THESIS

A COMPARISON OF ELECTROCOAGULATION AND CHEMICAL COAGULATION

TREATMENT EFFECTIVENESS ON FRAC FLOWBACK AND PRODUCED WATER

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ABSTRACT

A COMPARISON OF ELECTROCOAGULATION AND CHEMICAL COAGULATION

TREATMENT EFFECTIVENESS ON FRAC FLOWBACK AND PRODUCED WATER

Development and production of tight shale for crude oil and natural gas is increasing rapidly

throughout the United States and especially in the Wattenberg field of Northern Colorado.

Hydraulic fracturing is used to stimulate the shale formation, which allows previously trapped oil

and gas to flow to the surface. According to Goodwin (2013), approximately 2.8 million gallons

of water are required to hydraulically fracture a horizontal well. Freshwater makes up the vast

majority of water used to create these fracturing fluids with a small portion coming from

recycling of previously used fracturing fluid. In a semi-arid climate such as Northern Colorado,

there are multiple demands for freshwater, often exceeding the supply. Once a well is fractured,

water flows back to the surface along with the targeted oil and gas. This fluid is typically

referred to as flowback or produced water. In some areas around the United States as much as

10 barrels of water flows to the surface for every barrel of oil recovered. For the purposes of this

research, flowback is defined as water that flows to the surface within the first 30 days after

fracturing. After fracturing, up to 71% of the water (produced water) used to fracture the well

flows back to the surface along with oil and gas, with approximately 27% flowing back in the

first 30 days (Bai et al, 2013). The flowback and produced water is currently being disposed of

either by deep underground injection or in evaporation ponds. There has been very little effort to

capture, recycle, and reuse this flowback or produced water as it has traditionally been

considered a waste product. Due to the limited freshwater supply in Colorado, recycling and

reuse should be explored in greater detail and with a sense of urgency. The ultimate goal for the oil and gas industry should be to recycle and reuse 100% of flowback and produced water in the creation of hydraulic fracturing fluid for other production wells, creating a closed-loop system. Before flowback and produced water can be reused, treatment of the water is required. Treatment for reuse typically consists of removal of solids, organic compounds, and some inorganic ions. Historically, chemicals have been the dominant method used for coagulation to remove solids, as they are readily available and in many cases can be cheaper than other methods. Electrocoagulation (EC) is now also being considered as a produced water treatment method. EC involves running electric current across metal plates (sacrificial anodes) in a solution, which creates an *in situ* coagulant dose (Emamjomeh and Sivakumar 2008). There is a time component to water quality changes over the life of a well. Early flowback typically has higher concentration of aluminum, solids, and total organic carbon (TOC) as it is influenced mostly by the makeup of the fracturing fluid. At some point around the 30-day mark, a transition in water quality begins. The formation or connate water seems to have a greater influence on water quality than does the fracturing fluid. Treatment seems to correlate to the changing water quality, as treatment is less effective on the early flowback compared to produced water. TOC and low ionic strength may be the reason early flowback is more difficult to treat. Also, chemical coagulation (CC) is more effective than EC at removing TOC and aluminum in early flowback water compared to EC, while EC is more effective at removing iron. However, both treatments are effective after day 27.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

Development and production of tight shale for crude oil and natural gas is increasing rapidly throughout the United States and especially in the Wattenberg field of Northern Colorado. Many exploration and production companies are targeting the Niobrara formation in the Denver Julesburg (DJ) Basin, which lies approximately four to seven thousand feet below the surface to the north and west of Denver, CO. Due to the geology, stimulation of the tight shale formation is required to allow for the extraction of the oil and gas. Hydraulic fracturing is used to stimulate the formation, which allows oil and gas, previously trapped, to flow to the surface. Also, horizontal drilling has become the norm in the region due to the ability to access a larger portion of the formation with one well, ultimately increasing the volume of natural gas and crude oil produced and reducing the overall footprint. According to Goodwin (2013), approximately 2.8 million gallons of water is required to hydraulically fracture a horizontal well. Freshwater makes up the vast majority of water used to create these fracturing fluids with a small portion coming from recycling of previously used fracturing fluid. In a semi-arid climate such as Northern Colorado, there are multiple demands for freshwater, often exceeding the supply. Many energy and service companies are using groundwater sources, purchasing water from municipalities, or outbidding farmers at auction for the water rights. This has created some animosity, and somewhat of a negative perception in the view of the general public. Many in the general public are worried that an already scarce resource is being depleted without regeneration.

