS concentration was calculated by summing the anion and cation concentrations. pH was measured using a Hach (Hach, Loveland), HQ40d pH meter. TOC was measured based on Standard Methods¹¹⁶ 2540D 5130B. Cations were measured based on EPA2007¹⁸⁵ method 6010 C using a Varian ICP-AES, Liberty AX.

4.3.3Results and Discussion

Baseline Testing

Initial baseline samples, the typical composition for frac fluid using fresh water, for each frac fluid were tested and used as a control for the study (Figure 35). To identify all the variability and their sources, four samples were made (same frac fluid composition), each then was split among four viscometers. This method helped provide an understanding of all the machines' behavior. Both figures depict the apparent viscosity profiles of the multiple samples (splits) across multiple machines. The dashed lines represent the sample temperature throughout each test.

Also to determine if wait time impacted fracturing fluid rheology, one hour of wait time occurred between split runs 1 and 2. According to Figure 35a, wait time did not affect Fluid-A viscosity and the differences between split 1 and split 2 were negligible. However, the differences in Fluid-B

(Figure 35b) were significant, resulting in a higher peak and final viscosity, meaning that the longer the fluid sat, the higher viscosity profile was. To prevent this source of error, all spiked samples were tested immediately after being made for the duration of this study.

Defined criteria

All spiked sample tests were compared to the baseline tests to determine if a rheological change occurred. Rheological parameters include initial peak viscosity, final viscosity, and viscosity profile. Criteria for an acceptable rheology run were part of Service Company practices (Halliburton) and it may vary depending on each job. The criteria values were set at values higher than typically experienced because the frac fluid composition does not include the full chemical composition such as breaker and therefore a safety factor was considered. Table 11 shows the criteria used for both CMC and guar based fluids. Due to the huge difference in the chemical composition of these fluids, the presented criteria for each of these fluids are different. For example, a CMC fluid should reach a minimum peak viscosity of 1500cP and maintain a minimum viscosity of 1350cp in order to be accepted, while guar based fluid is acceptable at relatively lower viscosities. By comparing the results of the spiked water with the baseline runs, it is possible to determine which ions impact frac fluid viscosity.

Table 11- Viscosity ranges for acceptable run

	CMC based fluid	Guar based fluid
Expected Initial Peak Viscosity (cp)	2200	1750
Minimum Acceptable (cp)	1500	1250
Expected Final Viscosity (cp)	1500	1500
Minimum Acceptable (cp)	1350	1000

Results

Due to differences in chemical composition of the two frac fluid systems, gel formulations, crosslinkers, and their respective concentrations between the two fluid systems, ions had varying effects on each system. Figures 36-39 show the results of the rheology tests for Fluid-A and Fluid-B. From these results, it is clear that varying ions influence the fluid stability in different ways at different critical concentrations. Since ion concentrations were chosen based off of typical and extreme concentrations that may be encountered in the real application of recycling treated produced water and flowback, it can be difficult to directly compare different ions. However, the valence of each ion seems to alter its impact on the fluid stability.

Monovalent cation

The effect of monovalent cations on CMC based fluid and guar based fluid performances was studied and the results are shown in Figure 36 (a,b). Based on the results, it was concluded that both frac fluids are more tolerable to sodium and potassium. In other words monovalent cations did not affect the viscosity of the CMC based fluid until higher concentrations. This result is consistent with the findings from Haghshenas and Nasr-El-Din¹⁰⁰ (2014). Monovalent ions also had a greater influence on the guar-based fluid. Based on Figure 36, guar based fluid exhibited

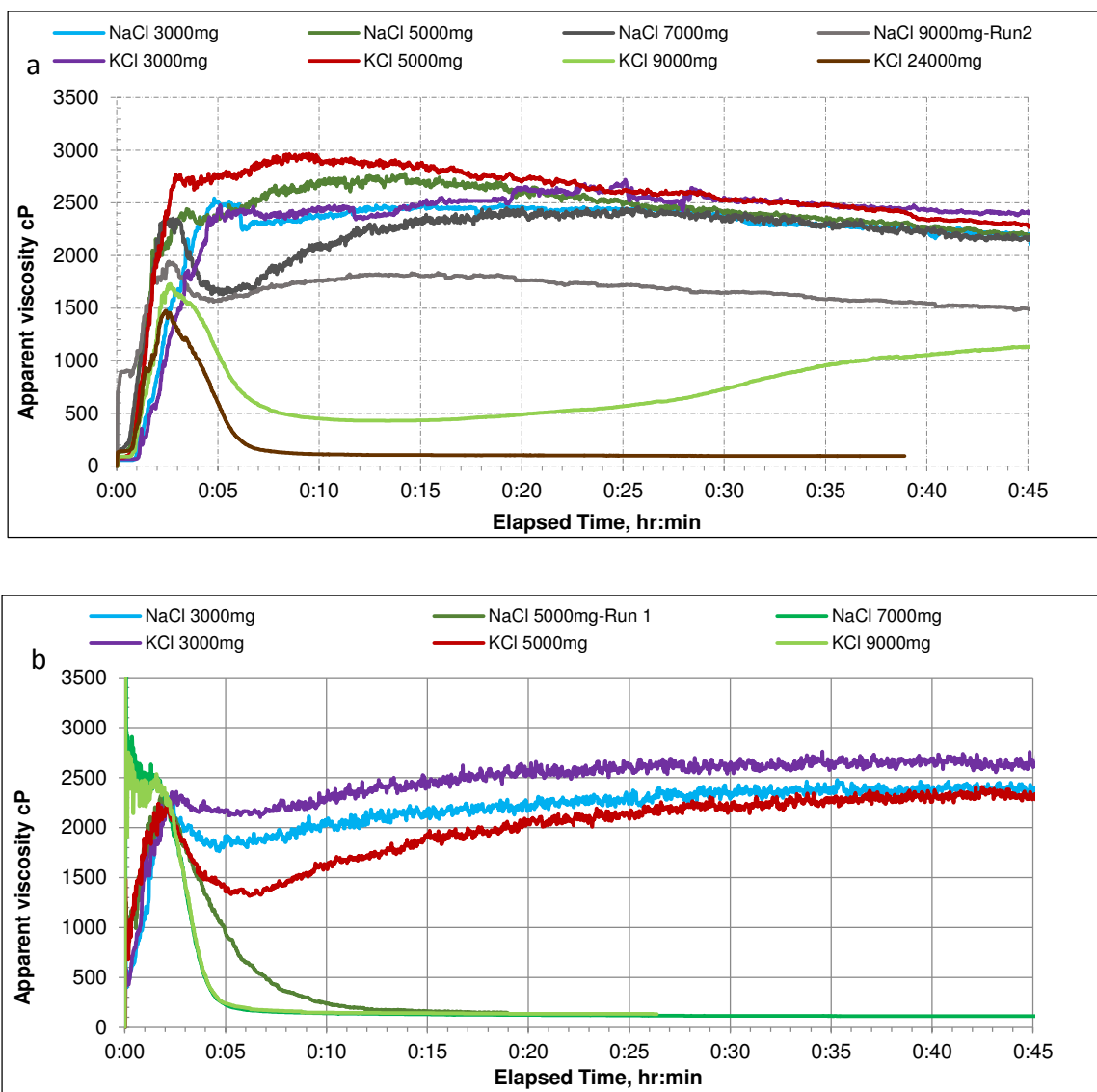


Figure 36- The impact of sodium and potassium on viscosity, a) CMC based fluid and b) guar based fluid

instability at a lower Na concentration (5000mg/l), while Na did not affect the CMC based fluid until 9000mg/l.

Divalent Cations

Viscosity profiles are shown for CMC and guar based fluids with varying concentrations of two divalent cations, magnesium and calcium, in Figure 37a and Figure 37b, respectively. Influence of magnesium at three concentrations of 25mg/l, 75mg/l and 125mg/l were studied. As previously mentioned, these concentrations represents three possible water quality types: typical water quality for water sources in the Denver-Julesburg Basin, an extreme condition and the minimal concentration expected.

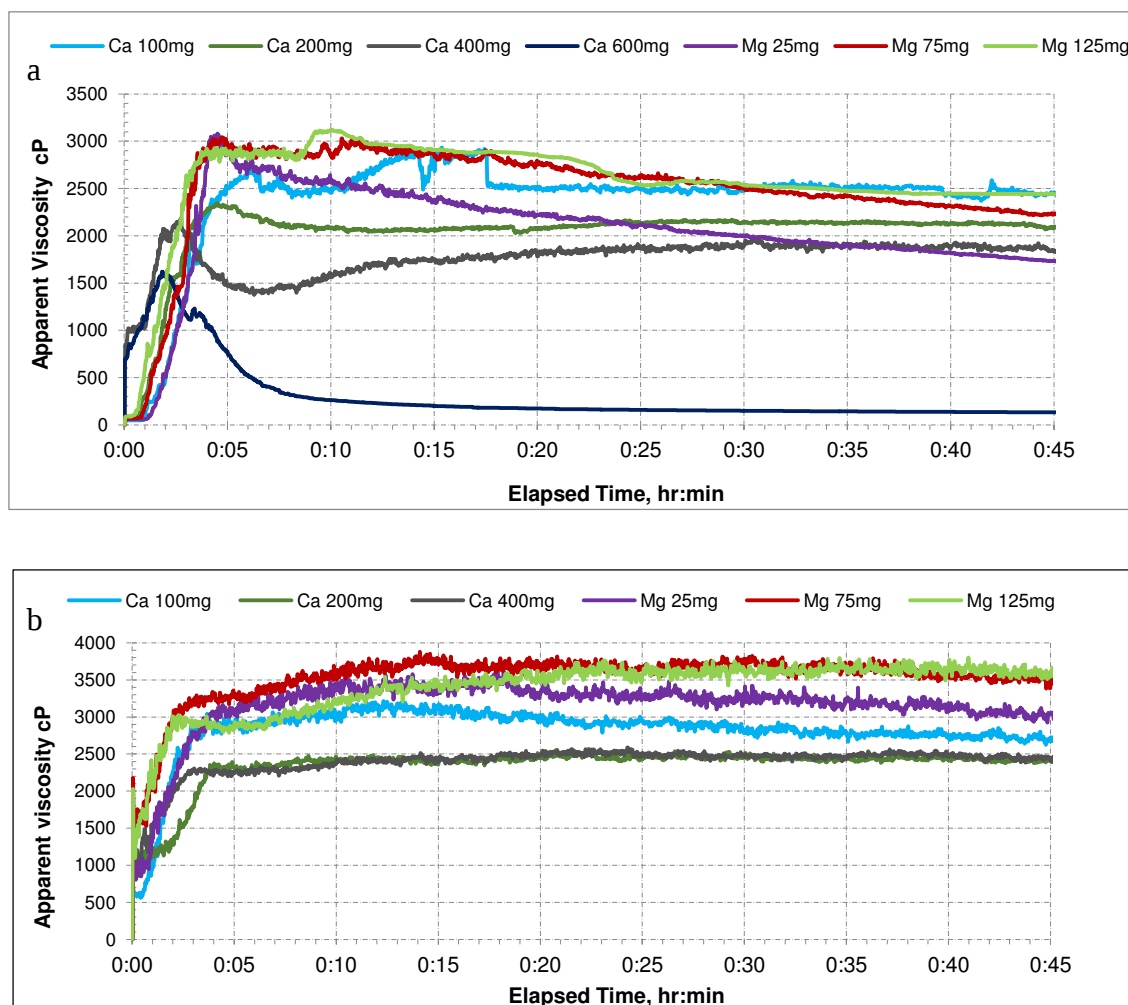


Figure 37- Viscosity profile for divalent cations, calcium and magnesium, a) CMC based fluid, and b) guar based fluid

As shown in Figure 37b, magnesium showed negligible impact on apparent viscosity for both fluids within the chosen concentration range.

An opposite influence was observed for calcium. At the highest concentration, calcium caused a negative impact on both frac fluids and viscosity profiles. This influence was more pronounced for the guar based fluid. This is a similar pattern to the impact of monovalent ions and confirms the fact that guar based fluid is more sensitive to TDS, salinity and some divalent cations.

Trivalent cations

Figures 38 illustrates the viscosity profile for trivalent cations over a 45 minute run. Aluminum and iron concentrations varied in each of these runs. According to figure 38a, aluminum did not affect the CMC based fluid performance in terms of peak and final viscosity, and the viscosity profile within the studied concentration range.

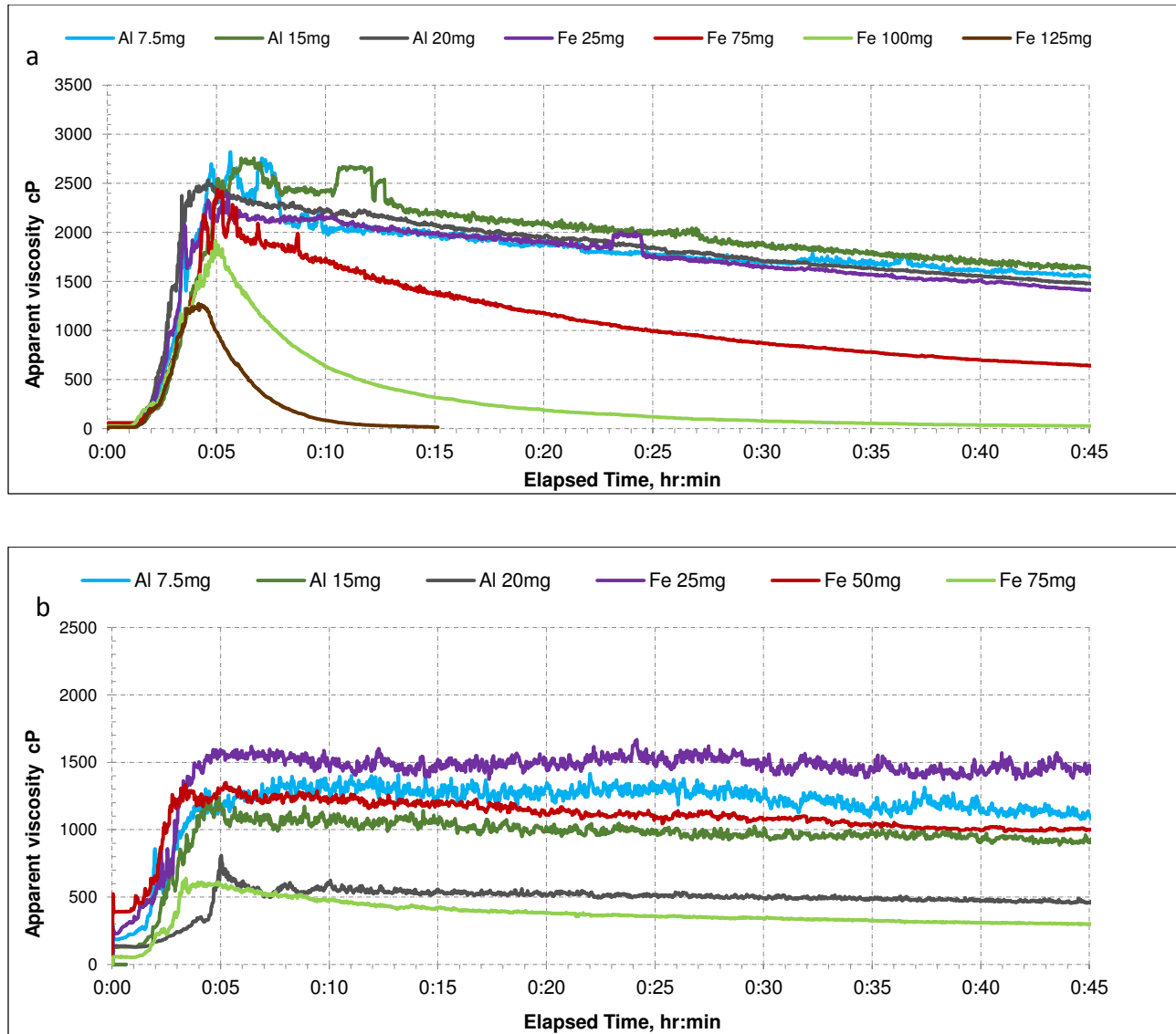


Figure 38- Aluminum and iron results a) CMC based fluid and b) Guar based fluid

However for guar based fluid, the peak viscosity was significantly lower at Al=20mg/l. Based on Figure 38, iron seemed to have a significant impact on both CMC and guar based fluids at concentrations of 75mg/L (iron was added in the ferrous state). Similar results were observed by Haghshenas and Nasr-El-Din¹⁰⁰ (2014). Guar based fluid showed more sensitivity to higher concentrations of iron and ultimately at Fe= 75mg/l, guar based fluid failed, while the CMC based fluid still was within an acceptable range and did not fail until Fe=100mg/l. Like monovalent and

divalent ions, guar based fluid behaved in the same manner to Al and Fe additives. This is in agreement with the monovalent and divalent ion impacts on CMC based fluid and show that guar based fluid is more tolerant to dissolved cations.

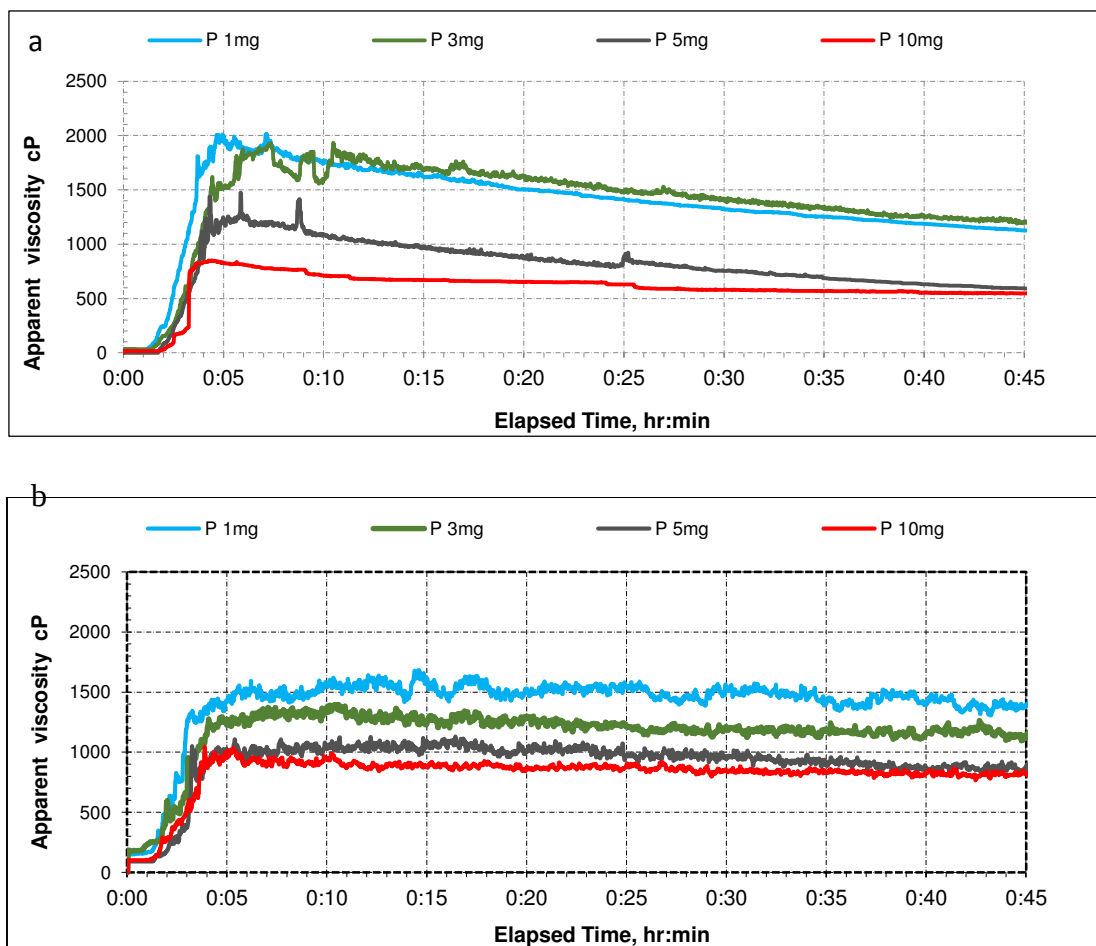


Figure 39- Viscosity profile in presence of phosphorus ion, a) CMC based fluid and b) guar based fluid.

Phosphate was another ion of interest in this study. Figure 39 shows the impact of phosphorous on CMC and guar based fluids performance. Like all other studied ions, the concentrations of phosphorous ion were chosen based on typical and extreme concentrations that may be encountered in treated produced water. Phosphorus caused a significant drop in the viscosity of both fluids and similar to the rest of studied ions this influence was higher for guar based fluid. The critical concentrations of phosphorus were 5mg/l and 3mg/l for CMC and guar based fluids, respectively.