Once a well is fractured, water flows back to the surface along with the targeted oil and gas. This fluid is typically referred to as flowback or produced water. In some areas around the United States as much as 10 barrels of water flows to the surface for every barrel of oil recovered. For the purposes of this research, flowback is defined as water that flows to the surface within the first 30 days after fracturing. Produced water will be defined as any water returning to the surface after the first 30 days after hydraulic fracturing occurs. The Niobrara shale formation in the DJ Basin is typically much drier and does not produce large volumes of connate water compared to other areas within the United States. After fracturing, up to 71% of the water used to fracture the well flows back to the surface along with oil and gas, with approximately 27% flowing back in the first 30 days (Bai et al 2013). This data suggests that a portion of the water used in hydraulic fracturing is consumed downhole creating a net water loss per well compared to other regions where each well produced a net water gain.

The water that does flow back to the surface is currently being disposed of either by deep underground injection or in evaporation ponds. There has been very little effort to capture, recycle, and reuse this flowback or produced water as it has traditionally been considered a waste product. Due to the limited freshwater supply in Colorado, recycling and reuse should be explored in greater detail and with a sense of urgency. The ultimate goal for the oil and gas industry should be to recycle and reuse 100% of flowback and produced water in the creation of hydraulic fracturing fluid for other production wells, creating a closed-loop system.

For reuse, water must be treated before fracturing fluids can be developed. Before treatment, water quality must first be understood. Water quality has a direct correlation to the subsurface

mineralogy by geographic location of the formation and chemical composition of the fracturing fluid used for stimulation. Many waters produced from oil and gas development in North America (up to 400,000 mg/L TDS) are more saline than seawater, which has total dissolved solids (TDS) concentration of roughly 35,000 mg/L (Gomes et al. 2012). Also, gel-based fracturing fluids have high solids and organic content, creating difficulties in treatment for reuse.

Treatment for reuse typically consists of the removal of solids, organic compounds, and some inorganic ions. Historically, chemicals have been the dominant method used for coagulation to remove solids, as they are readily available and in many cases can be cheaper than other methods. EC is now also being considered as a produced water treatment method. EC has been used to treat municipal wastewater in the United States since the early 1900s. EC involves running electric current across metal plates (sacrificial anodes) in a solution, which creates an in situ coagulant dose (Emamjomeh and Sivakumar 2008).

This thesis is organized around a journal article submitted to the American Water Works Association. Goals for this research are to compare treatment of flowback and produced water with EC and chemical coagulation (CC) and determine the efficiencies of each treatment and what could cause treatment to fail.

Chapter 2

Literature Review

The Greater Wattenberg field (GWA) is located in the DJ Basin of Colorado, just north of the city of Denver, CO and spans 50 to 70 miles from north to south (figure 1) (Moritz and Barron 2012). The GWA contains mostly unconventional reservoirs that consist of tight gas sands and some gas shale. The large volume of hydrocarbons present is difficult to develop due to the low porosity and permeability of the formation. The COGCC had the GWA ranked as the eighth largest gas field in the Unites States (COGCC). One of the top producing reservoirs is the Niobrara formation, which has been described as a shaly marl. The Niobrara formation was first discovered in 1912, in Goodland, KS by the Osborne and Dunn Co. when a strong flow of natural gas was encountered drilling the Goodland No.1 well (Sec. 24-T8S-R40W) (Brown et al. 1982). In 1919, the Beecher Island field was discovered in Yuma County, CO, and was further developed in 1972 with five additional wells drilled by Mountain Petroleum Corp. While further development was uneconomical at the time, significant gas reserves of the formation were proven. In 1974, a new foam fracture stimulation process was used, which increased production by 30 times. The Niobrara formation now extends from Chadron, NE, south to Kit Carson County, CO.

Figure 1. Map of the State of Colorado counties with the Wattenberg field highlighted in red. Courtesy of COGCC.

In 1978, widespread gas shortages in the United States led to the Natural Gas Policy Act (NGPA), where incentives were provided for exploration and development of new gas sources. In 1980, The Alternative Fuel Production Credit of the Internal Revenue Code (Section 29) was passed, sparking further development of unconventional gas sources (Kennedy et al. 2012). An unconventional reservoir is defined as a low quality reservoir that must be stimulated to produce at commercial flow rates and recover commercial volumes of hydrocarbons (Holditch 2013). Exploration and production of unconventional gas quickly increased in the GWA as it qualified for these incentives.

As development increased, technologies soon followed. Hydraulic fracturing was used to exploit these tight shale formations. Initially, frac fluids consisted of polymer emulsions to carry proppant downhole, but quickly transitioned to zirconium cross-linked gel fluids, which are still present today (Khachatrian et al. 2003). Stimulation increases oil and gas flow, which ultimately

makes the play commercially economical. Hydraulic fracturing is typically performed between

5,000 (1,524 m) and 10,000 (3,048 m) feet below the surface, at pressures between 2,000 - 8,000

psi (99-383 kPa), and with an average flow rate of 2,000 gallons per minute (7,571 liters per

minute) (Gruber 2013).

Fracturing fluids are comprised of 99.5% water and proppant and 0.5% chemical additives.   The

chemical additives are made up of surfactants to prevent emulsions from the formation, corrosion

inhibitors, scale inhibitors, gel-forming compounds to provide higher viscosity, a crosslinker for

proppant suspension, and breakers to reduce viscosity. Hazardous biocides are used as well, but

are being replaced in fracturing fluids with onsite UV disinfection. Generally, guar gum or

cellulose derivatives are used to form the gel, which will be cross-linked to carry the proppant

downhole (Bryant and Haggstrom 2012).

Hanes et al. (2003) provided research on quality assurance on recycled fracturing fluids.

Hydraulic fracturing has been used for more than 50 years and was first performed using oil as a

fluid. Through innovation, today's fracturing fluids are typically comprised of guar or a guar

derivative to control fluid loss during fracturing. Three main objective of fracturing fluids are: to

create a fracture downhole, to transport and place proppant in the fractures, and to flow back to

the surface leaving the proppant in place. Guar is a high molecular weight, water soluble,

polysaccharide, which creates the high viscosities needed, at generally low concentrations and

costs. The polysaccharide has been isolated from the endosperm of a guar bean. After the

fracturing process is complete and proppants are in place, the fluid viscosity must be lowered to

allow flowback to the surface. This is accomplished by the chemical addition of breakers during

6

the fracturing process, which degrades the cross-linked polysaccharides creating water like fluid. The breakers, commonly acids, enzymes, and oxidizers, hydrolyze acetal linkages and break the three-dimensional polymer network. There have been a few attempts to recycle this polymer-based fracturing fluid, but the fluid is typically not usable and is disposed. One reason recycling has been difficult is the inability to filter guar-based fluids. Removal of suspended solids is near impossible and is a required step in the recycling process. In conclusion, it was determined that lower molecular weight guar system that does not require the addition of breakers is superior to traditional guar based fracturing fluids and these fluids can be reused with minimal treatment and are more easily filtered.