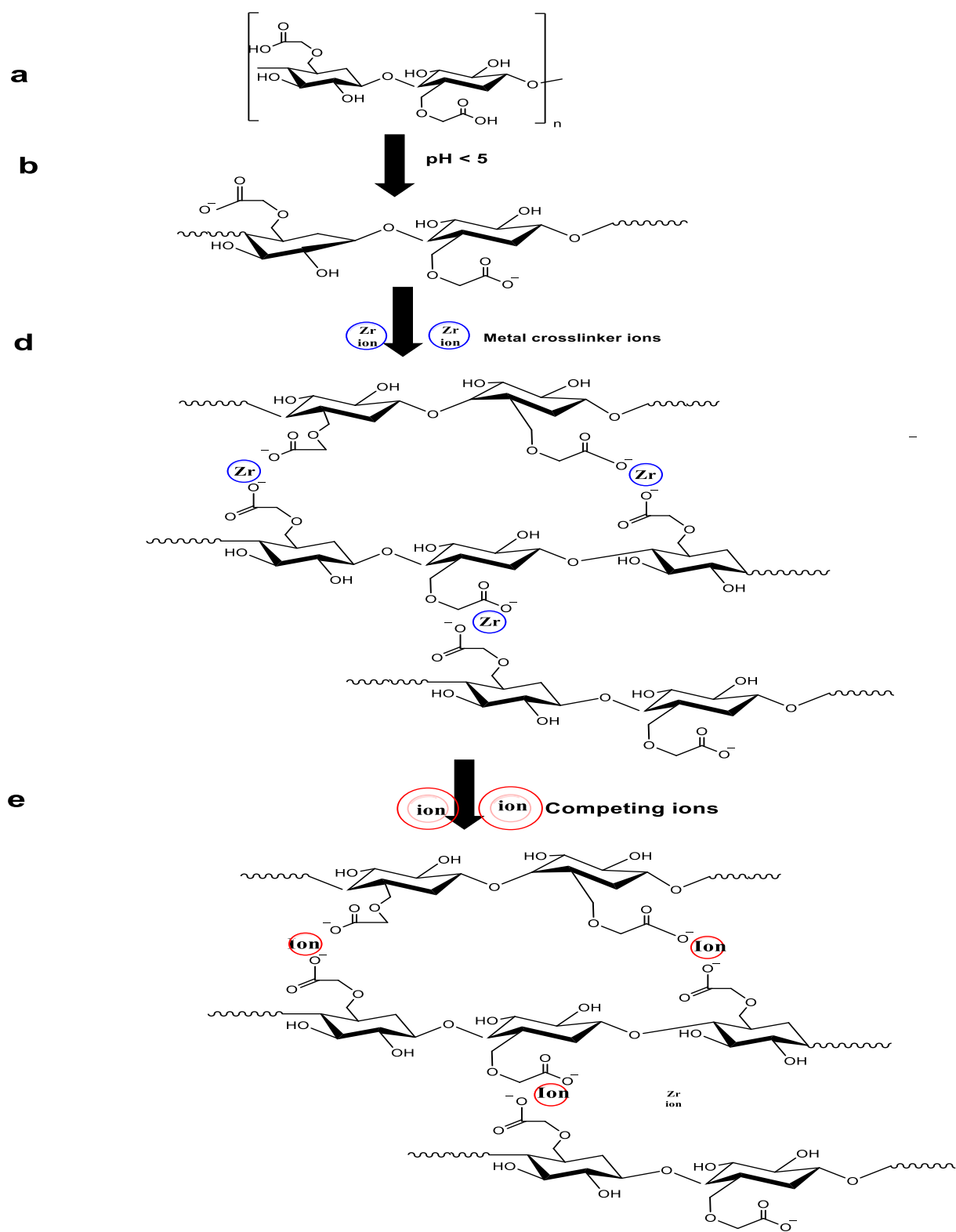


Figure 40- Crosslink mechanisms.

The initial viscosity of both CMC and guar based fluids is created through hydrating polymer gels in water. Figure 40 shows a chain of suggested reactions that need to happen to form a crosslinked-gel. Gels are typically derived from guar gum or cellulose (CMC). The gel unravels and forms polymer chains made up of sugar rings which are carboxymethylated with chloroacetic acid during the derivation process to improve solubility, thermal stability, and performance^{141,142}. Due to the carboxymethylation process, functional carboxylic acid groups exist on the polymer chain (Figure 40a). There have been limited studies on the mechanisms of inorganic ions influence on polymer formation and crosslinking and the complexity of the chemistry^{101,142}, but two scenarios have been postulated. Figure 6d and e show the potential mechanisms for ion interaction with frac fluids.

At higher pH values, this functional group begins to dissociate and form reactive carboxylate anions (Fig. 40b). A crosslinker can be added to replace the weak hydrogen bonds with much stronger bonds (Fig. 40d) which increases the viscosity of the fluid. Crosslinkers are typically metals that have been complexed with ligands. At least two of these ligands detach, typically in the presence of heat and shear, and the metal can now crosslink two available carboxylate sites¹⁶³. In the presence of spiked ions, a competition for available carboxylate sites may occur (Fig. 40e). Typically, this competition is not enough to impact stability, but as the ions approach a critical concentration, the crosslinker is unable to form a crosslink and viscosity is impacted. Previous studies have shown that in addition to the mechanisms shown, in the presence of high salt concentrations, shielding can occur. Shielding is a phenomena at which polymer molecules become surrounded by the dissolved ions in the solution. In other words, the ability of the polymer to disentangle is greatly reduced, reducing fluid viscosity^{100,143}. Instead of forming a competitive complex, the ions surround the active crosslink sites creating an interfacial double layer and preventing hydrogen bonds or crosslink complexes.

This effect becomes more pronounced as the ionic strength of the solution increases. Trivalent cations exhibit this behavior, possibly due to their increased ionic strength. They more easily compete with the typically quadrivalent crosslinker, resulting in less available crosslinking sites. It is possible that scenario (Fig. 40e) is not the only possible ion interaction. The ions may not form a crosslink at all, but instead interact with multiple functional groups on the same polymer, preventing any crosslinking at all, or complex with a single functional group rendering it inactive¹⁰¹. Whichever scenario exists, it is clear that the aluminum and iron behave in the same way as the calcium and magnesium at much lower concentrations. The same is true for the phosphorous. The phosphorous ion (+5 valence state) produced negative effects at very low concentrations (1-5mg/L), which leads to the conclusion that ionic strength is a definitive factor in ions and their impact on fracturing fluid.

Comparing hydration time and viscosity of all the spiked runs with a base run could be another way to confirm this hypothesis. Viscosity measurements were taken on the fluid as the gel hydrated for each sample. These measurements were then compared to the baseline viscosity measurements at 3,6, and 9 minutes and a weighted error was calculated based on the hydration delays at three points. The more negative the weighted error, the lower the hydration viscosity of the gel at each measurement interval.

Table 12- Weighted error for some ions in CMC and guar based fluids

Ion	Concentration (mg/L)	Weighted error-CMC based fluid	Weighted error- Guar based fluid
Phosphorous	1	0.9	0.8
Phosphorous	3	-0.4	0.1
Phosphorous	5	0.6	0.9
Phosphorous	10	0.5	-0.1
Aluminum	7.5	0.3	0.2
Aluminum	15	-0.1	1.0
Aluminum	20	0.7	0.9
Iron	25	0.5	0
Iron	50	0.2	-1.9
Iron	75	-0.5	-3.6
Iron	100	-1.1	
Iron	125	-2.2	
Magnesium	25	-1.9	-1.4
Magnesium	75	-5.7	-2.9
Magnesium	125	-6.3	0.8
Calcium	100	-4.1	
Calcium	200	-5.9	-4.2
Calcium	400	-7.7	-2.7
Calcium	600	-12.8	
NaCl	3000	-7.3	-6.0

NaCl	5000	-10.8	-9.5
NaCl	7000	-10.7	
NaCl	9000	-13.7	-10.3
KCl	3000	-7.5	-5.0
KCl	5000	-9.2	-7.6
KCl	9000	-11.3	-12.0
KCl	24000	-12.7	

Table 12 shows the calculated error for a subset of the ions tested. As seen in the table for both fluids, sodium and potassium significantly lower the ability of the gel to hydrate, further supporting the theory that at higher TDS values, more shielding is taking place and the polymer unfolding is more difficult and as a consequence the fluid has a lower viscosity with less stability.

Table 13- Summary of ions' effect based on spiked concentrations.

CMC based fluid					Guar based fluid			
Ion	Effect	Critical Concentration (mg/L)	Highest Concentration Tested (mg/L)	Notes	Effect	Critical Concentration (mg/L)	Highest Concentration Tested (mg/L)	Notes
Aluminum	None		20		Significant	15	20	Lowers Viscosity
Ammonium	None		50		Small		50	Increases Viscosity
Barium	None		15		None		15	
Bicarbonate	Small		3000	Increases Viscosity	Significant	1500	1500	Lowers Viscosity
Boron	Small		25	Increases Viscosity	None		25	
Bromide	None		200		None		200	
Calcium	Significant	600	600	Increases Viscosity	Significant		400	Increases Viscosity
Iron	Significant	75	125	Destabilizes Viscosity	Significant	75	75	Lowers Viscosity
Magnesium	Significant		125	Increases Viscosity	Significant		125	Increases Viscosity
Nitrate	None		100		Small		100	Increases Viscosity
Phosphorous	Significant	5	10	Destabilizes Viscosity	Significant	5	10	Lowers Viscosity
Potassium	Significant	9000	2400	Destabilizes Viscosity	Significant	5000	9000	Destabilizes Viscosity
Sodium	Significant	9000	9000	Destabilizes Viscosity	Significant	5000	5000	Destabilizes Viscosity
Strontium	None		60		Small		60	Increases Viscosity
Sulfate	None		1600		Significant		1600	Increases Viscosity

Table 13 summarizes the impact of each ion for the two fluid systems. The relative influence of each ion was determined based on the comparison of viscosity profiles between the individual ions and the base fluids. The critical concentration shown in the table represents the concentration found during testing that resulted in either an unacceptable peak viscosity, final viscosity, or a significant difference in the trend when compared to the baseline tests.

4.3.4 Conclusion

The effects of individual cations and anions on the rheological properties of high-pH crosslinked guar-based and low pH CMC-based polymers were examined in detail. Based on the results obtained, the following conclusions can be drawn:

- Compared to CMC-based fluid, the guar-based fluid was more sensitive to dissolved ions and metal additives (e.g. Al and Fe). Between these two fluid systems, hydraulic fracturing with CMC based fluids is more tolerant with saline and poor quality water sources.
- Calcium, iron, magnesium, phosphorous, potassium and sodium have significant impact on CMC-based fluid viscosity, albeit at vastly different concentrations.
- Higher valence state ions require lower concentrations to reach critical concentrations.
- CMC-based fluid and guar-based fluid were more tolerant to monovalent ions such as sodium and potassium at a significantly higher critical concentration 7,000 or 9,000mg/L.
- Divalent ions calcium and magnesium actually improve the apparent viscosity of both cellulose and guar based fluids until a critical concentration produces the counter effect.

The results of this study demonstrate that produced water can be used as a supplemental water source for hydraulic fracturing but when using gel-based polymers, a good understanding of the ionic interactions is required.

4.4 Recycling frac flowback water for use in hydraulic fracturing: influence of organic matter on stability of CMC based frac fluids

4.4.1 Introduction

Extraction of shale oil and gas using hydraulic fracturing and horizontal drilling is being conducted in many areas of the US. The practice requires varying and sometimes significant volumes of water as a primary component in the frac fluid. Typically, fresh water sources have been utilized to develop frac fluids due to specific viscosity requirements, but in water-short regions of the country (e.g. Texas and Colorado) oil and gas operators are increasingly looking to maximize use of flowback and produced water from existing wells. Although there are no clear definitions for frac flowback and produced water, the early time flowback (ETFB) water is distinguished by initially high flowback rates and significant concentrations of the broken frac fluid components. For the purpose of this research, ETFB is defined as water that flows back during the first 15 days. The quality of ETFB and produced water is generally very poor with high salinity and potentially high organic matter content^{33, 34}.

Hydraulic fracturing may require two to six million gallons for a single horizontal multi stage well⁴⁸. Currently fresh water from groundwater, ponds, rivers and lakes are the primary sources for oil and gas operations in many parts of the country. Water acquisition costs including rights and transportation can be significant at approximately \$4-5/barrel, depending on water source and its distance to the drilling field¹⁴⁴. The large quantity of water required also raises public concerns about water shortages and drought in arid climates¹⁰². Produced water that operators need to manage continues for the life of the well until permanent shut-in. Presently, injection into deep salt water disposal wells (SWDs) is the most common method for flowback and produced water

Society of Petroleum Engineers, N. Esmailirad*; C. Terry; Herron Kennedy; A. Prior; and K. Carlson, Colorado State University, Department of Civil & Environmental Engineering, * Corresponding author: nasimrad@colostate.edu

disposal with more than 90% of the wastewater disposed of in this manner⁵⁹ with associated costs including water hauling and disposal¹⁴⁴. The remaining produced water is discharged to surface water with treatment required to meet regulatory and legislative requirements, also a portion was recycled and reused in hydraulic fracturing^{33,34,60,61,102}. Recycling of produced water for reuse in fracturing fluids could reduce the costs of acquisition and disposal as well as address public concerns related to water shortages and environmental impacts. In recent years operators have been more motivated to recycle flowback water since more than 30% of total volume of water comes back to the surface in the first month of production⁹⁶. However, recycling flowback and produced water for use in frac fluids has not been well studied. Flowback water from broken gelled fracturing fluids contains more organic matter^{33,34,145} and lower total dissolved solids (TDS) while produced water (arbitrarily defined as well age greater than 30 days) contains higher TDS and a lower organic matter concentration. These characteristics are the main obstacle in successful traditional coagulation/filtration cost effective treatment^{33,34}. Temporal and spatial variability of produced water quality also makes recycling difficult for reuse in building suitable fracturing fluids⁹⁷.

Formulating fracturing fluids for acceptable rheological performance can be very sensitive to water quality. The composition of a typical gelled frac fluid consists of water, proppant, gelling agent, cross linkers, buffers, surfactant, breakers, biocides, friction reducers and scale inhibitors and potentially other additives based on geological and technical considerations^{100,146,149,150,151}. Polymers, such as cellulose derivatives, biopolymers and guar gum were introduced in the water based drilling fluids for their rheological performance and for ecological considerations. Guar gum and its derivatives are very common fracturing fluid polymers, they account for possibly 90% of all gelled fracturing fluids¹⁴⁹. The cellulose derivative is the next common polymer in hydraulic

fracturing due to its biodegradability and compatibility with other materials. CMC is produced by reacting cellulose obtained from wood pulp or cotton fibers with chloroacetic acid and NaOH. The presence of polar carboxyl methyl groups makes the cellulose soluble, chemically reactive and strongly hydrophilic⁹⁹. CMC is a white to almost white powder, non-toxic and biodegradable, odorless and does not ferment under normal conditions of use. It is also very soluble and it can be dissolved in hot or cold water. It is largely used in industry, due to its exceptional rheological properties in aqueous solutions⁹⁹. The crosslinkers work by chemically linking together the linear polymers in the fluid creating higher molecular weight polymer compounds. Common crosslinking agents include borates, aluminum, zirconium and titanium containing compounds. The selection of the correct crosslinking agent is based upon the type of gelling agent being used.

The viscosity of gelled frac fluid is a criterion for stability regarding transporting proppant while it is pumped downhole and having the ability of fracturing the formation in which the optimum production occurs⁶¹. The optimum hydraulic fracturing fluid composition for each well is typically chosen by the treatment objectives and evaluating the adequacy of the fluid system's performance in fluid-loss control, fracture conductivity, and proppant transport, as well as in the amount of formation permeability damage. Ideally, "the selected fluid system should promote the stimulation treatment, minimize associated risks, and maximize post-treatment production economics"¹⁵².

Therefore having a comprehensive knowledge and broad understanding of the frac flowback and produced water chemistry and its influences on frac fluid characteristics is important. In this paper we investigate the influence of oilfield wastewater organic matter and salinity on frac fluid stability. The objective of this study was to determine if organic matter from broken gelled frac flow back impacts fluid stability during the subsequent development of a gelled frac fluid. In addition, we qualify the influence and attempt to provide insight into the mechanisms involved.

4.4.2 Materials/Methods

Synthetic water and recycled water

Isolation and extraction methods are complex and may not be effective with the residual gel OM in this study and therefore actual water was collected for the experiments. For the first set of experiments, treated produced water (referred to subsequently as recycled water) was collected from an industrial facility that provided chemical treatment for flowback and produced water. The recycle water from this facility had a total organic carbon (TOC) concentration of greater than 1800 mg/L (**Table 14**). The facility uses a conventional ferric coagulation process so it is expected that 30-50% of the original organic matter is removed. Since the facility only collects wastewater from oil and gas operations, it is likely that the organic matter is made up of broken polymers from gel frac operations nearby.

Table 14- Water quality measurements for different waters tested.

Parameter mg/l	Recycled Water	Model water	ETFB water	Produced water	CSU Tap water
Gravimetric TDS	36580	27354		36520	
Ionic TDS	27354	24706	22412	26364	250
TOC	1868	0	1961	1397	<5
NH ₄	20	18	39	40	<0.5
Br	79	67	62	68	<1.0
Cl	16520	14886	13150	15550	19
SO ₄	290	73	<0.5	4.2	<0.5
HCO ₃	260	183	840	600	32
Al	1.3	1.3	1.3	1.3	<0.1
Ba	1.03	10.8	18.2	10.6	<0.1
B	10.1	8.8	14.8	18.5	<0.1
Ca	31.2	44.8	366	453	14.4
Fe	1.5	1.8	65.4	21.6	<0.1
K	351	517	51.6	46.2	0.89

Mg	10	10.2	41.8	68.2	1.8
Mn	0.1	na	0.8	0.3	<0.1
Na	9764	8877	7647	9372	3.6
Si	12.9	3.9	63.5	56.8	3.2
Sr	3.6	3.3	40.6	53.1	<0.1
Cu	Na	na	0.1	0.1	<0.1

For the second set of experiments in this phase of the research model or synthetic water was developed to be identical to the recycled water except for the presence of organic matter. The model water was created using low-TOC tap water and dissolving a specific amount of particular salts to reach the determined concentration such that total ions of modeled water was equal to ionic TDS (total sum of ions concentration) of recycled water. The added salts are: NaCl, FeCl₂, NaCO₃, NH₄Cl, NaBr, Na₂SO₄, BaCl₂, CaCl₂, KCl, MgCl₂, MnSO₄, FeSO₄, H₃BO₃, aluminum chloridehydrate and SrCl₂. The stock solution was then diluted with tap water to create samples with six different TDS values, 3000, 5000, 7000, 9000, 11000 and 13000 mg/l but no organic matter.

Early time flow back and produced water

The second part of the study was to explore the influence of different types of organic matter on frac fluid stability. For this aim, two water sources, ETFB (early time flow back) and produced water were used. Researchers^{33,34,145} have shown that organic matter characteristics are very different between ETFB and produced water. The ETFB water used in these experiments was not treated with a coagulation process so it represents all of the organic matter that is in the flowback water. The produced water was also not treated but was collected from a well that had been producing for more than 60 days. The difference in organic matter composition between the two waters is expected to be due to the well age and the washout of frac fluid compounds over time.

Stated differently, since the ETFB water was collected from a well that was in production for less than 5 days, the organic matter composition was likely dominated by the frac fluid. After 60 days, the flow rate decreased significantly and the organic matter composition is likely based on the formation water and possibly residual frac fluid that had undergone continued thermal breakdown. These water samples were taken from an operating oil and gas pad in the Denver-Julesburg Basin. Water quality analyses were conducted on both of these water samples and the results are compared with the recycled and model waters in Table 1. As with the other two water sources, several different TDS concentrations (5000, 7000, 9000, 11000 and 13000 mg/l) were studied by dilution with tap water (**Table B.1 through B.3**).

Table 15 shows a full description for all the abbreviations used in these experiments and the subsequent figures.

Table 15- Water sample descriptions

Abbreviation	Description
Recycled	Treated produced water
Model	The synthetic water made up based on recycled water ionic composition
Tap water-ETFB Tap water-PW	ETFB/ Produced water was diluted with CSU tap water to reach the targeted TDS value
Model-ETFB Model-PW	ETFB/ Produced water was diluted with model water and CSU tap water to reach the TDS and TOC values

Material

A frac package that included low residue CMC gel and zirconium crosslinker chemicals was used as the base fluid to determine if organic matter impacted the viscosity development. This fluid consists of low residue CMC based gel, buffer and a crosslinker (zirconium) as the base components. ETFB, produced water, model water and recycled water samples were used to prepare polymer solutions.

Water quality analysis

All water quality analyses were done using Standard Method procedures¹¹⁶. TOC, gravimetric TDS and pH analyses were conducted at the Colorado State University water quality laboratory. An independent, EPA-certified laboratory provided analysis of cations and anions. Gravimetric TDS was measured based on standard methods of water and wastewater¹¹⁶. The ionic TDS concentration was calculated by summing the anion and cation concentrations. pH was measured using a Hach (Hach, Loveland), HQ40d pH meter. TOC was measured using Standard Methods¹¹⁶ 2540D 5130B. Cations were measured by EPA 2007¹⁸⁵ method 6010 C using a Varian ICP-AES, Liberty AX.

Recycled water was diluted to achieve TDS values of 3000, 5000, 7000, 9000, 11000 and 13000 mg/l. As mentioned previously, the TDS of recycled water includes a significant amount of dissolved organic matter so the gravimetric TDS for this water is higher than the modeled water. Based on this observation, if there is any difference in frac fluid performance between the two waters, recycled and model, it is due to the organic content of the recycled water. To diminish and maintain the effect of salinity on the results, it was decided to build all the solutions based on ionic TDS and use ionic TDS as a label for samples. The TOC concentration of all samples at all TDS levels was measured and is shown in **Figure 41**.

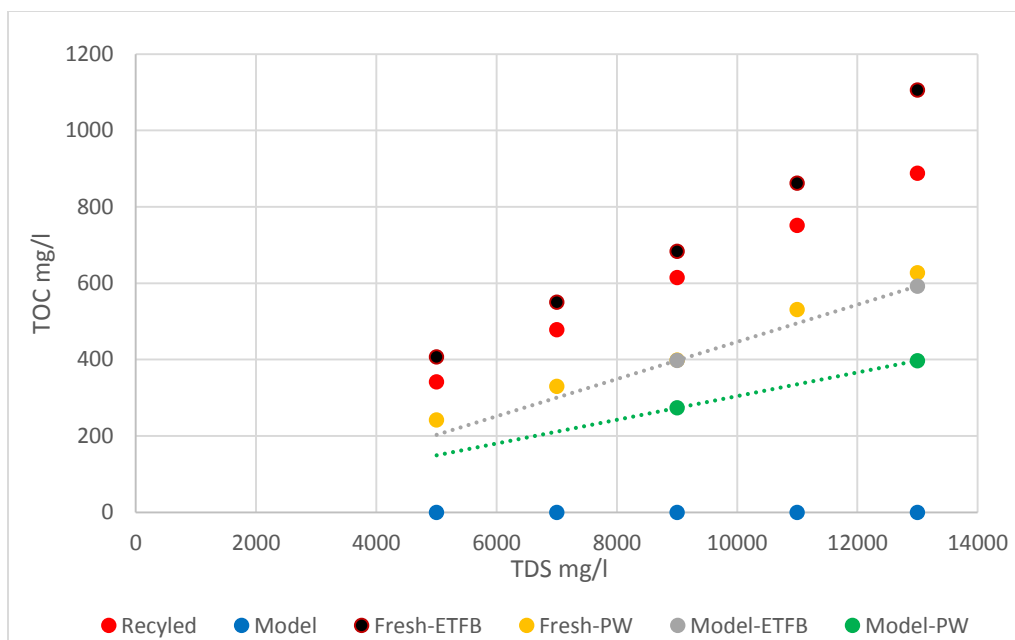


Figure 41-TOC quantity corresponding to TDS for different water samples

As shown in Figure 41, higher sample salinities correlated with higher TOC concentrations (except for the model water) since the dilution of the stock solution was less. The range of observed TOC concentration was between 180 and 1100 mg/l. Also the highest TOC level was seen with a mix of CSU tap water (fresh) and ETFB and the lowest TOC concentration was the model water.

Building frac fluid

The CMC gel that was used to make the frac fluid was buffered to a pH of approximately 5.0. All rheology tests were conducted at a service company in Brighton, CO. Fluid system loadings provide comparable viscosity to each other and are representative of actual formulations pumped in the field.

The following procedure was used to prepare all frac fluid samples:

1. A 1000 ml sample of water or salt water was placed in a 1000 ml blender to prepare the linear gel.
2. A blender was used at 1500 rpm circulating rate, which was needed to establish a vortex shape with no air bubbles trapped.
3. An appropriate quantity of CMC based gel was added slowly from the shoulder of the created vortex to reach the desired polymer loading. A timer was started at this time. Apparent viscosity was measured at 3, 6 and 9 minutes of adding polymer to water sample to study the polymer hydration phenomena.
4. Finally, the first buffer was added, followed by the cross linker and second buffer, mixed for 10 s before loading into the viscometer.
5. To minimize instrument variability, the tests were run on three dedicated viscometers that were calibrated regularly.

To have the same test conditions for all prepared fluids, viscosity measurements were conducted within two minutes of the initial hydration time to minimize viscosity changes¹³⁸.

Rheology tests

Viscosity was measured in the study using a Chandler Model 5500 HPHT Viscometer affixed with a R2 bob concentric cylinder geometry. A computer was directly connected to the viscometer and recorded viscosity and temperature of each test. All tests were performed using 78mL sample of fluid at a shear rate of 40s^{-1} for a run time of 45 minutes and a final temperature of 200°F. An example of the raw data of a run with the CMC is shown in **Figure 42**. Solid lines represent the

viscosity profile and dash lines represent temperature of the sample. TDS ranges varied between 3000 mg/l to 9000 mg/l. The temperature was raised from 75°F to 200°F within 15 minutes and was kept constant at 200°F.

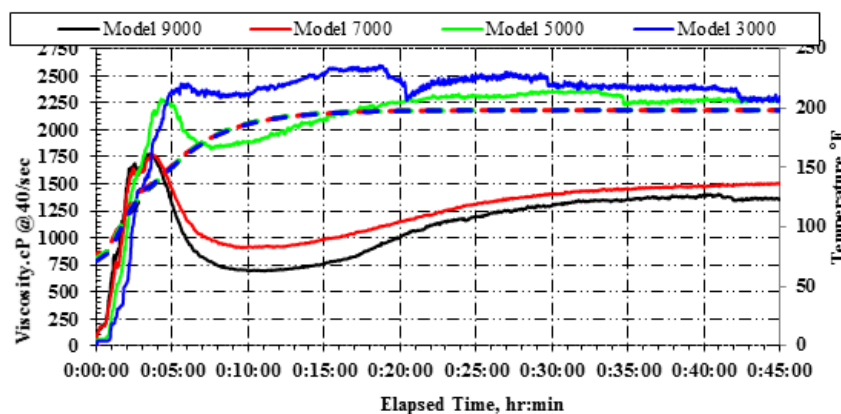


Figure 42-Low residue Carboxyl methyl cellulose (CMC): Model water with TDS ranging from 3000 to 9000.

4.4.3 Results and Discussion

The following graphs show the rheology tests results for a range of water quality conditions. Replicates were run for each condition and the actual number of runs is noted in each graph. The results shown are the average of the runs completed and the solid lines represent the viscosity profile and dash lines represent the temperature of sample during 45 minutes of testing.

Recycled water versus model water

Qualification analysis

The frac fluid system consisted of CMC based gel, buffer, and two zirconium based crosslinkers. Using this base fluid composition, different concentrations of salts were added for each case. The CMC gel requires a final pH of 5.0 for optimum efficiency; the pH was measured before and after

viscosity measurements. If the measured pH is higher, additional buffer was added and the experiment was repeated. The following plots are the average of three split runs unless noted otherwise. The actual number of runs for each sample is mentioned in parentheses. **Figure 43** shows the rheology results for both model and recycled water at five TDS values: 5000, 7000, 9000, 11,000 and 13,000 mg/l. The temperature profile is the same among all the runs and TDS levels, starting at less than $75\pm 5^{\circ}\text{F}$ and ramping up to 200°F within 15 minutes. As discussed previously, the only difference in the fluids is that one uses recycled water with more than 1800 mg/L of OM and the other is a model water made to mimic the inorganic composition of the recycled water but without OM.

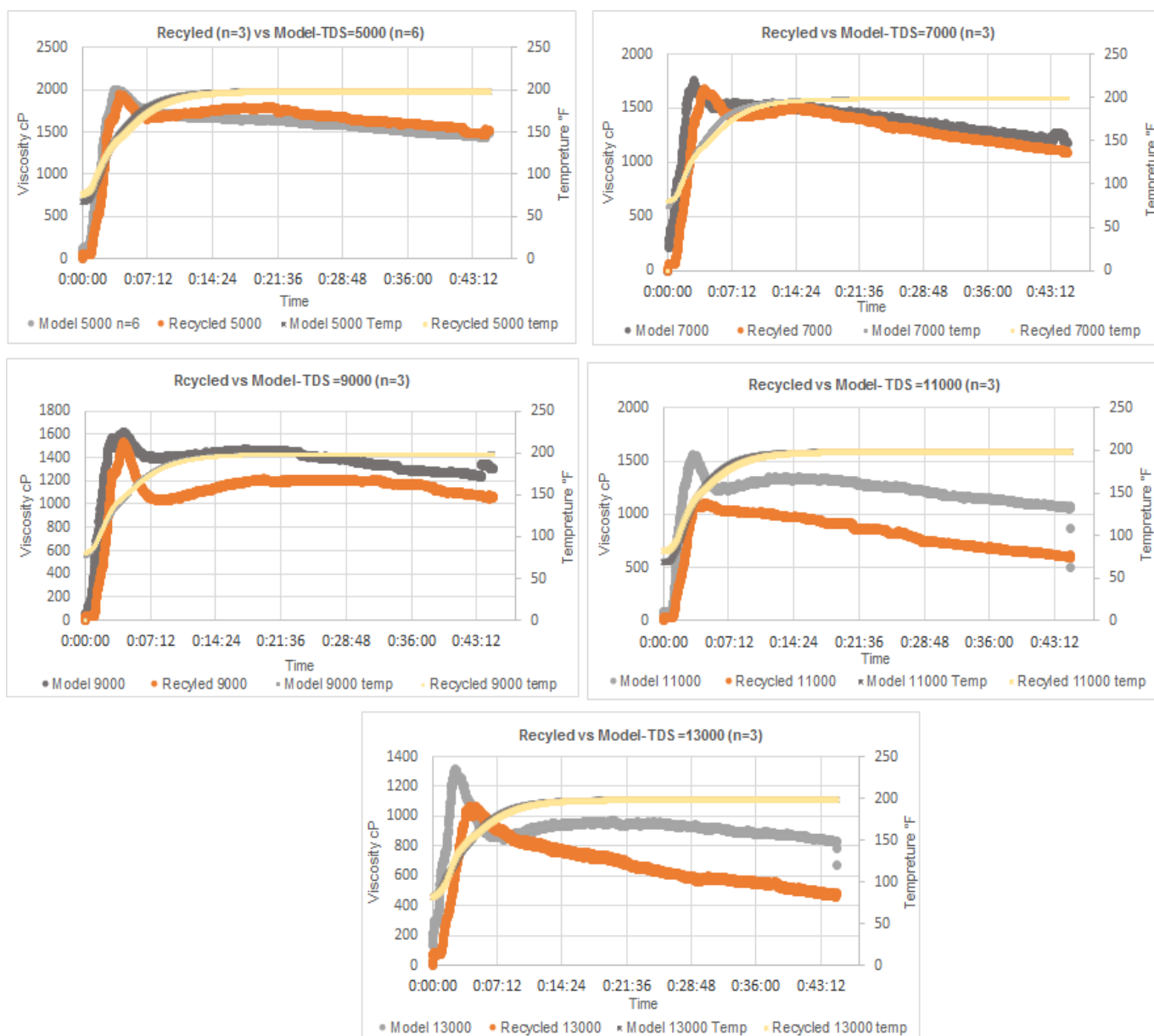


Figure 43- Recycle versus model water at five different TDS values: 5000, 7000, 9000, 11000 and 13000 mg/l.

At the lower TDS values (5000 and 7000 mg/L) both fluids exhibited similar viscosity profiles (Figure 43). Rheology parameters including peak viscosity, final viscosity and viscosity profile appeared to have minimal differences. However, at TDS values greater than 7000 mg/l, the rheology characteristics of the fluids created with different waters began to deviate. As the TDS

increased, the difference becomes more pronounced. Recycled water showed approximately 50% lower final viscosity at higher TDS concentrations than 9000 mg/l. According to Haghshenas¹⁰⁰ (2014) a good frac fluid needs to hold a viscosity of greater than 1500 cP for at least 30 minutes, to be able to carry proppant to the designated point in the formation^{146,149}. Clearly the presence of the organic matter in the recycled water reduced the viscosity stability of the CMC fluid tested.

In laboratory tests such as these, the final viscosity is an important criterion to evaluate whether a fluid will be successful but initial viscosity and the decline over time are also parameters that need to be examined. Despite the growing interest on reusing flowback and produced water in hydraulic fracturing, research has not been published on the influence of organic matter. There have been a few studies^{59, 100} on salinity effects on frac fluid behavior but all of them have studied influence of individual salts and none has investigated the impacts of organic residue from gels on frac fluid stability. Due to the lack of fundamental understanding and complexity of the subject, a few theories were postulated. The following may be considered^{59,100,153,154,155}:

- The formation of complexes with crosslinker and existing organic matter (for example broken linear CMC polymer chains or organic acids), leads to competitive crosslinking with long-chain polymers.
- The restricted mobility of polymer molecules by hydration of organic matter and/or existing ions.
- Salting out is a natural phenomenon that happens in saline waters meaning that solubility of polymer by addition of organic matter with hydrophilic ends and dissolved salt is reduced (**Figure 44**). Figure 44 illustrates that in presence of higher concentration of dissolved solids, ions shield the polymer molecules and prevent them from unfolding and dissolving in the water.

- Formation of aqueous biphasic system, due to the unfavorable polymer-salt interactions and the salting-out effect that is reducing polymer solubility in the presence of salts.

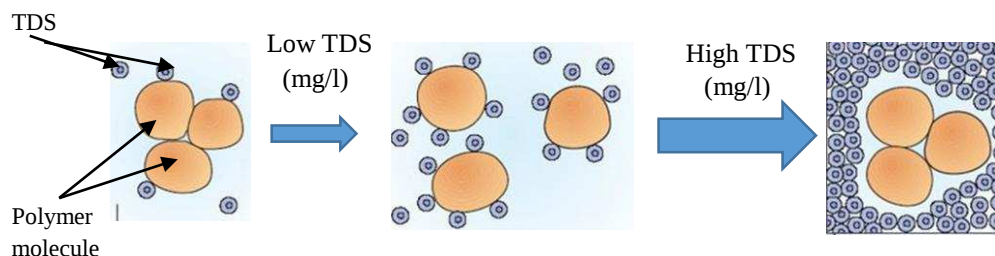


Figure 44-TDS concentration and salting out phenomena

Quantification analysis

The maximum observed viscosity for each run was recorded as peak viscosity. These peaks at different TDS values, for both model and recycled water, are shown in **Figure 45**.

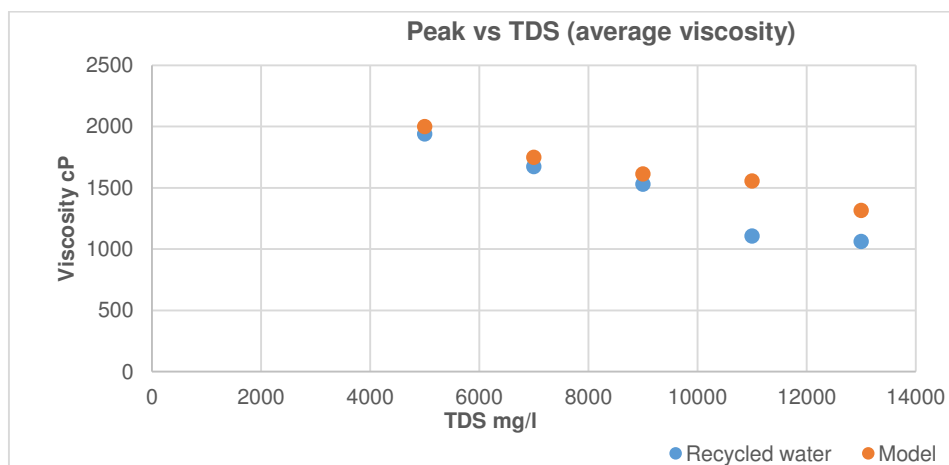


Figure 45-Peak viscosity versus TDS for model and recycled water

A strong correlation between the viscosity peak and TDS concentration. As observed in Figure45, the model water showed higher peak viscosity at all TDS values and the difference increased at TDS values greater than 7000mg/l.

A t-test was performed on the peak viscosity data for both waters and is shown in **Table 16 and FigureB.2**. A significance confidence level of 0.05 was chosen. The null hypothesis was that there is a significant difference between the two samples, model and recycle water. It was seen that for lower TDS values, 5000 and 7000mg/l, the null hypothesis was rejected, meaning there was not any difference between two water samples. However for TDS values of 9000 mg/l and above, p-values were lower than 0.05, indicating that model water and recycled water samples are significantly different.

Table 16-Calculated p-value for model and recycle water samples

TDS mg/l	5000	7000	9000	11000	13000
P value	0.375261	0.118994	0.00091	2.44E-05	0.023753

To confirm the negative impact of organic matter on frac fluid stability, the fluid viscosity sensitivity to organic matter as a function of TDS was investigated. The slope of the viscosity decline over time of the data shown in Figure 45 was analyzed by evaluating the change in viscosity for a unit change in TDS at a specific time. The delta viscosity/delta TDS versus time is presented in **Figure 46**.

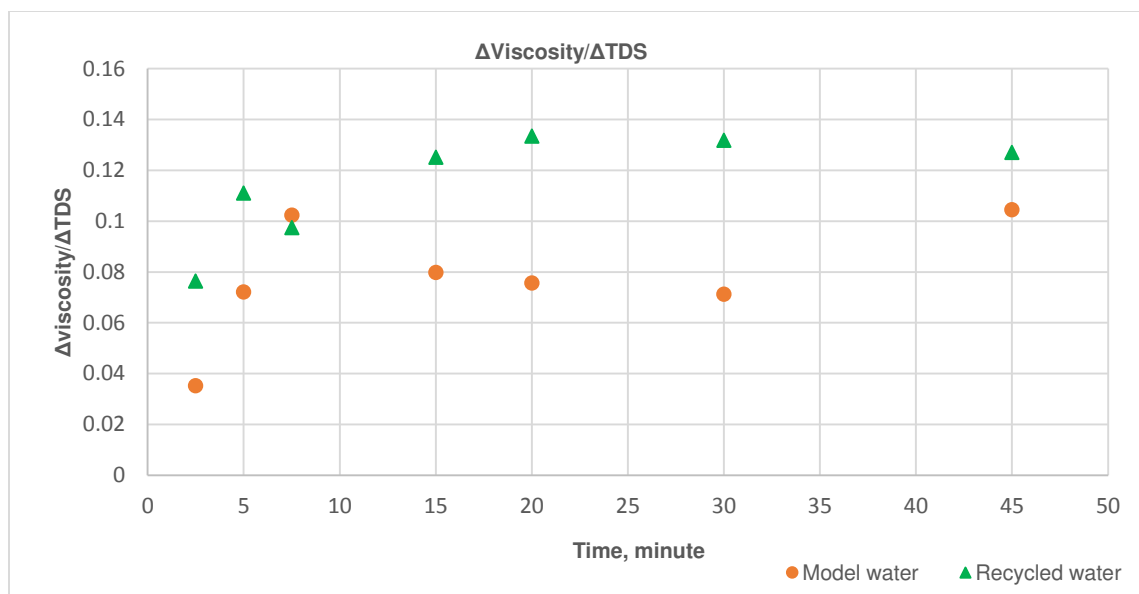


Figure 46-Δ Viscosity/ Δ TDS versus different times: 2.5, 7.5, 15, 20, 30 and 45 minutes

The data in Figure 46 indicates that recycled water showed a greater sensitivity to TDS concentration after the initial 10 minutes of fluid testing. The frac fluid developed with the model water exhibited a lower sensitivity to TDS and also its sensitivity was almost constant after 10 minutes of running the test.

ETFB versus Produced Water

Qualification analysis

Characteristics of organic matter present in frac flowback and produced water will vary significantly depending on well age, frac fluid originally used and formation. The results presented above are based on water obtained from an industrial recycling facility and was a composite of many different wells with a wide range of ages and frac fluids used. The water was also treated with a coagulation/filtration process as discussed previously, the early flowback water (ETFB) will have a higher concentration of organic matter since it is still dominated by the fluid used to frac the well.

The objective of this part of the study was to understand how water of a known origin would compare with the previous results. Two oil and gas wells in the DJ Basin were identified that had different well ages: (1) an ETFB well less than 7 days into production and (2) a produced water well that had been producing for more than 60 days. To study the source of organic matter and its' effect on frac fluid stability, CSU tap water was spiked with ETFB and produced water such that the TDS of the final solutions were: 5000, 7000, 9000, 11000 and 13000 mg/l. The viscosity plots are shown in **Figure 47**. The number of each runs are mentioned in the parentheses. The temperature profile is the same among all the runs and TDS levels, starting at 75°F and ramping to 200°F within 15 minutes remaining constant for the rest of the run.

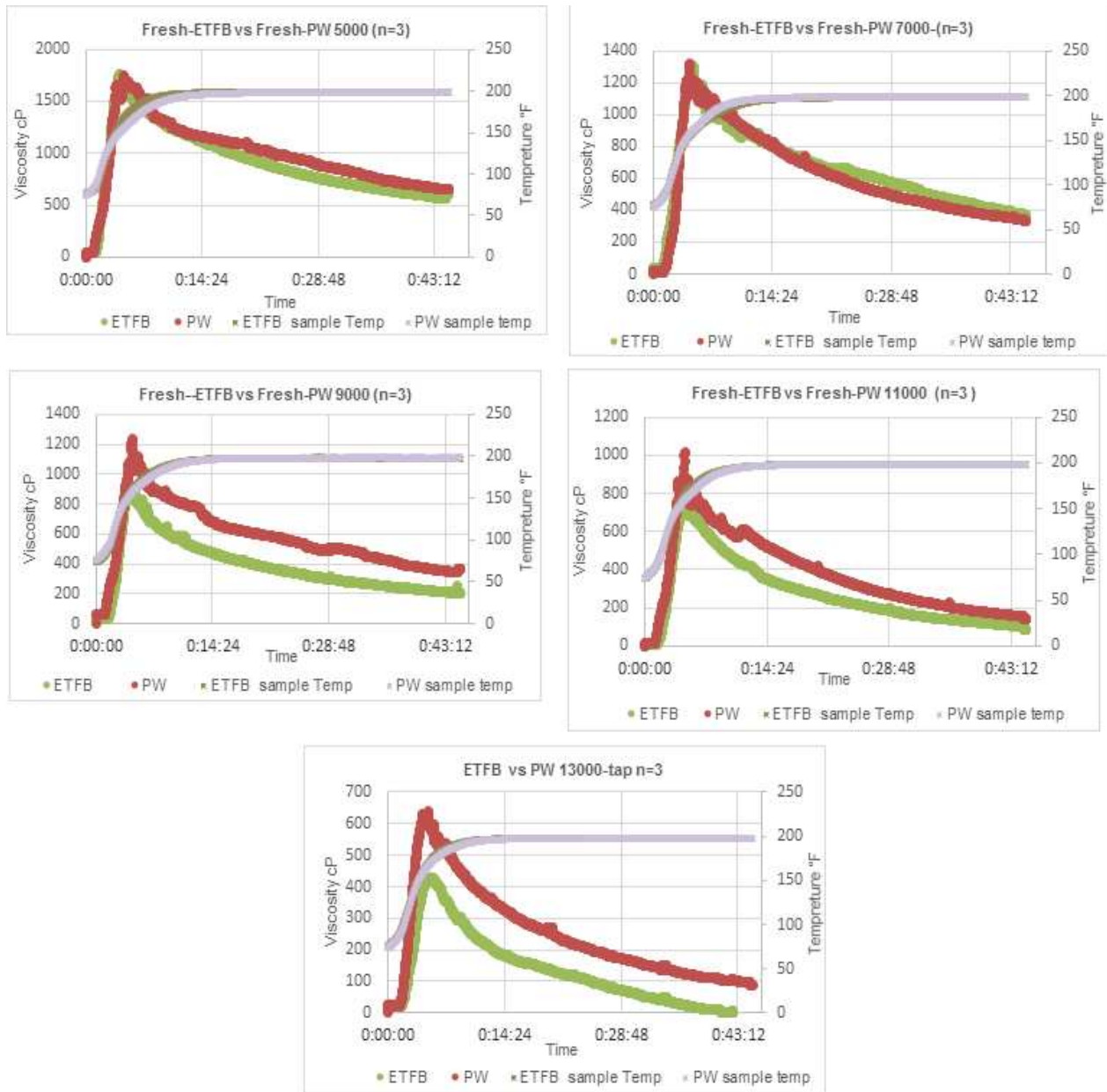


Figure 47-PW versus ETFB impacts on viscosity

Figure 47 shows that as TDS increased, the difference between ETFB and PW was intensified and produced water resulted in a frac fluid with higher viscosity profile and greater stability. ETFB fluid showed a stronger downward trend with lower viscosity.