In addition to hydraulic fracturing fluid advancement, drilling horizontal wells in the Niobrara has become the norm in the GWA. For low permeability reservoirs, long horizontal bore holes and multistage fracturing can effectively stimulate the formation (Holditch 2013). Approximately 3 to 5 million gallons (11,356-18,927 m^3) of water are required to hydraulically fracture a horizontal well (Goodwin 2013, Bryant and Haggstrom 2012).   Typically, 5% of the fresh water supply in the United States is used to create hydraulic fracturing fluids. It is predicted that in 50 years less than 3% of the fresh water supply in the United States will be used for hydraulic fracturing fluids. Western Resource Advocates state that 0.08% of the total fresh water available in the state of Colorado was used for oil and gas operations in 2011(Western Resource Advocates, 2013). Sources for freshwater include groundwater, surface water and municipal water, and recent advances are also allowing flowback and produced water to be used (Brown et al. 2011).

Approximately 27% (0.81-1.35 Mgal, 3,066-5,110 m^3) of injected water will flow back to the surface during the first 30 days (flowback water), and approximately 71% (2.13-3.55 Mgal, 8,063-13,438 m^3) over the lifetime (25-30 years) of the well (Bai et al. 2012). According to the produced water society (PWS), 65% of the water generated in the United States is injected back into the formation, 30% is injected into other deep formations and 5% is discharged to surface water bodies. During the produced water period, PWS states that in conventional oil fields, approximately three gallons (11.36 liters) of water are produced for every one gallon (3.79 liters) of crude oil. Tight shale does not produce as much water as conventional hydrocarbon reserves, but the volume of water that does return the surface creates a reuse opportunity for oil and gas companies (Gomes 2012).

Stewart and Takichi (2005) performed a case study of beneficial reuse of produced water in Colorado and Wyoming, USA. It was stated that the water produced is a constraint on the industry, and that the amount of energy that can be produced is directly related to how much water can be disposed of or released to the surface. The current industry standard is deep well injection, which requires a significant amount of energy. Also, it is believed that produced water could become part of a water right portfolio and ultimately a water resource in the water-short western United States. In 2005, 2.5 billion barrels of oil, 196 trillion cubic feet (5.55 trillion m^3) of natural gas, and 25 billion barrels of oil water were produced. The water, if usable, could support roughly 10 million people for a year (0.3 ac-ft/year/home, 370 m^3/year/home). It was estimated that 20% to 30% of the natural gas and electric energy used in the western United States is for moving water and roughly 30% of the energy (natural gas or oil) is being used to re-inject the associated water produced. The conclusion drawn is that there is a great need for

increased produced water research, as there is a lack of information regarding treatment, quality and volume. Also, the approach of having produced water as a resource will benefit water providers as well as energy companies.

Electrocoagulation

While popular in the early 1900s, by the 1930s all EC treatment plants has been abandoned as operating costs were considered to be higher than CC, but EC has recently been rediscovered in the wastewater industry (Holt et al. 2002). EC has been used in various industries to remove suspended solids and organics for some time, but is not considered a desalination technique (Bryant and Haggstrom 2012). According to Kennedy (2012), EC treatment is the preferred method to remove suspended solids and heavy metals from flowback and produced water in the Marcellus region of Pennsylvania.

Emamjomeh and Sivakumar (2008) performed a review of pollutants removed by EC. EC was defined as a mechanism for destabilizing suspended or dissolved contaminants in an aqueous solution by introducing electrical current to the solution. Sacrificial electrodes are the metal plates submerged in the solution and are typically made of destabilizing agents such as aluminum or iron, or a combination of the two. These metal anodes produce cationic species of iron or aluminum in situ, which may have the same effect as the addition of coagulant salts and will destabilize charged particles allowing for flocculation and solid-liquid separation. The entire process has three main mechanisms: electrode oxidation, gas bubble generation, and flotation and sedimentation of formed floc.