Similar to the data presented previously comparing recycled and model water, there was minimal difference at lower TDS levels (5000 and 7000 mg/l). ETFBs' peak viscosity dropped dramatically

(40%) starting at TDS of 9000 mg/L associated with a 50% increase in TOC according to Figure 41. This observation supports the idea of organic matter impacting the frac fluid stability. Researchers^{33,34,145} reported that there is a difference in organic matter content of ETFB and produced water and each has a different chemical composition profile. According to Figure 47 and referenced studies, it was seen that the ETFB frac fluid had approximately 50% more dissolved organic matter, potentially the cause of the decrease in frac fluid stability that was observed. One explanation for the decrease in fluid peak viscosity and stability could be the presence of broken polymer chains that interact with the subsequent frac fluid cross-linkers creating a polymer structure of short chains and random crosslinking.

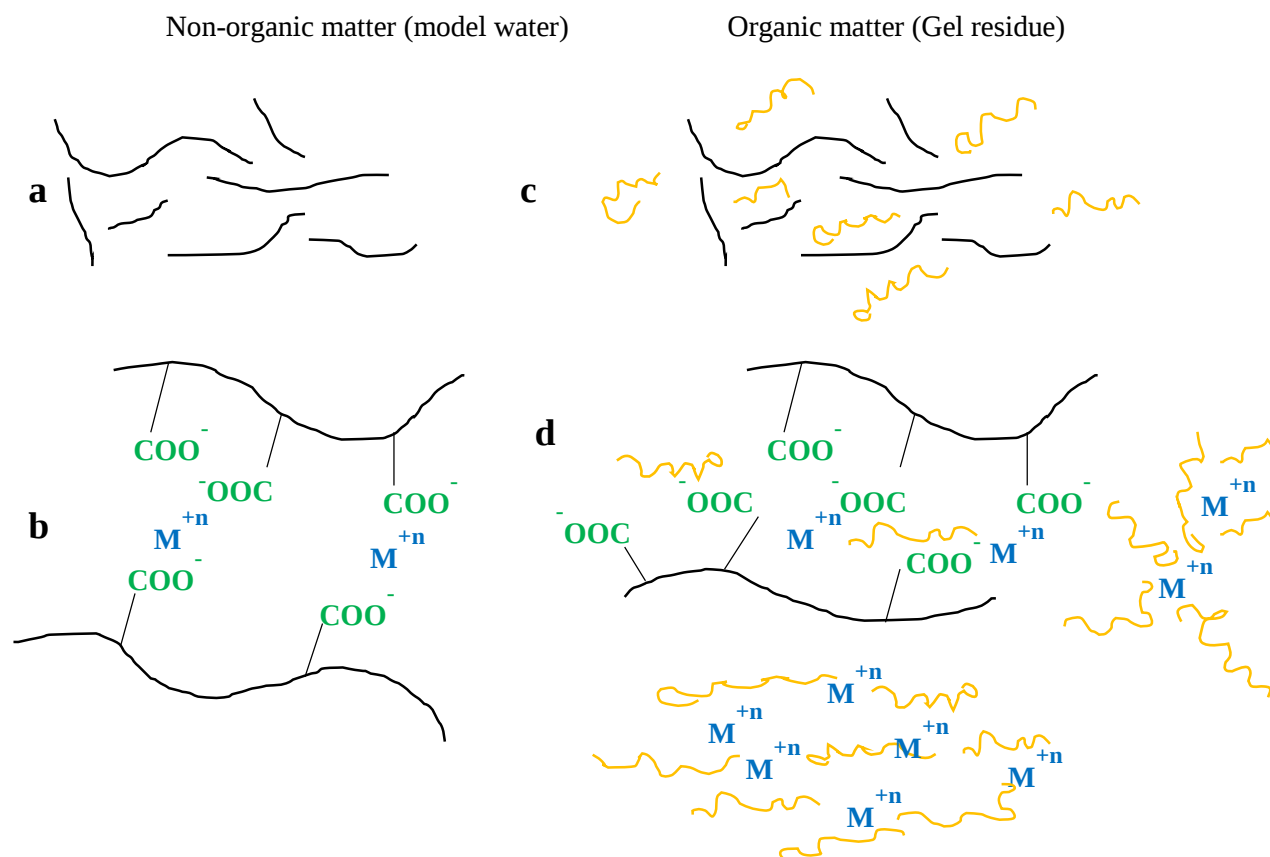


Figure 48-Speculated mechanisms of cross linking in presence of organic matter

Figure 48 postulates cross-linking mechanisms with and without the presence of organic matter for a CMC based fluid. Without residual flowback organic matter, non-crosslinked polymer branches separately (a), and then adding zirconium crosslinkers (b) forms a strong ionic bond and well organized polymer structures that lead to high and stable viscosity. According to Figure 48(c), non-crosslinked polymers (a) with residual organic matter have similar elongated branches of polymers but after adding zirconium crosslinkers to the solution (d), two possible mechanisms are suggested: formation of metal-organic complexes and/or crosslinking of organic matter. Complexation of cations, the zirconium crosslinker, with hydrophobic organic matter due to electrostatic forces, swapping the zirconium ions and therefore creating a deficiency in zirconium crosslinker concentration for crosslinking of CMC chains. The second potential mechanism was that instead of crosslinking of linear CMC chains, the recycled organic matter molecules that are residues of the frac fluids, react with the zirconium ions and form a weak and unstable crosslinked structure.

Quantification analysis

Results of t-tests comparing peak viscosity values between the ETFB and PW fluids are shown in **Table 17 and Figure B.3**. A significance level of 0.05 was considered for the null hypothesis of non-equivalency. Based on the calculated p values, the peak viscosity for the fluid developed with ETFB water was significantly less when the viscosity was increased to 9000 mg/L or above.

Table 17-Calculated p-value for PW and ETFB water samples, peak viscosity

TDS mg/l	5000	7000	9000	11000	13000
P value	0.375261	0.118994	0.00091	0.003932	0.003559

Treating produced water or not? Does treatment make any difference?

Treatment of flowback water and produced water can pose challenges due to the presence of high concentrations of organic matter. Esmailirad, et al.^{33,34} reported that when a high organic content is present, traditional flocculation-coagulation processes are not successful at reasonable coagulant doses and costs. Based on these results, a comparison was run between recycled water samples and un-treated ETFB and produced water samples.

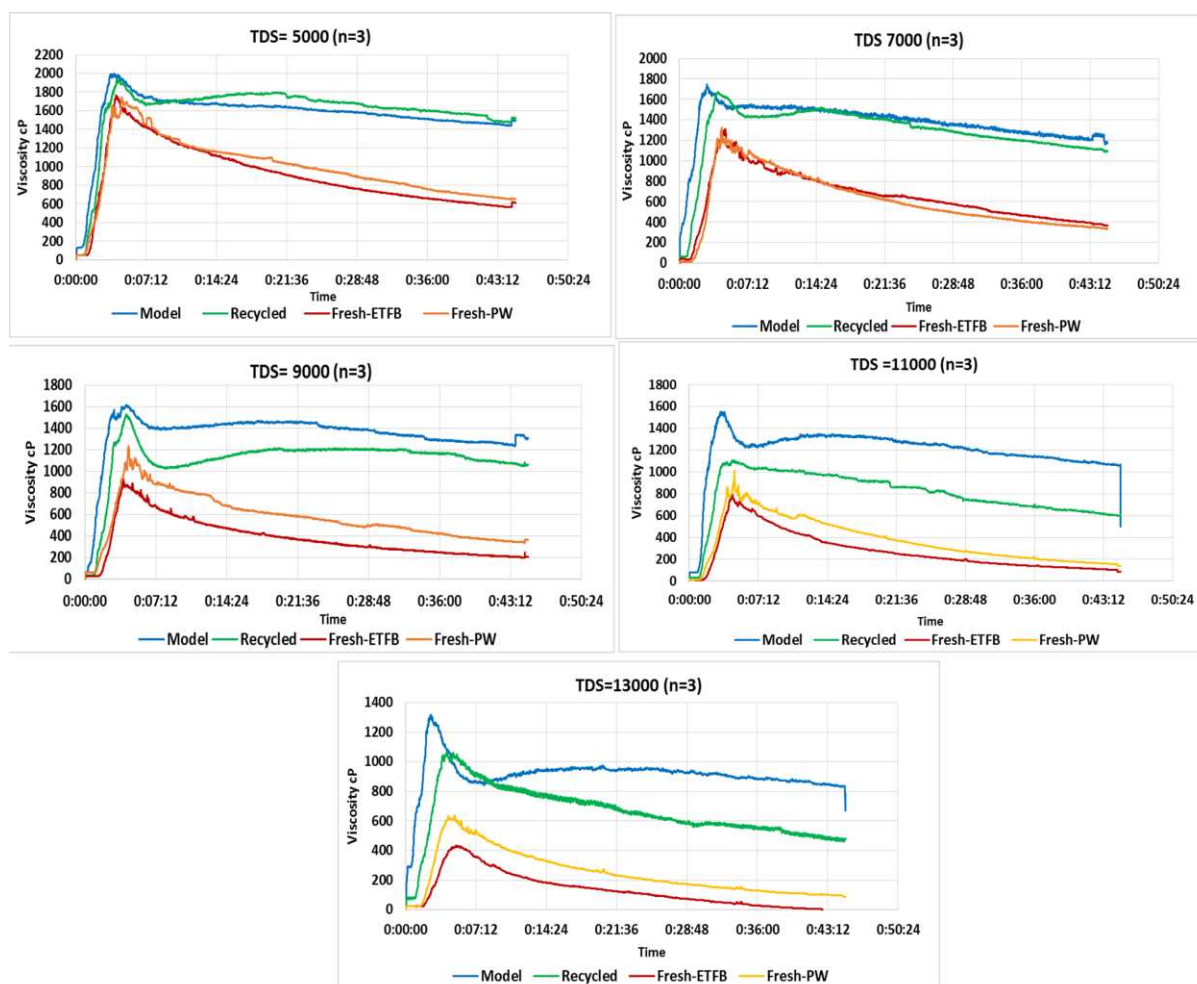


Figure 49-Comparing viscosity of recycled water and non-recycled water

Figure 49 represents viscosity profiles for all three types of waters at TDS values of 5000 to 13000 mg/l. The lowest viscosity profile was seen for the ETFB water while the highest viscosity profile

was seen for recycled water and this difference was more pronounced with increased TDS. According to Figure 49, un-treated ETFB and produced water behaviors were similar but there is a significant gap between treated and un-treated waters. The results indicate coagulation/filtration treatment removes organic matter that may be particularly surface-active and disruptive to the development of an acceptable frac fluid.

Organic matter quantity

Organic matter is a persistent obstacle in produced water and flowback water recycling. Yet, its strong presence in the flowback and produced water and its sources has not been characterized to an acceptable level. The objective of this part of the study was to determine whether TOC quantity is responsible for the decrease in stability of frac fluid when non-fresh water is used. To attempt to answer this question, model water was spiked with both ETFB and produced water and was diluted by CSU tap water to reach the TDS ranges of 7000 to 13000 mg/l.

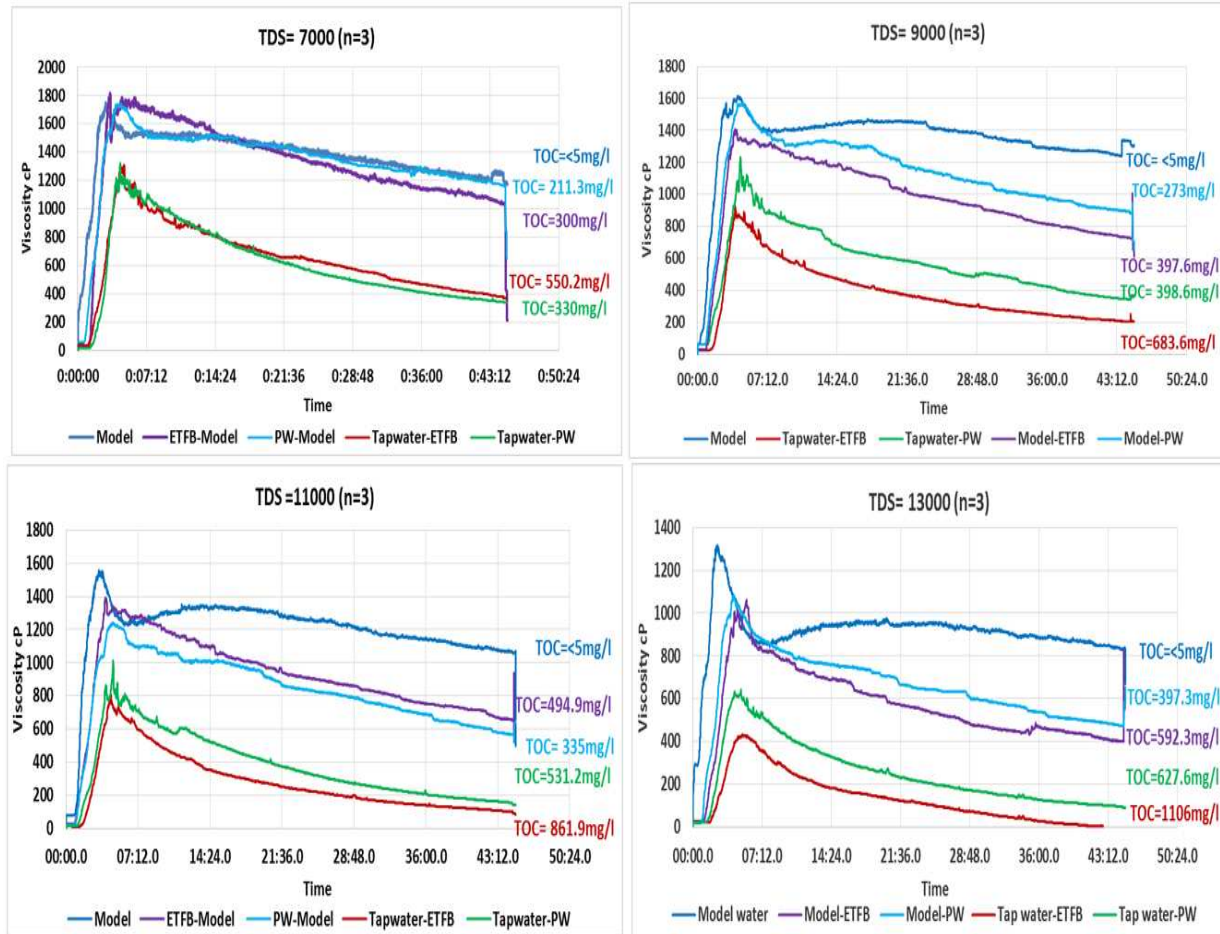


Figure 50-Viscosity profile for different water samples at TDS of 7000, 9000, 11000 and 13000mg/l.

Figure 50 illustrates the viscosity profiles for four different frac fluid samples at TDS levels of 7000, 9000, 11000 and 13000mg/l during 45-minute runs. Fresh-ETFB and Fresh-PW terms refer to CSU tap water, which was spiked with ETFB or produced water, respectively in such a way that TDS was obtained at the desired value. Model-ETFB and model-PW represent the frac fluid samples that were made by spiking model water with ETFB/PW and then the solution was diluted by CSU tap water. The required volume of each water, was calculated based on the desired TDS value. Therefore the only difference between all five waters is TOC concentration (Figure 41). Based on Figure 41, the TOC concentration with these five frac fluid samples are: Model < Model-

PW< Model-ETFB< Fresh-PW< Fresh-ETFB. As observed in Figure 50, the viscosity profiles are ordered equivalently to the order of TOC concentrations. Model water appeared to have the highest peak and final viscosities. The viscosity gap becomes more pronounced as TDS increases.

In an aqueous environment with a high ionic strength, the water molecules surround the charges of the ions and organic molecules. In fact, the effect of addition of salts in solutions of polymers is very complex, mainly because a large number of different types of intermolecular interactions come into play between the ion and water, ion and polymer, and polymer and water. This is further complicated by the fact that the magnitude of the interactions varies in relation to the types of ions and polymers involved¹⁵⁴. At a certain ionic strength, the water molecules are no longer able to support the charges of both the ions and the organics^{156,157,158,159}. The result is the precipitation of the least soluble solute, such as polymers and large organic molecules^{156,157}. Due to the complexity of the subject and lack of studies, this could lead to speculation based on literature^{156,157,158,159} and observed results that improper polymer dissolution in saline water leads to a two-phase solution. In other words, the higher TDS values (greater ionic strength) and broken polymers result in a non-homogenous frac fluid with poor rheology parameters, resulting in weak and unstable viscosity.

Peak viscosity for the five frac fluid samples are shown in **Figure 1-B**. As expected, peak viscosity as well as sensitivity of frac fluid samples to TDS show significant differences and a downward trend with increased TDS was seen for all of the frac fluid samples. The peak viscosity was: model water> model-PW>model-ETFB>fresh-PW> fresh-ETFB which was the opposite of TOC values: model water<model-PW<model-ETFB<fresh-PW< fresh-ETFB.

4.4.1 Conclusion

The oil and gas industry is increasingly relying on recycling the produced and flowback water. Results of this study showed that Model water produced a more stable frac fluid and significant organic matter influence was seen at TDS concentrations of 9000 mg/l and greater and organic matter had a negative impact on the peak viscosity. Presumably the organic matter residues from gelled frac fluids, were crosslinked and formed metal complexes. Therefore a weak and loose association caused unstable viscous frac fluid. Also untreated produced water samples showed slightly more frac fluid viscosity stability than untreated ETFB samples. Based on the OM content of samples, ETFB samples seem to be more sensitive to TDS. The destabilizing influence of organic matter on carboxyl methyl cellulose (CMC) based gel frac fluid is suggested to be due to secondary cross-linking of the short chain polymer residuals in the flow back resulting in lower initial viscosity and stability. Finally, coagulation treatment of produced water or early time flow back water seemed to be a necessary strategy in recycling the water and reuse in hydraulic fracturing.

4.5 Optimization of Carboxyl Methyl Cellulose Frac Fluid Part I: Influence of pH and Crosslinker Concentrations in High Salinity Water Sources

4.5.1 Introduction

Nearly all the hydraulic fracturing operations in the US use water as their base fluid to recover oil and gas deposits from shale formations. Hydraulic fracturing requires a large quantity of water and traditionally fresh water resources have been used for this purpose. A typical horizontal multi-staged well requires between 2-5 millions of gallons of water for fracturing⁴⁸. In 2012 the estimated water consumption for hydraulic fracturing operations was more than 5,000 million gallons and is predicted to grow in 2015 to over than sixty three billion gallons of water¹⁶⁹.

Fifty six percent of hydraulically fractured wells in the United States are in regions experiencing short to long-term drought conditions¹⁷⁰. Areas experiencing prolonged drought conditions include California and much of Texas, Colorado, Oklahoma, New Mexico, Arkansas and Louisiana. Operating in drought conditions makes it more difficult to physically source water. It can also lead to increasing groundwater depletion, competitive pressures over existing water resources and loss of social license to operate.

Water is also is the largest by-product of the shale oil and gas developments. More than 30% of the water flows back to the surface within the first thirty days of a well production and often is referred to as flowback water³³. Flowback water has been known to have a high quantity of TOC (total organic carbon), and low TDS (total dissolved solids). The high organic content of this water has been referenced to residual of polymers and other chemicals in the frac fluids^{33,34,35}. Returned water is often referred to as produced water later in the production cycle of a well and it is more characteristics of formation water with higher TDS and lower TOC concentration. Over 90% of

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the produced water in the US is reinjected into class II wells^{33,59,101}. Reusing this water will represent a good opportunity for oil and gas operators to reduce the burden on drinking water resources and optimize the use of this valuable resource. Although reuse of produced water has been explored in Colorado, little research has been conducted to use produced water in crosslinked gel-based hydraulic fracturing fluids¹⁰¹.

Selection of the optimal fracturing fluid is crucial in economic shale gas and shale oil development and due to the huge variability in the geology and nature of formations of oil and gas deposits. Formulating fracturing fluids for acceptable rheological performance can be very sensitive to water quality. The composition of a typical gelled frac fluid consists of water, proppant, gelling agent, cross linkers, buffers, surfactant, breakers, biocides, friction reducers and scale inhibitors and potentially other additives based on geological and technical considerations^{27,100, 146,149, 150, 151}. A fracturing fluid should provide sufficient viscosity to suspend and transport proppant into the fracture, and should break into a low-viscosity fluid after the proppant has been placed. This will facilitate the fracture to clean up by allowing rapid flowback of fluid to the surface.

The viscosity of gelled frac fluid is a criterion for stability regarding transporting proppant while it is pumped downhole and having the ability of fracturing the formation in which the optimum production occurs⁶¹. The optimum hydraulic fracturing fluid composition for each well is typically chosen by the treatment objectives and evaluating the adequacy of the fluid system's performance in fluid-loss control, fracture conductivity, and proppant transport, as well as in the amount of formation permeability damage. Ideally, the selected fluid system should stimulate fluid flow, minimize associated risks, and maximize post-treatment production economics¹⁵².

Polymers, such as cellulose derivatives, biopolymers and guar gum are introduced in the water based drilling fluids for their rheological performance and for ecological considerations. Guar gum and its derivatives are the most common fracturing fluid polymers, accounting for up to 90% of all gelled fracturing fluids¹⁴⁹. The cellulose derivative is the next common polymer in hydraulic fracturing due to its biodegradability and compatibility with other materials. CMC is a white to almost white powder, non-toxic and biodegradable, odorless and does not ferment under normal conditions of use. CMC is produced by reacting cellulose obtained from wood pulp or cotton fibers with chloroacetic acid and NaOH⁹⁹. It is largely used in industry, due to its exceptional rheological properties in aqueous solutions⁹⁹. The mechanism of sol-gel process is composed of gelling of organic polymers containing hydroxyl or carboxyl groups by using organometallic cross-linkers consisting of di-, tri-, or tetra-valent cations complexed by organic ligands. The main advantage of polymer gels is that gel strength can be reduced as desired. For example, in the oil industry, very weak gels are needed to reduce water production without affecting oil recovery¹⁷².

The proper crosslinking agent is designated based on the type of gelling agent being used. In the past decade zirconium lactate or citrate has been used in hydraulic fracturing¹⁷¹ not only because it is considered to have minimal environmental impacts and is not toxic, but also because of the improved crosslinking kinetics^{172,173} and consequently final structure and homogeneity of the gels.

Although a minimum viscosity of 500 cP has been reported for optimally placing the proppant downhole¹⁰¹, and creating the desired conductivity, a lack of sufficient evidence and knowledge of downhole conditions has led to ambiguity regarding the required viscosity of a frac fluid system. Though more studies need to be conducted in this area and define the minimum required viscosity for the frac fluid, a viscosity contour map based on input parameters such as gel loading, crosslinker dose and pH is a critical tool for understanding use in the field.

A well-defined water management system is essential in order to reduce the impact of horizontal fracturing on fresh water resources and address community, landowner and regulator concerns regarding the use of freshwater resources. Therefore a comprehensive operation plan that integrates both oil and gas operator's goal and service companies expertise, is required such that other water resources such as seawater and brine can be used. The objective of this study was to generate a three-dimensional contour map of apparent viscosity as a function of pH and, zirconium crosslinker and gel loadings.

4.5.2Material/Method

Synthetic water

For experiments in this phase of the research, model or synthetic water was developed to be identical to locally sourced recycled water except for the presence of organic matter. The model water was created using low-TOC tap water and dissolving a specific amount of particular salts to reach the determined concentration such that total ion concentration of modeled water was equal to ionic TDS (total sum of ion concentrations) of recycled water. The added salts were: NaCl, FeCl₂, NaCO₃, NH₄Cl, NaBr, Na₂SO₄, BaCl₂, CaCl₂, KCl, MgCl₂, MnSO₄, FeSO₄, H₃BO₃, aluminum chloridehydrate and SrCl₂. The water quality characteristics of model water is shown in **Table 18**. To represent a brackish, medium salinity water quality, a TDS of 15,000 mg/L was chosen. The stock solution was then diluted with tap water to create samples with TDS level of 15000mg/l.

Table 18- Water quality composition for model water

Parameter	Model water (mg/L)
Gravimetric TDS	27354
Ionic TDS	24706
TOC	0
NH4	18
Br	67
Cl	14886
SO4	73
HCO3	183
Al	1.3
Ba	10.8
B	8.8
Ca	44.8
Fe	1.8
K	517
Mg	10.2
Mn	na
Na	8877
Si	3.9
Sr	3.3
Cu	na

Material

A frac package that included CMC gel and zirconium crosslinker chemicals was used as the base fluid for this study. This fluid consists of CMC based gel, buffer to adjust pH and a metal crosslinker (zirconium) as the base components.

Design of experiments

In order to generate a well-covered 3-D map for apparent viscosity, design of experiments (DOE) using Minitab was performed. There are three aspects of this study that were analyzed by DOE: factors, level and response. Factors are variables in each experiment that typically are classified as either controllable (independent) or uncontrollable (dependent) variables. In this case there were three controllable factors: pH, crosslinker concentration and gel loading. Likewise, there could be

other types of factors such as changes in chemicals, viscometer variation but these were controlled by dedicating chemicals and conducting control runs on different viscometers. However to simplify the DOE, only the maximum and minimum levels of each three factors were considered. Viscosity was the response or outcome of the experiments and was measured and analyzed to determine the factors and their settings that will provide the best overall outcome for the critical characteristics, both measurable variables and assessable attributes.

Water quality analysis

All water quality analyses were done using Standard Method procedures¹¹⁶. TOC, gravimetric TDS and pH analyses were conducted at the Colorado State University water quality laboratory. An independent, EPA-certified laboratory provided analysis of cations and anions. Gravimetric TDS was measured based on standard methods of water and wastewater¹¹⁶. The ionic TDS concentration was calculated by summing the anion and cation concentrations. pH was measured using a Hach (Hach, Loveland), HQ40d pH meter. TOC was measured using Standard Methods¹¹⁶ 2540D 5130B. Cations were measured by EPA 2007¹⁸⁵ method 6010 C using a Varian ICP-AES, Liberty AX.

Building frac fluid

The CMC gel that was used to make the frac fluid was buffered (ammonium acetate) to a pH of approximately 5.0. All rheology tests were conducted at a service company in Colorado. Fluid system loadings provide comparable viscosity to each other and are representative of actual formulations pumped in the field.

The following procedure was used to prepare all frac fluid samples:

1. A 1000 ml sample of water or salt water was placed in a 1000 ml blender to prepare the linear gel.
2. A blender was used at 1500 rpm circulating rate, which was needed to establish a vortex shape with no air bubbles trapped.
3. An appropriate quantity of CMC based gel was added slowly from the shoulder of the created vortex to reach the desired polymer loading. A timer was started at this time. Apparent viscosity was measured at 3, 6 and 9 minutes of adding polymer to water sample to study the polymer hydration phenomena.
4. Finally, the first buffer was added, followed by the cross linker and second buffer, mixed for 10 s before loading into the viscometer.
5. To minimize instrument variability, the tests were run on three dedicated viscometers that were calibrated regularly.

To have the same test conditions for all prepared fluids, viscosity measurements were conducted within two minutes of the initial hydration time to minimize viscosity changes¹⁷⁴.

Rheology tests

Viscosity was measured in the study using a Chandler Model 5500 HPHT Viscometer affixed with a R2 bob concentric cylinder geometry. A computer was directly connected to the viscometer and recorded viscosity and temperature of each test. All tests were performed using 78mL sample of fluid at a shear rate of 40s^{-1} for a run time of 45 minutes and a final temperature of 200°F. An example of the raw data of a run with the CMC is shown in **Figure 51**. Solid lines represent the

viscosity profile and dash lines represent temperature of the sample. The temperature profile is the same among all the runs, starting at less than 75±5°F and ramping up to 200°F within 15 minutes. Fracturing fluids are considered as non-Newtonian fluids due to their non-direct proportionality between shear stress and rate of shear and furthermore they are classified as thixotropic fluids because of their decrease in viscosity over time at constant shearing rate¹⁷⁵.

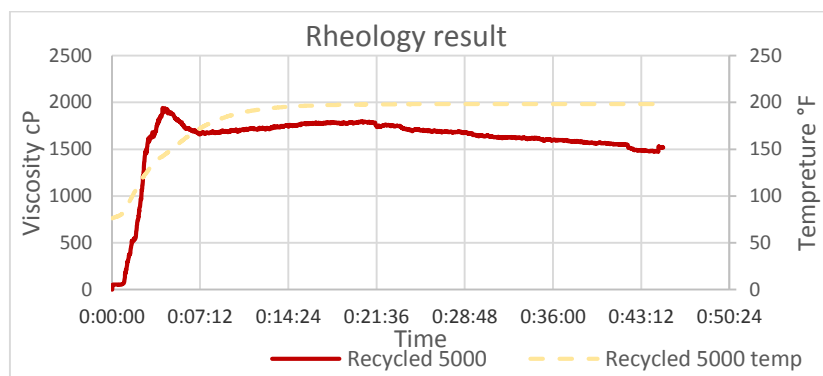


Figure 51-Low residue polysaccharide: Model water

Control runs

In order to control and observe any viabilities such as effect of different viscometers on the result, one control run was conducted for each set of tests. The control runs were defined based on a typical frac fluid composition at suggested concentrations by the Service Company. CSU tap water was used as the water source and typical chemical composition of a field frac operations were added to the water. Three sets of experiments were conducted at different gel loadings.

4.5.3 Results and Discussion

The effects of pH, and crosslinker concentration on stability and apparent viscosity of CMC frac fluid at TDS levels of 15000mg/l at different gel loadings were studied in this paper. A CMC loading of 45 pound per thousand gallons of water (ppt) has been used for typical fresh water sources. Four different set of experiments were conducted using different gel loadings of 40 ppt,

45 ppt, 50ppt and 55ppt. At each of these runs, pH and cross linker concentrations were also varied. pH ranged from 5.0 to 6.0 with increments of 0.25 and zirconium crosslinker concentrations were in the range of 1 to 3 gallon per thousand gallons of water (gpt). Apparent viscosity versus time was then plotted for all runs. The assessment for all the runs included a visual viscosity profile, peak viscosity and a final viscosity. A failure run exposed a sudden drop in apparent viscosity within the 10 minutes of start point and viscosity of zero was assigned to it. Contour plots were generated at four CMC gel loadings at the TDS of 15000mg/l.

Effect of pH on crosslinker concentration at different gel loadings

Gel loadings of 45ppt, 50ppt and 55 ppt were chosen to optimize the frac fluid composition for use with high salinity water. 3-D contour maps of apparent peak viscosity were developed for each gel loading. Y- axis shows crosslinker concentration, gpt, X- axis shows pH, and apparent viscosity values are color-coded with scale shown on the side bar. A peak viscosity of 1500cP has been reported¹⁰¹ to be the minimum required viscosity for a frac fluid. In order to make a comparison among the runs, a higher minimum peak viscosity of 2000cP was picked to provide a safety factor for the full chemical composition of CMC frac fluids, such as breakers.

Gel loading of 45ppt

The first set of frac fluid optimization experiments were conducted at the suggested gel loading of 45 pounds per thousand gallons of water. A pH range of 5 to 6 with 0.25 increments was studied. **Figure 52** illustrates the contour map of peak viscosity at a gel loading of 45ppt. The warmer colors represent higher apparent viscosity and cooler colors represent lower values. The minimum peak viscosity was observed at combinations of high pH-low crosslinker concentrations and low pH-high crosslinker concentrations. These areas are shown in blue. The minimum viscosity was

at 270cP. The maximum viscosity of 1845cP occurred at higher pH and higher crosslinker concentration.

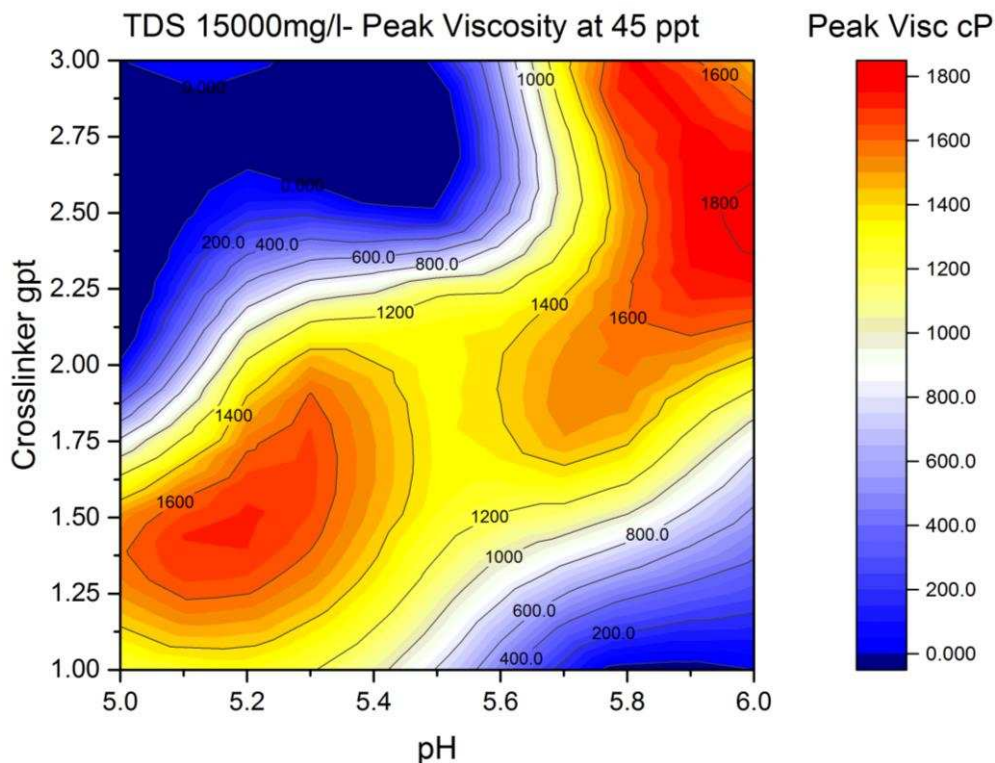


Figure 52-Viscosity map at gel loading of 45ppt

According to Figure 52, combinations of low pH-low crosslinker concentration and high pH- high crosslinker concentration resulted in fluids with viscosity values higher than 1400cP. Approximately 40% of the samples had viscosity greater than 1500cP. A potential explanation follows:

1. The mechanism of gelling a CMC fluid consists of complexation of organic polymers containing hydroxyl or carboxyl groups by organometallic cross-linkers consisting of di-, tri-, or tetra-valent cations, zirconium in this case, and organic ligands.

2. The carboxylic acid functional groups on the CMC backbone dissociate and release hydrogen ions at higher pH values, which then creates negatively charged carboxylate functional groups.
3. At higher pH values, more carboxylate functional groups appear on the polymer backbone, resulting in more crosslinking sites and vice versa for lower pH^{101,174, 176}.

This also supports the observation of low viscosity at the combination of higher pH-lower crosslinker concentration since the higher concentration of carboxylate functional groups at pH>5.5 demand more crosslinker cation. Therefore to generate a highly viscous fluid (viscosity> 1200cP), one needs to increase the crosslinker concentration at pH>5.5. The other approach that is more cost effective could be gelling CMC fluid at pH 5 and lower concentrations of crosslinker.

Gel loading of 50ppt

Since the gel loading of 45ppt did not result in peak viscosity greater than 1800cP (suggested peak viscosity is higher than 2500cP), it was decided to raise the gel loading to 50ppt. The contour map of peak viscosity is shown in **Figure 53**.

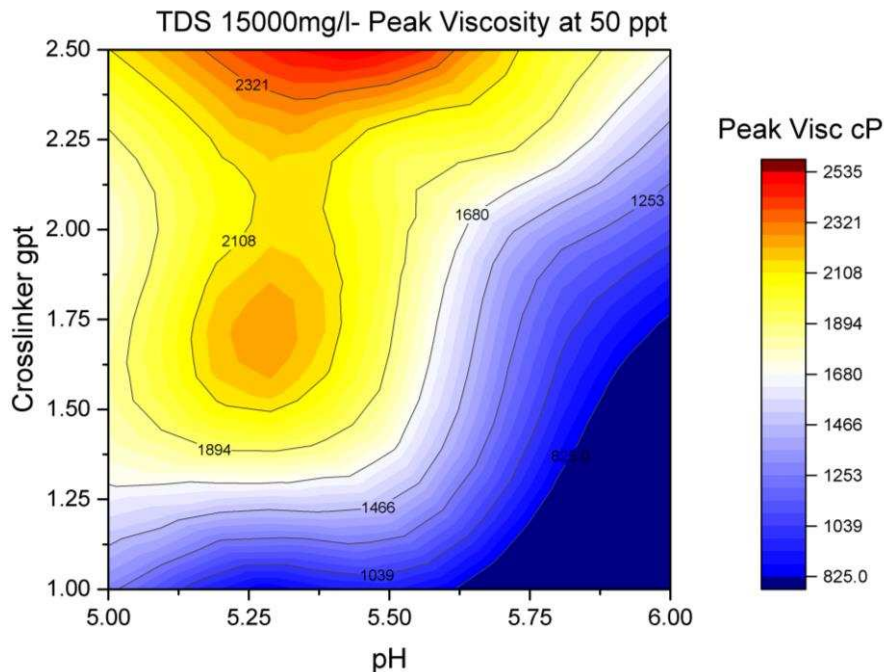


Figure 53-Viscosity map at gel loading of 50ppt

According to Figure 53, the minimum and maximum peak viscosity was improved to 825cP and 2535cP. A similar pattern for viscosity was observed at gel loading of 50ppt and combination of high pH-low crosslinker concentration appeared to be least effective. However the viscosity seemed to be less sensitive to pH changes, as the warmer areas (higher peak viscosity than 1500cP) are more dominant and cover close to 60% of the map, almost double the gel loading of 45ppt. This could be explained as higher concentration of CMC polymer, more carboxylate functional groups introduced into the solution (counterbalancing the number of carboxylate sites at low pH) and consequently raising the crosslinker sites on CMC backbones requiring more crosslinker, Zr ion. This result is consistent with the findings from previous studies^{177, 178, 179}. They reported that the rheological behavior of a CMC solution is largely affected by CMC and its concentration.

Gel loading of 55ppt

A gel loading of 55ppt was studied in the third set of experiments and the rheology map is illustrated in **Figure 54**. pH ranged from 5 to 6 and crosslinker concentration varied between 1gpt and 3gpt.

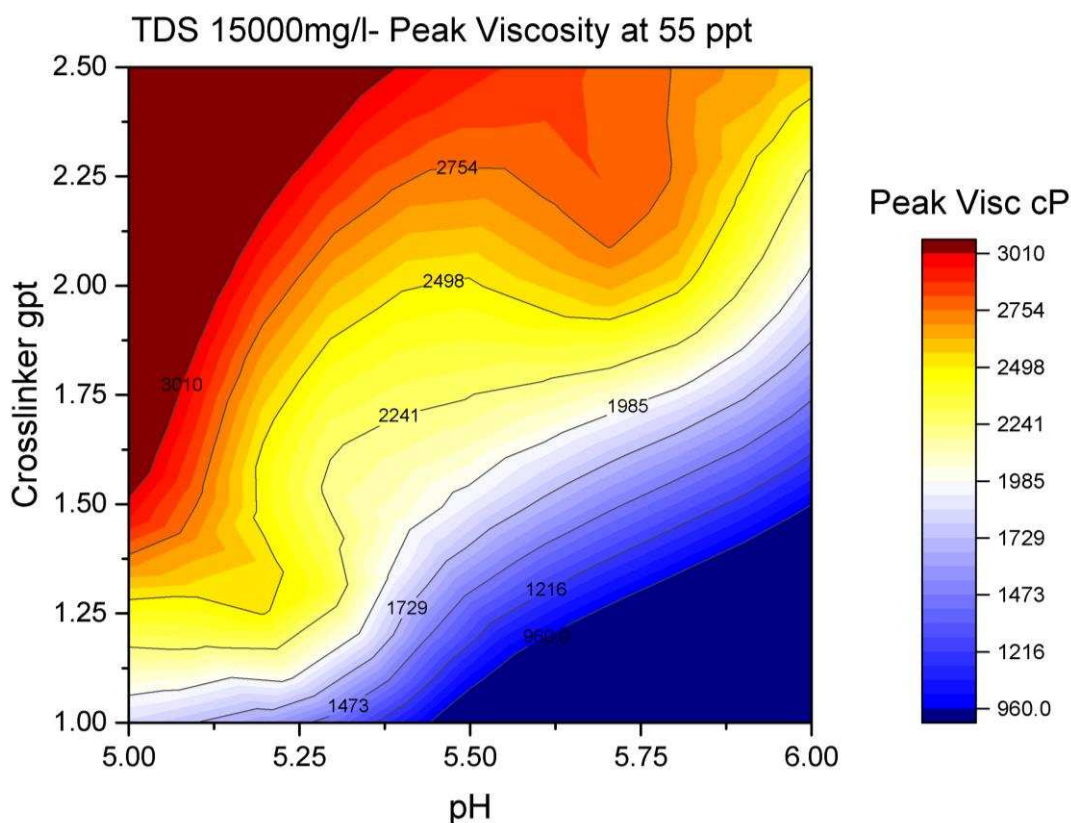


Figure 54-Viscosity map at gel loading of 55ppt

According to Figure 54, more than half of the samples showed peak viscosity of greater than 1985cP. This excludes the combination of high pH-low crosslinker concentration, which is consistent with the results obtained at gel loadings of 45ppt and 50ppt. The experiments resulted in a minimum and maximum viscosity at 960cP and 3070cP both greater than gel loadings of 45ppt and 50ppt. More than 80% of frac fluid samples tested exhibited peak viscosity of greater than

1500cP. This suggests that increasing gel loading will result in samples less sensitive to pH and crosslinker concentration changes, a characteristic that could be important in field operations.