Various uses for EC were found, beginning with Kaliniichuk et al. (1976) who used EC to treat refinery wastewater. Results showed that aluminum hydroxide formed due to the dissolution of aluminum anodes and the hydroxide floc adsorbed the oil, which was then floated to the top by the hydrogen bubbles formed at the cathode. Balmer and Foulds (1986) studied the effectiveness of a sacrificial iron anode on oil separation from oil in water. Key findings were as follows: the production rate of a reagent is controlled by the electrical current, several different anode materials are effective for treatment, energy consumption is optimized by using high electrolyte water with small electrode plate spacing, and the consumption rate of the sacrificial anode is dependent on the current applied. Ibanez et al. (1995) also treated oily wastewater and found that aluminum electrodes are more efficient than iron electrodes. This is likely due to the high adsorption capacity of hydrous aluminum oxides.

EC was used to treat municipal wastewater to study effects on microfiltration (Pouet and Persin 1992, Pouet and Grasmick 1995). An EC cell consisting of 15 aluminum electrodes was used followed by a microfiltration system. Chemical oxygen demand (COD), total suspended solids (TSS), and turbidity were measured as key result parameters. Results suggested that microfiltration in combination with EC could improve removal efficiency of turbidity up to 30%, COD by 20%, and TSS by 65%.

EC has also been used in treatment of oily wastes containing high COD concentration (Calvo et al. 2003). A laboratory scale EC unit was used at two different currents of 7 and 10 Amperes (A). At 7A COD removal ranged between 50% and 78%, while at 10A COD removal increased to 90%. Also, Dimoglo et al. (2004) studied EC treatment for COD removal, along with

turbidity, phenol, and hydrocarbons. Petrochemical wastewater was treated with two laboratory scale EC units containing aluminum and iron electrodes. Results show that using a combination of iron and aluminum electrodes more effectively treats wastewater. This was determined by comparing removals efficiencies for each separately. It was found that aluminum was more effective at removing hydrocarbons and phenols, while iron was more effective are removing turbidity and grease. There was no difference between electrodes for COD removal. Also, results suggested removal efficiency increases as electrolysis time increases.

Holt et al. (2005) conducted a review of EC to determine its future as a water treatment technology. An experiment was performed as well, comparing a batch EC reactor with a continuous flow EC reactor. While EC is not a new technology, in recent years a renewed interest has been found in continuously fed water treatment facilities for industrial applications. During the review of EC, several shortcomings in literature and research were found. It appears there is no real systematic approach to EC design and operations, leaving little to be known regarding different reactor performance; and in addition, most science behind reactor design is empirical and heuristic. Also, there seems to be very little research data published regarding batch reactor treatment. Finally, the performance of an EC cell is directly related to the operational state of the electrodes. Typically, an oxide forms a layer on the surface of the electrode preventing further metal dissolution and electron transfer, ultimately limiting coagulant dose created in situ. A key driver for the development of any application of EC has been the removal of a specific pollutant.

EC reactors can be broken into two main categories, batch and continuous reactors. A continuous reactor consists of a constant flow of wastewater and is essentially in steady state. An advantage for continuous reactors is that the coagulant requirement dose remains relatively consistent. Batch rectors are used with a fixed volume of wastewater for each cycle. A disadvantage here is that the conditions in the reactors change with time creating uneven coagulant dosing due to corrosion. Within each category, another distinction can be made by the presence of flotation. Hydrogen bubbles created at the cathode can be used to separate aggregated particles by flotation. If flotation is not used, separation by settling is typically the method of choice. It has been found that a low current produces a low bubble density, which creates a low flotation momentum for separation. Thus, as current increases, bubble density increases, leading to a greater upward momentum and allowing for the possibility of separation by flotation.

It was determined that the best EC design for a water treatment plant would be a batch reactor system with vertical plate electrodes, and the use of flotation for separation. This led to an experiment discussed later (Holt et al. 2002), where potter's clay was used as the pollutant and the electrodes were made of aluminum. It was found that turbidity removal was independent of initial load as influent loads of 1.6 g/L and 0.1 g/L produced turbidity of 4.3 and 3.6 NTU, respectively.