These results are consistent with previous studies^{101, 172, 173}. Although it is known that zirconium hydrolyzes and polymerizes in water, little is known on Zr speciation in polymer solutions^{101, 180}. Rose et al., (2003) reported dominance of Zr-dimers, the better candidates for crosslinking phenomena at lower pH while cyclic tetramers were dominant at higher pH. At pH 6 and low concentrations of Zr crosslinker, not only the ratio of OH⁻ ion to organic ligands is 10-fold compared to pH 5, but also hydroxyl group OH⁻ are stronger ligands than organic ligands^{172, 173}. Therefore Zr polymerization increases with pH. Prevalence of tetramers and other complexations of Zr-OH result in less crosslinking function leading to a lower viscosity.

Based on Figures 52, 53 and Figure 54, it was seen that in order to generate a frac fluid with a particular peak viscosity, one could utilize a broad range of combinations of polymer and crosslinker concentrations at different pH values. However the frac fluid chemical composition should always consider the quantity of chemicals so that not only are lesser amounts of chemicals injected downhole but also costs can be minimized.

DOE results

Empirical rheological properties of a CMC based fluid with zirconium crosslinker were studied in this paper. These experiments were conducted to investigate the effects of one or more factors including gel loading, crosslinker concentration and pH on the response, which was the apparent peak viscosity. When an experiment consists of two or more factors, the variables can impact the response individually or jointly^{181,182}. Often, one factor at a time experimentation is studied and therefore the experimental design does not allow one to properly assess the joint impacts of the

factors. In this study it was tried to generate a 3D correlation between the viscosity and three factors (gel loading, crosslinker concentration and pH).

To investigate the joint effects of all these factors, factorial experiments were conducted. Factorial experiments include all possible factor-level combinations, both high and low levels, for all variables being tested. The individual and joint impacts of all three factors are shown in the following figures. To determine the significant factors, a Pareto chart was used for identifying the effects that are statistically significant¹⁸². Both individual and joint influences for all three factors, gel loading, crosslinker concentration and pH, are shown in **Figure 55a** and **55b**.

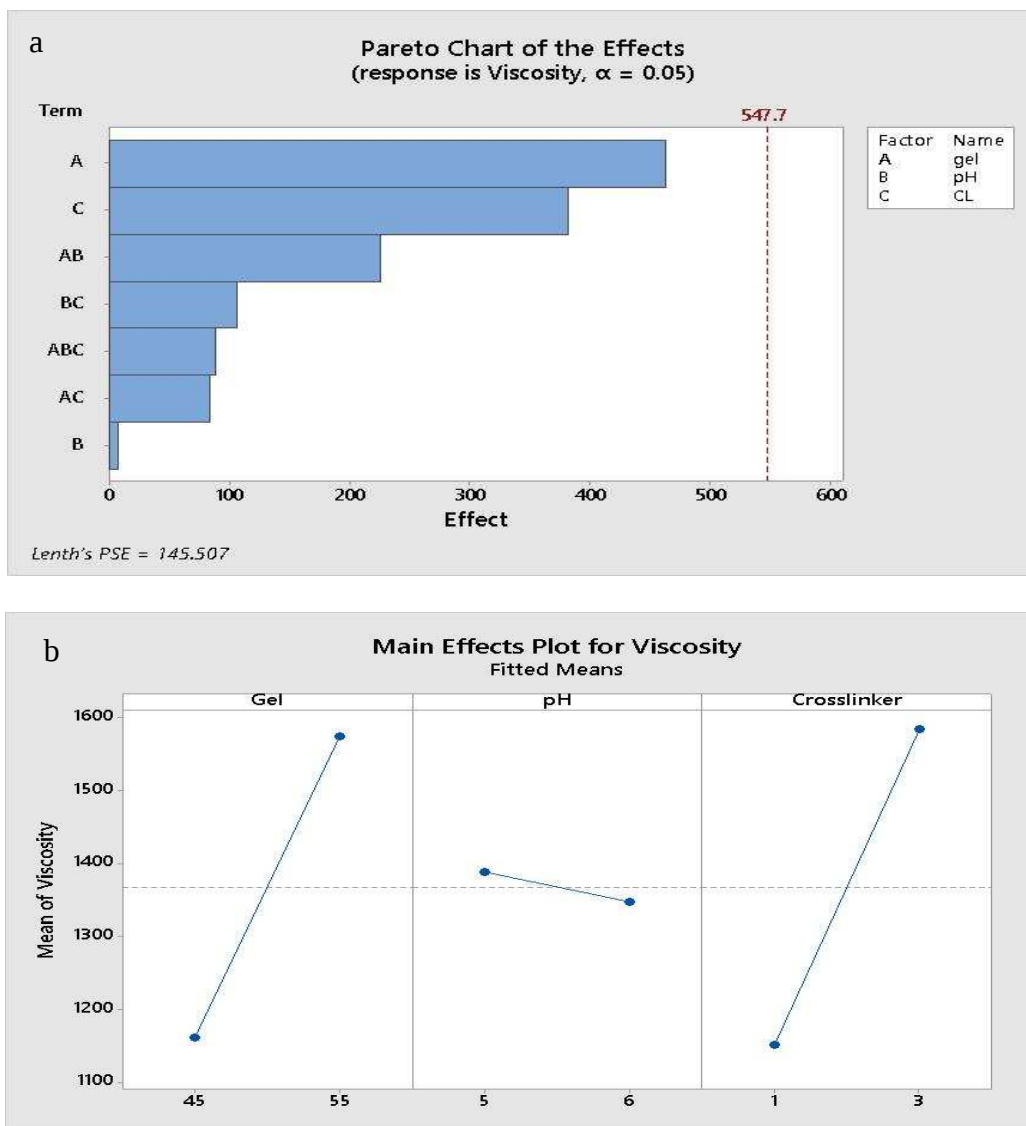


Figure 55-Statistical analysis, a) Pareto graph; b) main effects

Figure 55a, represents the Pareto chart of significant effects for both individual and joint combinations of gel loading, crosslinker concentration and pH. The analysis suggested that crosslinker concentration and gel loading were important in producing high viscosity CMC frac fluids. Figure 55b also shows the main effect for the three variables. Gel loading and crosslinker concentration have a direct correlation with peak viscosity, meaning that an increase in the

concentration of gel and crosslinker will result in an increase in peak viscosity. These results confirm the observed data and are in agreement with previous rheological studies^{172, 173, 101, 180}. A significant effect was not observed for pH at the range of 5 to 6.

Prediction equations are useful to analyze what-if scenarios for different combinations of factors. Moreover it generates a 3-D surface response which could be applied in similar conditions to calculate the peak viscosity. Since data cannot be collected at all levels and factors, a prediction equation can be used to estimate the output. A prediction equation was generated by DOE for the process by quantification of the factor interactions in terms of $Y = f(X_1, X_2, X_3, X_4 \dots X_n)$

Where

Y is the response of experiments, peak viscosity here;

$X_1 \dots X_n$ are the variable factors in the experiments.

The prediction equation for peak viscosity based on three factors of pH, crosslinker concentration, and gel loading is given in Eq. 1, where gel is gel loading pounds per thousand gallons and “cl” is the crosslinker concentration gallon per thousand gallons of water.

$$\begin{aligned} \text{Peak viscosity (cP)} = & 11182 - 123 \text{ gel} - 19755 \text{ CL} - 1671 \text{ pH} + 408 \text{ gel} \times \text{CL} + 17.1 \text{ gel} \times \text{pH} \\ & + 312.3 \text{ CL} \times \text{pH} - 62.2 \text{ gel} \times \text{CL} \times \text{pH} \dots \dots \dots (1) \end{aligned}$$

4.5.4 Conclusion

Optimization of chemical composition of CMC frac fluid for use with water with a TDS of 15000 mg/l was described in this paper. Three gel loadings of 45ppt, 50ppt and 55ppt at a pH range of 5

to 6 and crosslinker concentration range from 1 gpt to 3 gpt were chosen. The main conclusions that emerged from the results are:

- Application of brackish, medium salinity waters including produced water and briny ground water in the development of hydraulic fracturing fluids is feasible.
- The frac fluid chemical composition should always consider the quantity of chemicals so that not only are lesser amounts of chemicals injected downhole but also costs can be minimized.
- The viscosity of a CMC frac fluid directly correlates with CMC concentration.
- At high pH values, the required crosslinker concentration to obtain a viscosity higher than 1500cP increases.
- The influence of pH and crosslinker concentration on rheology of fluid was minimized by an increase in the gel loading.

4.6 Optimization of Carboxyl Methyl Cellulose Frac Fluid Part II: Influence of pH and Crosslinker Concentrations in Low Salinity Water Sources

4.6.1 Introduction

This is the second part of an article described the optimization of frac fluid chemical composition for using low salinity waters such as brine ground waters or any industrial treated waters. The first part focused on the replacing fresh water resources with high salinity water sources such as sea water with TDS of 15000mg/l. For a general introduction into hydraulic fracturing including water consumption and frac fluids see (part I). An average of two to six million gallons of water has been used for a single horizontal multi stage well in hydraulic fracturing¹⁷⁴. Dedication of this amount of water in areas with water scares crisis, is very competitive especially if agricultural activity is the largest water consumer in that area. Moreover environmental activists' and public concerns associated with water depletion and consumption of drinking water resources is another main challenge for survival of oil and gas operations in semi-arid to arid areas. Oil and gas operators should consider alternative water sources to fresh water; large volume is the first important characteristic of an alternative water resource, low organic content is the second important properties of the replacement water source. Researchers have shown that high total organic carbon (TOC) interferes with crosslinking phenomena in a gelled frac fluids¹⁷⁴ and therefore high TOC waters such as produced water, cannot directly be used in hydraulic fracturing. Any brackish water resources comprising of treated produced water, sea water and municipalities water, could be the remedy for the water sourcing in hydraulic fracturing. These water sources are not suitable for drinking water utilization due to the high total dissolved solids (TDS) content and could be of interest for oil and gas activities. However the solution to water shortage regarding hydraulic

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fracturing seems simple, but it requires a thorough understanding of the chemical composition of CMC frac fluid and its interaction with water pollutants (high TDS). There has been few scientific and industrial studies on produced water reuse in hydraulic fracturing where the influence of individual cations on frac fluid stability was examined^{100,101,183}, however this was one element in many associated with poor water resources usage in hydraulic fracturing. The fresh water sources replacement with poor quality water could be lucrative on dynamic of hydraulic fracturing, yet frac fluid chemical composition also need to be optimized based on the different constituents existing in the water. In this paper a synthetic brackish water was used and the chemical composition of CMC frac fluid was optimized by varying three main components of gelled frac fluid: pH, gel polymer concentration and crosslinker concentration. The results of this study are reported in 3-dimensional contour map of viscosity at different gel loading.

It is hoped that the work summarized in these papers be valuable in enabling the oil and gas industry to a better understand on the interaction of frac fluid chemicals with total dissolved solid (TDS) content of water sources at two level of high and low. Application of these generated viscosity maps at poor quality waters, will assure the oil and gas producers of the feasibility of using other water sources than fresh water sources and therefore lessen the burden on drinking water resources.

4.6.2Material/Method

Synthetic water

For this set of experiments a model or synthetic water, is called model water in this paper, was developed to be identical to a recycled produced water except for the presence of organic matter. The model water was created using low-TOC tap water and dissolving a specific amount of particular salts to reach the determined concentration such that total ions of modeled water was equal to ionic TDS (total sum of ions concentration) of recycled water. The added salts are: NaCl, FeCl₂, NaCO₃, NH₄Cl, NaBr, Na₂SO₄, BaCl₂, CaCl₂, KCl, MgCl₂, MnSO₄, FeSO₄, H₃BO₃, aluminum chloridehydrate and SrCl₂. The water quality characteristics of model water is shown in **Table19**. The stock solution was then diluted with tap water to represent low salinity water samples with TDS level of 2500 mg/l.

Table 19- Water quality composition for model water

Parameter mg/l	Model water
Gravimetric TDS	27354
Ionic TDS	24706
TOC	0
NH ₄	18
Br	67
Cl	14886
SO ₄	73
HCO ₃	183
Al	1.3
Ba	10.8
B	8.8
Ca	44.8
Fe	1.8
K	517
Mg	10.2
Mn	na
Na	8877

Si	3.9
Sr	3.3
Cu	na

Material

A frac package that included CMC gel and zirconium crosslinker chemicals was used as the base fluid for this study. This fluid consists of CMC based gel, buffer to adjust pH and a metal crosslinker (zirconium) as the base components.

Design of experiments

In order to generate a well-covered 3-D map for apparent viscosity, design of experiments (DOE) using Minitab was performed. There are three aspects of this study that were analyzed by DOE: Factors, level and response. Factors (inputs to the experiments) are basically variables in each experiments and typically are classified as controllable or uncontrollable variables. In this case there were three controllable factors: pH, crosslinker concentration and gel loading. Likewise, there could be other types of factors such as changes in chemicals purity, viscometer variation, but they were controlled during the experiments by dedicating some chemicals to this experiments and conducting control runs on different viscometers. In this study levels of each factors was referred to the range of each factor. However to simplify the DOE, only two levels, the maximum and minimum of each three factors was considered. Viscosity the response or outcome of the experiments, was measured and analyzed to determine the significant factor/factors.

Water quality analysis

All water quality analyses were done using Standard Method procedures¹¹⁶. TOC, gravimetric TDS and pH analyses were conducted at the Colorado State University water quality laboratory. An independent, EPA-certified laboratory provided analysis of cations and anions. Gravimetric TDS was measured based on standard methods of water and wastewater¹¹⁶. The ionic TDS concentration was calculated by summing the anion and cation concentrations. pH was measured using a Hach (Hach, Loveland), HQ40d pH meter. TOC was measured using¹¹⁶ Standard Methods 2540D 5130B. Cations were measured by EPA 2007¹⁸⁵ method 6010 C using a Varian ICP-AES, Liberty AX.

Building frac fluid

The CMC gel that was used to make the frac fluid was buffered (Ammonium acetate) to a pH of approximately 5.0. All rheology tests were conducted at a service company in Colorado. Fluid system loadings provide comparable viscosity to each other and are representative of actual formulations pumped in the field.

The following procedure was used to prepare all frac fluid samples:

1. A 1000 ml sample of water or salt water was placed in a 1000 ml blender to prepare the linear gel.
2. A blender was used at 1500 rpm circulating rate, which was needed to establish a vortex shape with no air bubbles trapped.
3. An appropriate quantity of CMC based gel was added slowly from the shoulder of the created vortex to reach the desired polymer loading. A timer was started at this time. Apparent viscosity

was measured at 3, 6 and 9 minutes of adding polymer to water sample to study the polymer hydration phenomena.

4. Finally, the first buffer was added, followed by the cross linker and second buffer, mixed for 10 s before loading into the viscometer.

5. To minimize instrument variability, the tests were run on three dedicated viscometers that were calibrated regularly.

To have the same test conditions for all prepared fluids, viscosity measurements were conducted within two minutes of the initial hydration time to minimize viscosity changes^{138, 174}.

Rheology tests

Viscosity was measured in the study using a Chandler Model 5500 HPHT Viscometer affixed with a R2 bob concentric cylinder geometry. A computer was directly connected to the viscometer and recorded viscosity and temperature of each test. All tests were performed using 78mL sample of fluid at a shear rate of 40s^{-1} for a run time of 45 minutes and a final temperature of 200°F. An example of the raw data of a run with the CMC is shown in **Figure 56**. Solid lines represent the viscosity profile and dash lines represent temperature of the sample. The temperature profile is the same among all the runs, starting at less than $75\pm 5^\circ\text{F}$ and ramping up to 200°F within 15 minutes. Fracturing fluids are considered as non-Newtonian fluids due to their non-direct proportionality between shear stress and rate of shear and furthermore they are classified as thixotropic fluid because of their decrease in viscosity over time at constant shearing rate¹⁷⁶.

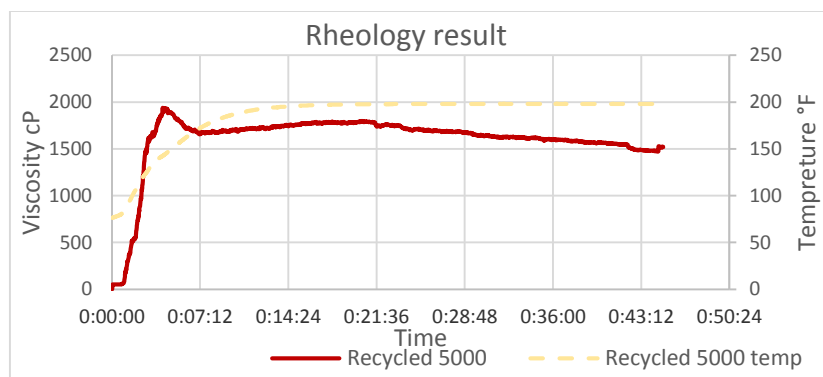


Figure 56-Low residue polysaccharide: Model water

Control runs

In order to control and observe any viabilities such as effect of different viscometers on the result, one control run was conducted for each set of tests. The control runs was defined based on a typical frac fluid composition at suggested concentrations by Service Company. CSU tap water was used as the water source and typical chemical composition of a real fracking job was added to the water. Three sets of experiments were conducted at different gel loadings.

4.6.3 Results and Discussion

To understand the frac- water interaction at low TDS water level of 2500mg/l, optimization of a CMC based frac fluid was studied in this paper. Therefore influence of pH, crosslinker and CMC concentration as the main three components of a frac fluid, on frac fluid stability was assessed. Five CMC concentrations of 25ppt, 30ppt, 35ppt, 40ppt and 45 ppt were chosen to optimize the frac fluid composition for using low salinity water. Five set of rheology experiments were conducted. pH and crosslinker concentration were varied at each of the sets. Zirconium crosslinker concentrations varied between 1 gallon per thousand gallon of water (gpt) to 3gpt and pH ranged from 5 to 6. In the first part of data analysis, apparent peak viscosity was plotted versus time. Second part of data analysis was to assess the runs based on three criteria: visual viscosity profile,

peak viscosity and a final viscosity. Then a failure run exposed a sudden drop in apparent viscosity within the 10 minutes of start point and viscosity of zero was assigned to it.

Contour plots were generated at four CMC gel loadings at high TDS of 15000mg/l. These generated maps will help the industry to understand their specific needs by optimizing the chemical composition of CMC based fluid and consequently will lower the injected chemicals into the formation rock.

Effect of pH on crosslinker concentration at different gel loadings

Five gel loadings of 25ppt, 30ppt, 35ppt, 40ppt and 45 ppt were chosen to optimize the frac fluid composition for using low salinity water. 3-D contour maps of apparent viscosity are shown in following Figures. Y- axis shows crosslinker concentration, gpt, X- axis shows pH, and apparent viscosity are color-coded with scale shown on the side bar. Peak viscosity of 1500cP has been reported¹⁰¹ to be the minimum required viscosity for a frac fluid. In order to make a comparison among the runs, a higher minimum peak viscosity of 2000cP was picked to compensate a safety factor for the full chemical composition of CMC frac fluids, such as breakers.

Gel loading of 45ppt

The first set of frac fluid optimization experiment was conducted at the suggested gel loading of 45 pounds per thousand gallons of water. This is the typical gel loading for a frac job using fresh water source. A pH range of 5 to 6 with a 0.25 increments was studied. **Figure 57** illustrates the contour map of peak viscosity at gel loading of 45ppt.

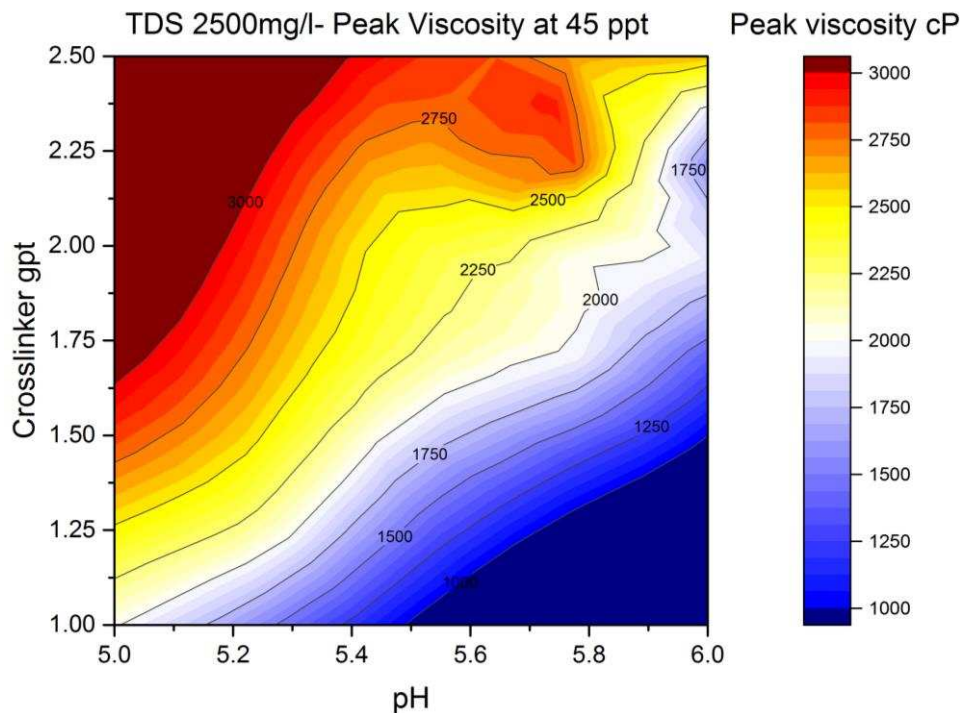


Figure 57- Apparent viscosity at gel loading of 45ppt

The warmer colors represents the samples with higher peak viscosity while cooler colors represents lower peak viscosity. The minimum and maximum peak viscosity occurred at combination of high pH-low crosslinker and low pH-high crosslinker, respectively. This is consistent with previous results (part I). According to Figure 57, 84% of the samples exposed greater viscosity of 1500cp. Peak viscosity of 1500cp was reported to be the minimum peak viscosity of a frac fluid. The observed minimum peak viscosity was near to four times than same gel loading (45ppt) at high TDS water samples. (Part I) These observations indicate the gel concentration is higher than it is needed, hence lower gel concentrations were studied in the next set of experiments. Since the mechanisms of gelling CMC and Zr crosslinker is the same as previous study, these observations were on agreement with the suggested mechanisms in part I. the higher pH, the more crosslinking sites becomes available on CMC backbone and therefore it demands higher crosslinker concentrations. Also as Rose et al. (2003) reported, as pH raise, the ratio of $[\text{OH}]^{-1}$ to organic

ligands increases and therefore lessen the crosslinker cations chance to sit and do the actual crosslinking job.

Gel loading of 40 ppt

Apparent viscosity was studied at gel loading of 40ppt in different pH ranges and Zr crosslinker concentration. **Figure 58** represents the resulted map at TDS level of 2500mg/l. Based on the Figure 50, the minimum viscosity was dropped significantly, more than 50%, compare to the gel loading of 45ppt while not a visual effect was seen on the maximum viscosity did not changed.

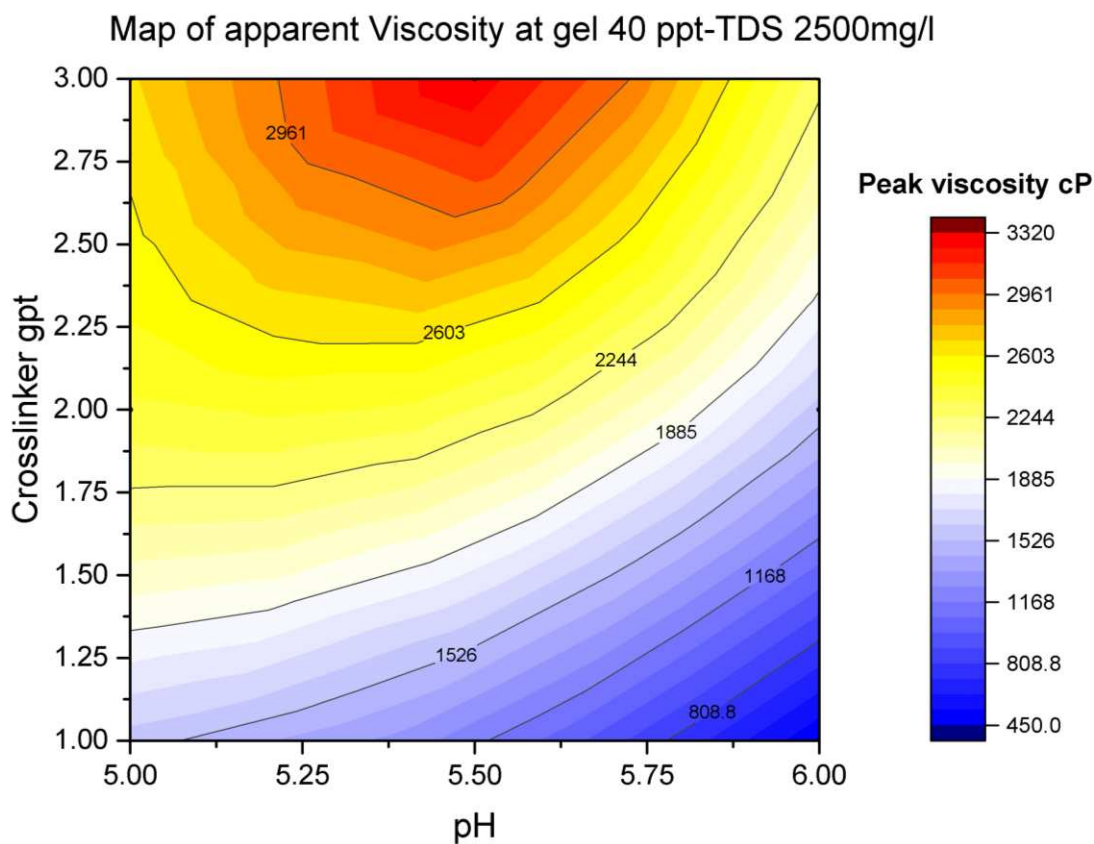


Figure 58- Viscosity map for gel loading at 40ppt

According to Figure 58, more than % 83 of the frac fluid samples showed a viscosity of 1500cP, which is very close to what was seen at gel loading of 45ppt. The fact that by decreasing the gel

loading to 40ppt, not a significant influence on peak viscosity was observed; suggested that oil and gas industries could use less chemicals with no effects on CMC frac fluid stability. This is a great opportunity in hydraulic fracturing, since not only it drops the polymer loading in the formation but also will illuminate the obstacles and challenges in downstream of treating produced and flowback water. In order to determine the minimum gel concentration with no negative impacts on frac fluid stability, lower concentrations studied in following experiments sets.

Gel loading of 35 ppt

The next set of experiments was conducted at gel loading of 35ppt. this gel loading is less than 22% of the suggested concentration by Service Company. In **Figure 59**, 3-D contour map of the apparent peak viscosity for the frac fluid samples at gel loading of 35ppt is shown.

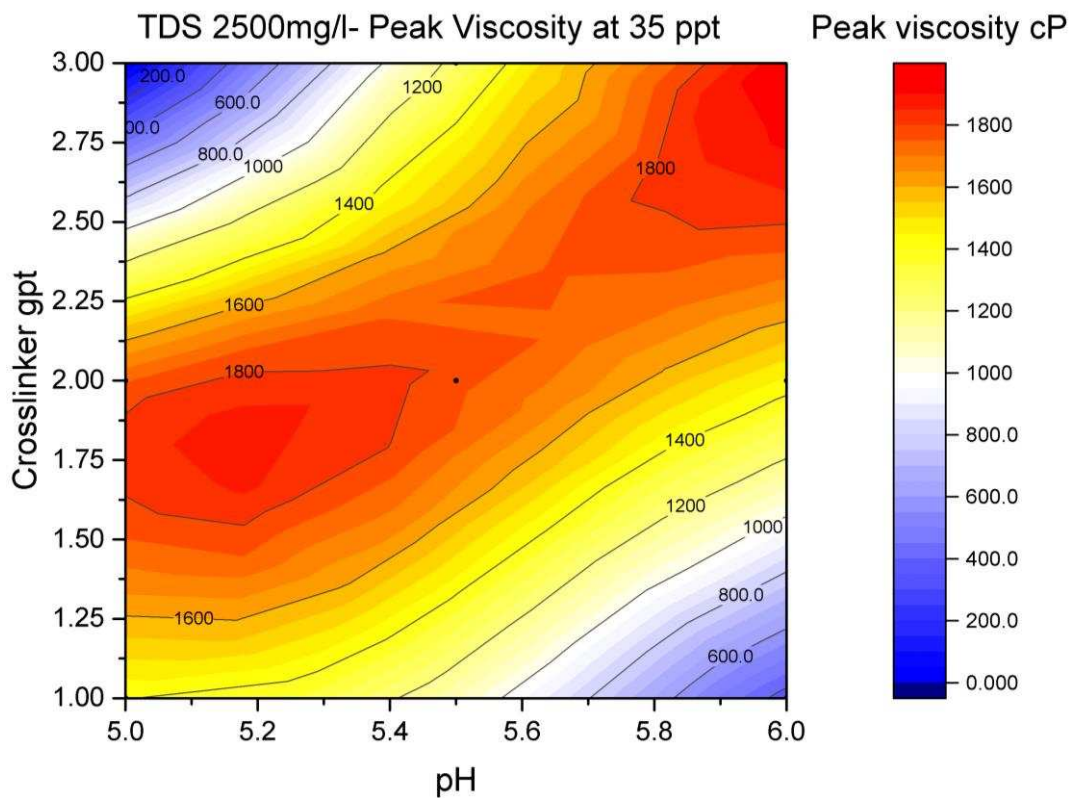


Figure 59- Contour map of apparent peak viscosity at gel loading of 35ppt

According to the Figure 59, at gel loading of 35ppt, the profile of contour map is slightly different comparing to previous maps; likewise, the combination of low pH-high crosslink was resulted in lower frac fluid stability. Therefore to generate a high viscose CMC fluid, one could use two combinations of low pH-low crosslink or high pH- high crosslinker concentration. Although it is clear that low pH-low crosslink combination not only is the cost effective option but also has lower environmental impact associated with downhole chemicals injection. This confirmed the theory suggested by Esmaeilirad et al.,¹⁷⁴ they reported that higher pH results in more negatively charged carboxylic sites on CMC backbone, as a consequent the number of crosslinking sites increases which results in higher demand for crosslinker cations. Hence pH and crosslinker concentration directly correlate and increasing one, the other should raise too.

Decrease in CMC concentration lead to a significant influence on both minimum and maximum peak viscosity. The 20% drop in CMC concentration comparing to the original concentration, resulted in 64% and 35% drop in minimum and maximum viscosity, respectively. However the number of samples with viscosity greater than 1500cP significantly dropped to 38% which is almost half of the number of samples at higher gel loadings. This observation indicate the important role of gel concentration in generating high viscose samples. This is in agreements with previous studies that shown CMC concentration directly impact the viscosity^{177, 178, 179} (part I).

Although there is not much knowledge on the crosslinking phenomena^{101, 172, 173} and that what exactly are the kinetics and chemistry of it, Rose et al (2003) studied the kinetics and speciation of Zr lactate crosslinking in polymer solutions. They reported that Zr-dimers which are the best Zr oligomers for crosslinking, govern in polymer solutions at lower pH while tetramers and other complexes of Zr prevail at higher pH. Moreover OH⁻ which are stronger ligands than organic ligands are dominate at higher pH values which in consequent Zr polymerization increases with

pH and viscosity drops. Prevalent of tetramers and other complexations of Zr-OH results in rendering Zr crosslinker incapable of crosslinking function leading to a lower viscosity (Part I).

Gel loading of 30 ppt

Although rheology experiments showed a significant drop in peak viscosity at gel loading of 35ppt but the maximum peak was still higher than the recommended value of 1500cP. Hence, CMC concentration was decreased to 30ppt and rheology experiments were conducted on the samples at different pH and crosslinker concentration. The viscosity map at gel loading of 30ppt is shown in **Figure 60**.

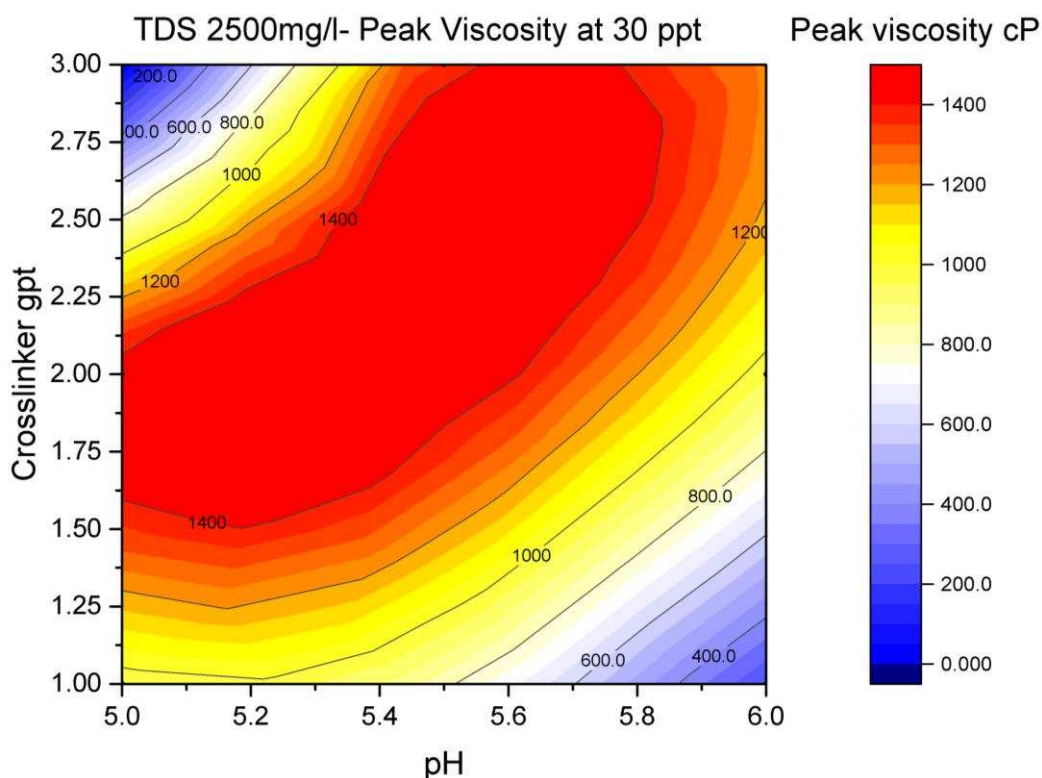


Figure 60- Contour map of viscosity at gel loading of 30ppt

According to Figure 60, the general profile was similar to gel loading of 35ppt, showing the combination of high crosslinker-low pH and low crosslinker-low pH resulted in lower viscosity compare to rest of samples. However, the CMC loading was only a third of the suggested concentration (45ppt), yet this resulted in a huge drop in maximum viscosity. The Maximum viscosity reduced by slightly more than 50%, from 3000cp to 1400cp. Subsequently none of the samples showed peak viscosity higher than 1500cP. This fact confirmed that gel loading is definitely plays a key role in building a stable frac fluid^{177, 178,179}.

Gel loading of 25 ppt

The objective of this paper was to optimize the chemical composition of CMC frac fluid for using a replacement of fresh water resources and this couldn't be successful without determination of a minimum CMC concentration. As the result, CMC concentration was lowered to 25ppt and rheological characteristics of CMC fluid samples were examined. **Figure 61** illustrates the results of this examination.

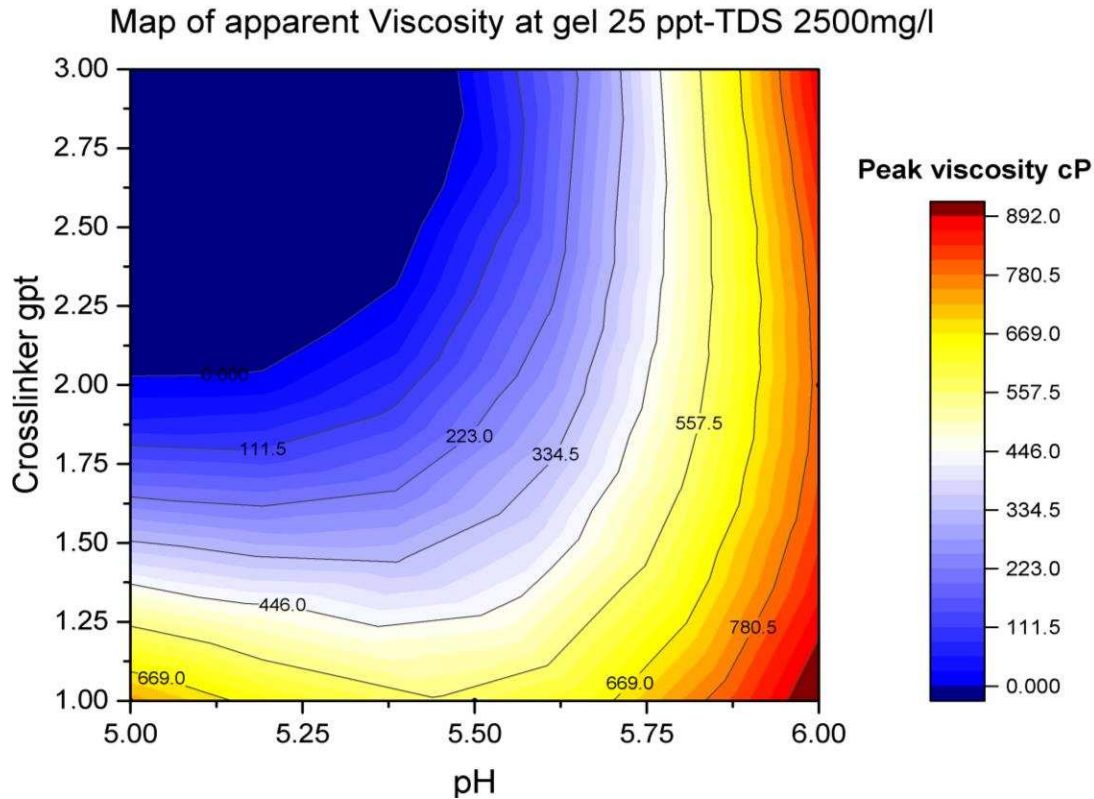


Figure 61- Contour map of viscosity at gel loading of 25ppt

According to Figure 61, the viscosity map at gel loading of 25ppt is different than the previous maps. As it was mentioned earlier, increasing the crosslinker sites on CMC backbone could be achieved by increasing the gel loading or increasing pH of the polymer solution. Since the gel loading is the lowest concentration studied here, the only way to generate sufficient number of crosslinking sites (deprotonated carboxylic sites) was to raise the pH. This could be the reason of which a different profile map was observed and combination of high pH-low crosslinker resulted in high viscosity contrariwise the rest of gel loadings. As it was expected none of the samples exposed viscosity greater than 1500cP as well.

Although a minimum viscosity of 1500cP has been reported for a good frac fluid¹⁰¹, it is yet ambiguous due to the lack of knowledge on the downhole environment and the sufficient viscosity

of CMC fluid. These maps will be very useful in case of future studies on the minimum required viscosity for both academic and industrial application.

DOE results

Experimental optimization of the CMC farc fluid was conducted to determine the importance of each of three components of pH, CMC polymer and crosslinker concentration. In order to confirm the observed results from the experiments, statistical analysis using design of experiments (DOE) were conducted. Since all the experiments consisted of three factors (gel loading, pH and crosslinker concentration) the variables can impact the response individually or jointly^{181, 182}. Each of these factors had at least low and high levels. Factorial experiments were used in here and it included all possible factor-level combinations, both high and low levels, for all variables being tested, in the experimental design.

To determine the significant factors/factor, the Pareto chart was used. The Pareto chart has been described as a useful tool for identifying which estimated effects are the most important¹⁸². Normal plot of the effects was also used to compare the magnitude and statistical significance of main and interaction effects in factorial design. The Pareto chart and Normal plot of the effects were shown in **Figure 62**.

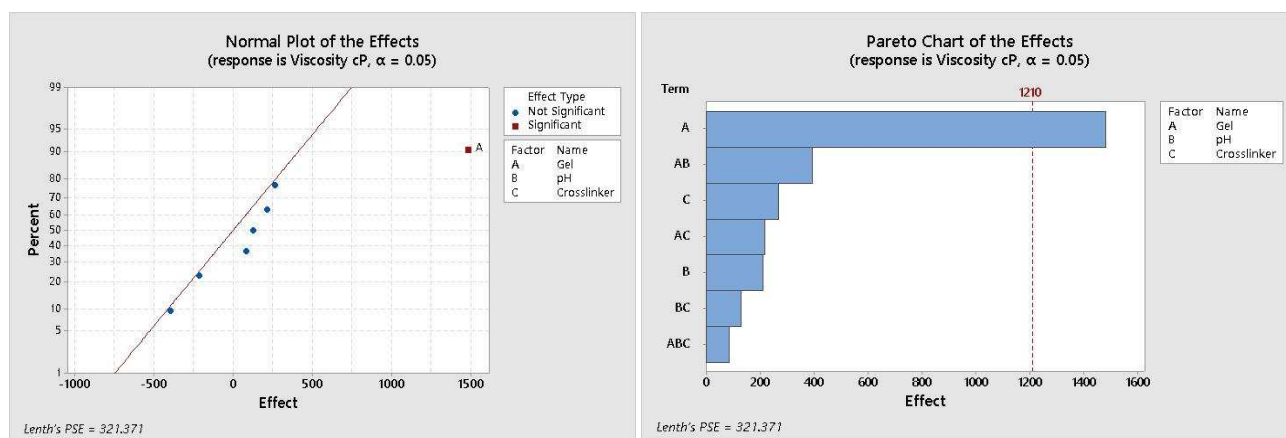


Figure 62- Pareto chart and Normal plot of the effects

Based on Figure 62, gel loading appeared to be statistically significant effect among the factors at 5% significant level. According to Normal plot of the effects, gel loading had a positive correlation on peak viscosity as it was seen in the experiments. This is in agreement with the results of experiments and previous studies^{177, 178, 179}.

However in part I of this study, where optimization of CMC frac fluid was done at higher TDS of 15000mg/l, no significant effect was observed, although the gel and crosslinker dosing showed higher impact on frac fluid peak viscosity. The TDS could interfered the results as gel loading was significant effect the viscosity while none of factors were significant in higher TDS.

In order to see the interaction between the individual factors and the main effect for each factors **Figure 63** reveals the individual and joint effects for all three factors, gel loading, crosslinker concentration and pH. The Interaction plot for peak viscosity was plotted to see if there is any interaction between the individual factors. The combination of gel and pH, as it was anticipated, the interaction plot indicated that significant interaction exists.