Mass balance was also measured and the mass added to the reactor was a combination of initial pollutant loading and coagulant addition. Results showed that the lower the pollutant loads, the greater the percent mass recovered at the surface (flotation). Also, the greater the current

density, the greater the mass collected at the surface. Current density directly determines the

coagulant dose and the bubble density. Results showed that settling is the main mechanism for

separation with low current density as less bubbles are produced to float colloids, while

floatation is the main removal mechanism at higher current density rates as larger number of

bubbles are produced.   Two key findings from this experiment are that operating current density

is the key parameter affecting both response time and the pollutant separation method, and

operating an EC system at the highest available current may not be the most efficient method for

operation. The latter was determined by more mass being removed at the surface from a current

density of 14 A/m^2 with the same coagulant dose as a current density of 27 A/m^2.

It was also stated that even with over a century of use, there is still no consensus on the most

effective design for any given application. A likely reason for EC being such an enigmatic

technology is the fact it uses three fundamental physic-chemical processes of electrochemistry,

coagulation, and flotation.   There is research about each one separately but not much is known

regarding the interaction of them all together. EC needs to be researched in a way where

mechanistically-based mathematical modeling can replace current "enlightened empiricism."

Few studies can be found regarding treatment of frac flowback and produced water with EC.

However, Gomes et al. (2012) studied the effects of EC on COD removal in produced water. In

addition to COD, different electrodes, residence time, current density, and pH were also studied

to optimize treatment conditions. EC was performed in a beaker-size reactor as well as a larger

flow-through apparatus (FTEA). Both iron and aluminum electrodes were used to make a

comparison. Flow rate for the FTEA was 0.525 L/m and for the reactor a total of 450 ml of water

was used for treatment. For the FTEA each sample was run two times and for the reactor each treatment was performed four times, totaling 45 minutes. COD removal was found to be 68 ± 12 mg/L when using the FTEA and 67 ± 3 mg/L with the reactor. It was found that aluminum electrodes increase removal of COD compared to iron electrodes. It was also found that EC can effectively remove metal ions with adsorption of iron oxides/hydroxides/oxyhydroxides and aluminum oxides. It was determined that EC can be used to treat produced water, but more work needs to be completed to optimize the conditions for removal of COD, metal ions, and organic species.

Chemical Coagulation

CC consists of delivering a coagulant as a salt, which disassociates in solution (Holt et al. 2002). In the United States, aluminum and iron salts are the most commonly used coagulants (Carlson and Gregory 2000). CC involves the addition of positively charged metal salts and polymers, typically aluminum or iron, to induce coagulation and flocculation. The mechanism for coagulation and flocculation is through charge neutralization of negatively charged particles, which are initially stable and hydrophilic. The colloids are de-stabilized, repulsion is reduced, and subsequently the colloids aggregate or flocculate into particles that can be removed through settling or filtration (Cardoso et al. 2012).

Cardoso et al. (2012) conducted an experiment involving treating produced water from offshore oil and gas operations with oxidation followed by coagulation and flocculation (CF). Typically, offshore produced water has higher TDS but lower benzene, toluene, ethylbenzene, and xylenes (BTEX) compared to onshore produced water. CF is a widely used process for removal of

14

colloidal partials, organic and inorganic, from wastewater. Most high molecular weight organic matter such as humic substances and fulvic acids can be removed by CF in industrial and municipal water treatment facilities. However, many uncharged, low molecular weight substances, such as carbohydrates, cannot be removed by CF and typically require a biological process for removal. Aluminum and polyaluminum based coagulants do have the ability to form complexes with some of the uncharged, low molecular weight organic material. The mechanism for removal is the polyaluminum ions attach so that the hydrophilic end of the organic substance faces the surface of the aluminum compound and the hydrophobic end faces the aqueous phase, allowing for aggregation.