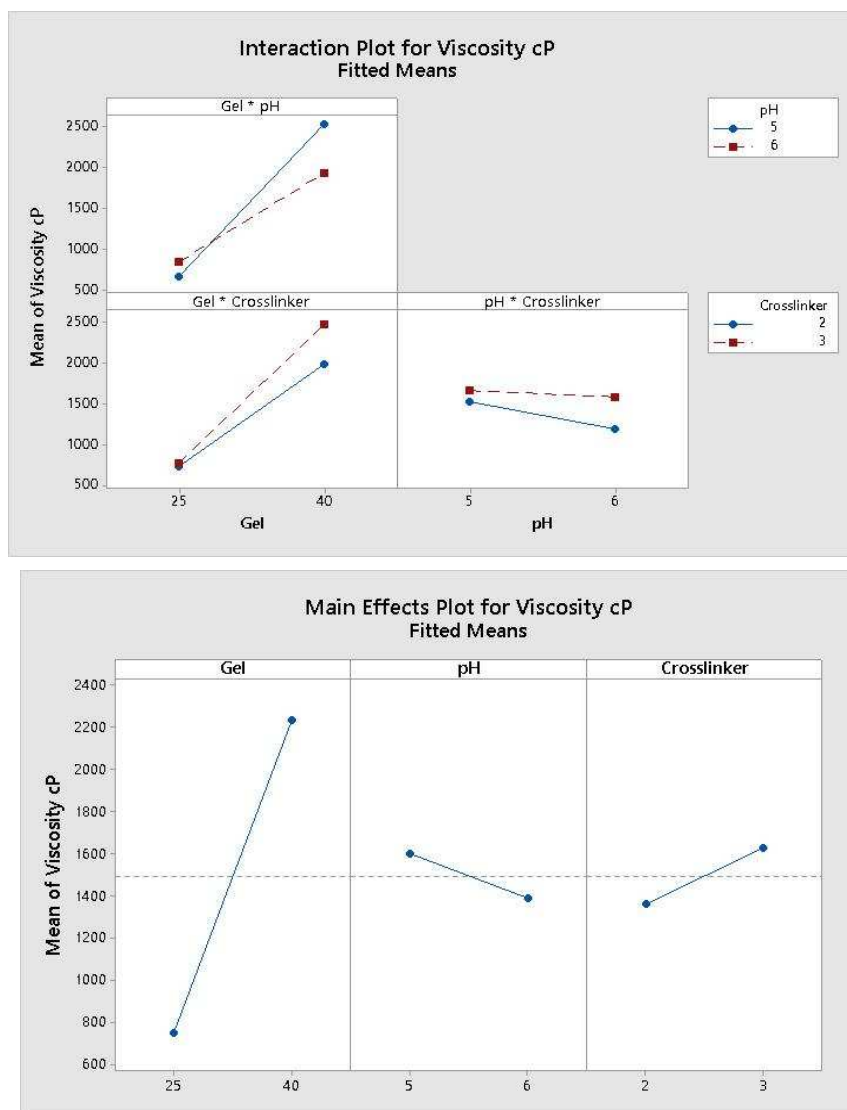


Figure 63- Interaction and individual effects for all three factors, gel, pH and crosslinker concentration

The effect of one of the independent variables on the dependent variable while ignoring the effects of all other independent variables was shown by main effect plot (Figure 63). There is a main effect when different levels of a factor affect the response differently. A main effects plot graphs the response mean for each factor level connected by a line. The steeper the slope of the line, the greater the magnitude of the main effect. Based on Figure 63, the line was not horizontal, therefore there was a main effect. Different levels of the gel loading affected the viscosity differently.

Although the line for pH and crosslinker was not completely horizontal, but according to the Pareto chart and Normal plot of effect, they are not significant.

Prediction equations are useful to analyze what-if scenarios in future studies. Moreover it generates a 3-D surface response which could be applied in similar conditions to calculate the peak viscosity. Many times data cannot be collected at all levels and factors so a prediction equation can be used to estimate the output. A prediction equation was generated by DOW for the process by quantification of the factor interactions in terms of $Y = f(X_1, X_2, X_3, X_4 \dots X_n)$ where

Y is the response of experiments, peak viscosity here;

$X_1 \dots X_n$ are the variable factors in the experiments.

Regression equation in uncoded units is as bellow:

$$\begin{aligned} \text{Peak viscosity (cP)} = & -14679 + 622.4 G + 2662 \text{ pH} + 1883 \text{ CL} - 108.3 G \times \text{pH} - 93.53 \text{ Gel} \times \text{CL} \\ & - 464.8 \text{ pH} \times \text{CL} + 22.27 G \times \text{pH} \times \text{CL} \end{aligned}$$

Where

G is the gel loading in pounds per thousand gallon of water

CL is the crosslinker concentration in gallon per thousand gallon of water.

This regression equation can be applied to all CMC based fluid cross-linked with Zr crosslinker at acidic pH.

4.6.4Conclusions

In this paper, it was tried to evaluate using poor quality waters, TDS level of 2500mg/l, as the main water sources in hydraulic fracturing, by developing three-dimensional viscosity maps. Carboxymethyl cellulose frac fluid gelled with zirconium based crosslinker was the base fluid in the experiments. Five gel loadings of 45ppt, 40ppt, 35ppt, 30ppt and 25ppt at pH range of 5 to 6 and crosslinker concentration at 1gpt to 3 gpt were chosen. The following conclusions where derived:

- Low salinity waters could be a great replacement for fresh water in hydraulic fracturing.
- The 3-dimentional counter maps could be used for optimization of frac fluid chemical composition and for lessen the amount of injected chemicals downhole.
- The peak viscosity should be determined, in order to optimize the chemical composition of CMC frac fluids for using saline waters.
- The viscosity of a CMC frac fluid directly correlates with CMC concentration and gel concentration has a significant effect on viscosity.
- Combinations of high pH-high crosslinker concentration and low pH-low crosslinker concentration could be used to build a high viscose frac fluid.
- The influence of pH and crosslinker concentration on rheology of fluid was eliminating by increasing the gel loading.
- The drawn regression equation could be applied to all the CMC based fluid gelled with zirconium crosslinker.

Chapter 5 : Conclusion

5.1 Summary

It is well known that hydraulic fracturing in unconventional oil and gas development consumes large volumes of water. In Colorado, much of the oil and gas operations are coincident with areas of intensive agricultural operations. Due to the complex nature and intensive water requirements of unconventional resource developments the risk of environmental impact is higher than with conventional energy development. The effective use of water in oil and gas operations plays a vital role in an operating company's success in the industry. A variety of water management techniques for hydraulic fracturing in Colorado were studied and are presented in this dissertation. Successful development of these water management techniques could lead to significant cost savings and reduced environmental impacts through reduced freshwater usage and elimination of water disposal operations thereby reducing water trucking impacts, and seismic issues. To address these issues, five hypotheses were proposed for the research described in this dissertation with the corresponding results

- I. Divalent cations removal with EC can be optimized by consideration of sequencing pH values.

Softening before EC is more efficient in removing not only divalent cations such as Ca, Mg, Sr and Ba, but also is more effective in removing TOC for produced water samples (older than 30 days). However, both sequences showed no significant success in treating early time

flowback water samples. Analysis of the data suggests that the challenges associated with treating flowback water are due to the high organic content (TOC), which is the residue from polymers and surfactants of the frac fluid. Flowback water quality, then, resembles fracking fluid chemistry while produced water has more characteristics of formation water with high TDS and low TOC values.

- II. The cost of treatment can be optimized by understanding the solubility of target salts and their pKa values.

It was found that depending on the target water quality, in order to precipitate specific constituents, different pH levels are required. Since magnesium solubility is very high, it will dictate the pH level required for softening or metal precipitation processes. Equilibrium modeling results in section 4.2, predict that removal efficacy of Ca and Sr will be minimally impacted by lowering pH from 10.2 to 9.5. Therefore, depending on the target removal, cost of treatment which is typically associated with chemical handling, could be cut.

- III. Recycling of flowback and produced water can be optimized by understanding minimum water quality targets for frac fluid formation.

According to Section 4.2, it was seen that treatment can be optimized by understanding the required water quality standard for produced water reuse and recycling in hydraulic fracturing. Based on the rheological study of CMC and guar based frac fluids, two water quality standards

were developed. It was determined that for the chosen concentrations for this study, aluminum, iron, phosphorous, potassium, and sodium all have negative impacts on fracturing fluid stability. Calcium and magnesium improved fluid rheology characteristics until a critical concentration was reached, beyond which the frac fluid becomes less stable. Results show that CMC based fluids were more suitable for waters with higher TDS values and poor quality waters.

- IV. Organic matter residuals in frac fluid and produced water could impact frac fluid development and stability by interfering with the crosslinking mechanism.

The rheological parameters of CMC based frac fluid samples built using model water, with no organic content, exhibited a more stable fluid than the frac fluid samples built using recycled water, with significant amounts of organic matter. The negative impact of organic matter on frac fluid stability was more pronounced at organic matter content greater than 600mg/l, resulting in a lower viscosity profile. Analysis of the results suggests that the organic matter residues from gelled frac fluids crosslink and form metal complexes with the transitional metal crosslinker. This crosslinking and formation of metal complexes yield loose and weaker crosslinked polymers resulting in a less stable and less viscous frac fluid.

- V. The water quality range that is compatible with acceptable frac fluid can be increased by optimizing pH, gel loading, and cross linker concentration.

Analyses of CMC based fracking fluids at high and low TDS levels show that, depending on the source water quality, the primary chemical composition of frac fluid could be adjusted. Several 3-D contour maps of apparent peak viscosity were developed based on the samples' rheological data. The contour maps depict that at a TDS level of 15,000mg/l, a stable and high viscosity (greater than 1500cP) could be formed at lower pH with only an 11% increase in gel loading (45 ppt to 50ppt). The optimization of chemical composition of the CMC frac fluid at low TDS level of 2500mg/l led to 40% lower gel loading compared to the original gel loading of 45ppt (loading used in the field and suggested by Service Company).

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Chapter 7 Appendix

Appendix A: P-Values for the frac fluid samples

Table A-1 T-tests and P-value for guar based frac fluid

Guar Based Frac Fluid		
Ion	Paired concentration mg/l	P-value
Na	3000, 5000	4.8579E-175
	5000, 9000	0
	3000, 9000	0
K	3000, 5000	0
	3000, 9000	0
	3000, 24000	0
	5000, 9000	0
	5000, 24000	0
	9000, 24000	2.3309E-175
Ca	100, 200	0
	200, 400	2.10351E-65
	100, 400	0
Mg	25, 75	0
	75, 125	5.2938E-263
	25, 125	9.3155E-301
Al	7.5, 15	1.2591E-267
	15, 20	0
	7.5, 20	0
Fe	25, 75	0
	75, 125	0
	25, 125	0
P	1, 3	0
	3, 5	0
	5, 1	0
	3, 1	0

	1, 5	0
	1, 1	0

Table A-2 T-tests and P-value for CMC based frac fluid

CMC Based Frac Fluid		
Ion	Paired concentration mg/l	P-value
Na	3000, 5000	1.2591E-267
	5000, 9000	0
	3000, 9000	0
K	3000, 5000	5.2864E-205
	3000, 9000	0
	3000, 24000	0
	5000, 9000	0
	5000, 24000	0
	9000, 24000	0
Ca	100, 200	0
	200, 400	7.3925E-301
	100, 400	0
Mg	25, 75	0
	75, 125	0
	25, 125	1.36114E-16
Al	7.5, 15	9.9136E-244
	15, 20	1.8597E-106
	7.5, 20	8.8565E-34
Fe	25, 75	0
	75, 125	8.90515E-25
	25, 125	1.2249E-138
P	1, 3	3.02672E-14
	3, 5	0
	5, 1	0
	3, 1	0
	1, 5	0
	1, 1	0

Appendix B: Water quality tables

Table B.1- Water quality parameters for water samples at TDS = 5000mg/l and TDS = 7000mg/l.

Parameter mg/l	TDS= 5000 mg/l			
	High Sierra	Model	ETFB	Produced water
Gravimetric TDS	6686.4	5000.0	5481.9	4876.4
Ionic TDS	5000.0	4515.9	5000.0	5000.0
TOC	341.4	0.0	399.1	229.2
NH4	3.66	3.29	8.7	7.5
Br	14.44	12.25	13.83	12.90
Cl	3019.67	2720.99	2933.58	2949.04
SO4	53.01	13.34	0.00	0.80
HCO3	47.53	33.45	187.39	113.79
Al	0.24	0.23	0.28	0.24
Ba	0.19	1.97	4.06	2.01
B	1.85	1.60	3.30	3.51
Ca	5.70	8.19	81.65	85.91
Fe	0.27	0.33	14.59	4.10
K	64.16	94.50	11.51	8.76
Mg	1.83	1.86	9.32	12.93
Mn	0.02	Na	0.18	0.05
Na	1784.75	1622.61	1705.94	1777.39
Si	2.36	0.72	14.17	10.77
Sr	0.66	0.61	9.06	10.07
Cu	na	Na	0.02	0.02

Parameter mg/l	TDS= 7000 mg/l			
	High Sierra	Model	ETFB	Produced water
Gravimetric TDS	9360.9	7750.2	7674.6	6827.0
Ionic TDS	7000.0	7000.0	7000.0	7000.0
TOC	478.0	0.00	558.7	321.0
NH4	5.1	5.10	12.2	10.6
Br	20.2	18.9	19.4	18.1
Cl	4227.5	4217.7	4107.0	4128.7
SO4	74.2	20.7	0.00	1.1
HCO3	66.5	51.9	262.4	159.3
Al	0.3	0.4	0.39	0.34
Ba	0.26	3.06	5.68	2.81
B	2.58	2.48	4.62	4.91
Ca	7.98	12.69	114.31	120.28
Fe	0.38	0.52	20.43	5.73
K	89.82	146.48	16.12	12.27
Mg	2.56	2.89	13.05	18.11
Mn	0.03	na	0.25	0.08
Na	2498.65	2515.14	2388.32	2488.34
Si	3.30	1.11	19.83	15.08
Sr	0.93	0.94	12.68	14.10
Cu	na	na	0.03	0.03

Table B.2- Water quality parameters for water samples at TDS = 9000mg/l and TDS = 11000mg/l.

Parameter mg/l	TDS= 9000 mg/l			
	High Sierra	Model	ETFB	Produced water
Gravimetric TDS	12035.53	9964.62	9867.41	8777.58
Ionic TDS	9000.0	9000.0	9000.0	9000.0
TOC	614.61	0.00	718.38	412.71
NH4	6.58	6.56	15.66	13.65
Br	25.99	24.41	24.90	23.21
Cl	5435.40	5422.73	5280.45	5308.26
SO4	95.42	26.59	0.00	1.43
HCO3	85.55	66.66	337.31	204.82
Al	0.43	0.46	0.50	0.43
Ba	0.34	3.93	7.31	3.62
B	3.32	3.19	5.94	6.32
Ca	10.27	16.32	146.97	154.64
Fe	0.48	0.67	26.26	7.37
K	115.49	188.33	20.72	15.77
Mg	3.29	3.72	16.78	23.28
Mn	0.03	Na	0.33	0.10
Na	3212.55	3233.75	3070.69	3199.30
Si	4.24	1.43	25.50	19.39
Sr	1.19	1.21	16.30	18.13
Cu	na	Na	0.04	0.03

Parameter mg/l	TDS= 11000 mg/l			
	High Sierra	Model	ETFB	Produced water
Gravimetric TDS	14710.1	12178.9	12060.2	10728.2
Ionic TDS	11000.0	11000.0	11000.0	11000.0
TOC	751.19	0.00	878.02	504.43
NH4	8.04	8.01	19.14	16.69
Br	31.77	29.83	30.43	28.37
Cl	6643.27	6627.78	6453.88	6487.88
SO4	116.62	32.50	0.00	1.75
HCO3	104.56	81.48	412.26	250.34
Al	0.52	0.57	0.61	0.53
Ba	0.41	4.81	8.93	4.42
B	4.06	3.90	7.26	7.72
Ca	12.55	19.95	179.63	189.00
Fe	0.59	0.81	32.10	9.01
K	141.15	230.19	25.32	19.28
Mg	4.02	4.54	20.51	28.45
Mn	0.04	na	0.40	0.12
Na	3926.45	3952.36	3753.07	3910.25
Si	5.19	1.75	31.17	23.70
Sr	1.46	1.48	19.93	22.15
Cu	na	na	0.05	0.04

Table B.3- Water quality parameters for water samples at TDS = 13000mg/l.

Parameter mg/l	TDS= 13000 mg/l			
	High Sierra	Model	ETFB	Produced water
Gravimetric TDS	17384.660	14393.346	14252.928	12678.727
Ionic TDS	13000.000	13000.000	13000.001	13000.002
TOC	887.768	0.000	1037.663	596.141
NH4	9.505	9.471	22.621	19.723
Br	37.545	35.255	35.961	33.530
Cl	7851.137	7832.834	7627.314	7667.491
SO4	137.823	38.412	NA	2.071
HCO3	123.565	96.292	487.220	295.852
Al	0.618	0.668	0.725	0.626
Ba	0.490	5.683	10.556	5.227
B	4.800	4.604	8.584	9.122
Ca	14.828	23.573	212.289	223.368
Fe	0.699	0.963	37.934	10.651
K	166.813	272.039	29.929	22.781
Mg	4.753	5.367	24.245	33.628
Mn	0.048	NA	0.473	0.141
Na	4640.345	4670.971	4435.443	4621.204
Si	6.131	2.063	36.832	28.007
Sr	1.725	1.747	23.549	26.183
Cu	na	na	0.058	0.049

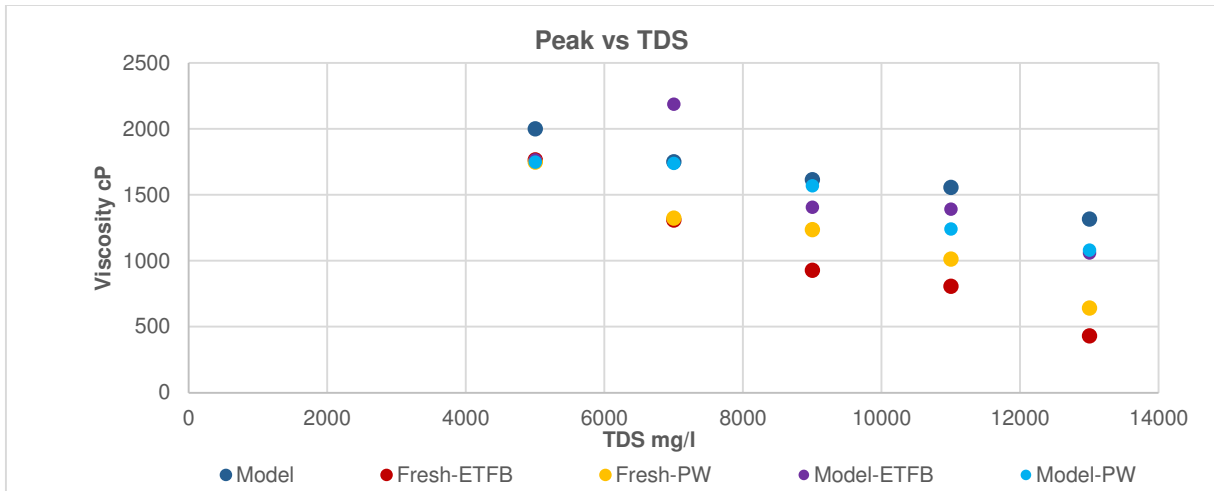


Figure B.1- Viscosity peak for recycled, model, ETFB and PW waters.

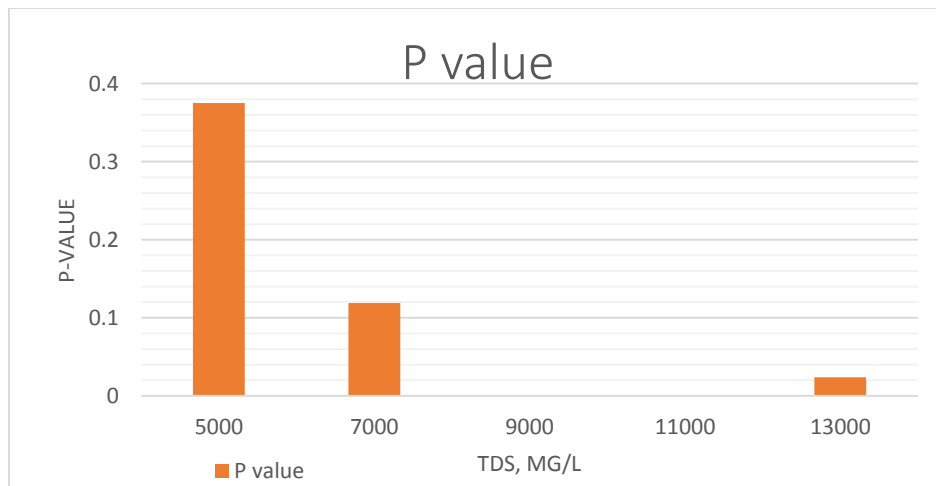


Figure B.2- p-Value for the paired t-test.

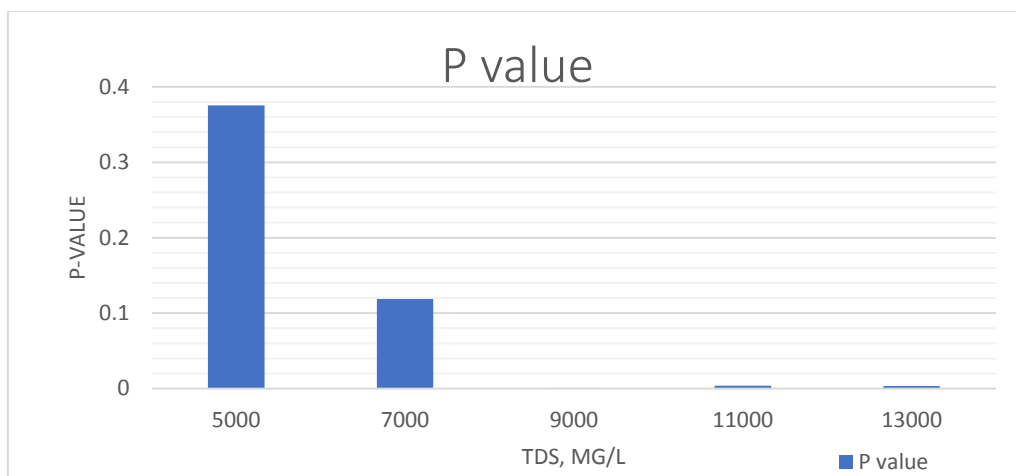


Figure B.3- p-Value for the paired t-test.