The water quality parameters measured in this study were apparent color, turbidity, pH, total oil and grease (TOG), and TSS. Samples were collected from a produced water tank stored on site before batch treatment. A jar-testing unit was used to agitate and mix oxidant and coagulant. First, oxidation methods were tested using organic oxidants and hydrogen peroxide. Results showed TOG and turbidity were significantly reduced with low doses of organic oxidants and lower than what high doses of hydrogen peroxide could obtain. Results, of CF treatment show a complete removal of TOG from 118 mg/L, a turbidity decrease form 2100 NTU to an average of 44 NTU, and a TSS reduction form 590 mg/L to an average of 128 mg/L. Treatment 5, containing the highest dose of oxidant and coagulant was found to perform the best under current conditions. TSS was found to be unaffected by coagulant dose or pH. Experimental results show the oxidation and CF process is reliable for treatment of produced water containing hydrocarbons and high concentrations of dissolved solids.

Electrocoagulation vs. Chemical Coagulation

Few studies can be found comparing treatment of produced water with EC and CC. However, Holt et al. (2002) conducted a quantitative comparison between chemical dosing and EC on treatment of a solution spiked with clay particles at different chemical doses and electrical currents. Normalized turbidity removal was used to determine treatment effectiveness. Chemical addition was delivered via jar testing mixers using aluminum sulphate (alum) at three different doses (1, 4, and 20 mg/L). EC was run on a bench scale unit at different currents, which will deliver different in situ coagulant dosages. Optimal CC treatment occurred at pH 4.2 and aluminum dose of 4 mg/L, while optimal EC treatment occurred at pH 8.3-8.8 and aluminum dose of 20 mg/L (longer run time). It was determined that a direct comparison of CC and EC is not practicable, as they do not operate equivalently. The coagulant addition for CC is delivered in a discrete method compared to EC, where coagulant addition is a function of time and current. Another difference is pH drops with CC treatment due to the disassociation of alum, creating additional sulfate ions. No salts are added with EC treatment, thus pH remains relatively steady. Also, pollutant removal processes are different for both processes, as settling is the only method in CC while flotation and settling can be used with EC. To more accurately compare these removal mechanisms, pH was increased in the CC runs to simulate pH of the EC samples, while the time was increased for EC runs to match the amount of coagulant concentration being delivered with CC. Both EC and CC were below optimal turbidity removal levels at low coagulation dose and high pH (8.3-11.4). EC was found to out perform CC at a 20 mg/L aluminum dose and lower current. This is a result of hydroxyl ions OH^- (aq), which are formed at the cathode and improve sweep flocculation in a greater sense than the sulphate ion, SO_4^{-2},

which is from the alum. However, CC was found to be more effective than EC at lower pH

levels.

Yilmaz, Boncukcuoğlu, and Kocakerim (2007) conducted a quantitative comparison between CC

and EC for boron removal. Removal of boron was used to determine treatment effectiveness

while pH, current density, coagulant dose, temperature, and initial boron concentrations were

used to determine optimal operating conditions. For EC, a laboratory scale batch reactor with

two groups of alternating aluminum plates aligned vertically was used. Current intensity ranged

from 1-5 A, and the theoretical amount of coagulant dose was calculated using Faraday's second

law. Chemical coagulation was completed using a standard jar testing mixer and using

aluminum chloride as the coagulant. The dose of coagulant delivered was equal to the dose

calculated using Faraday's second law for the EC treatments. Sodium hydroxide and

hydrochloric acid were used to manipulate pH to desired values. For both treatments, boron

removal increased as pH increased up to 8.0 and then decreased. EC effectively removed 94% of

the boron concentration compared to 24% for CC. As initial boron concentration increased

treatment efficiency decreased for both treatments. Increasing coagulant dose for both

treatments yielded greater removal efficiency. However, aluminum was used more effectively as

a coagulant during the EC treatment compared to CC, which allowed for increased boron

precipitation. This is a result of increasing the current density. Both treatments showed an

increase in boron removal as temperature increased. EC with aluminum plates significantly

outperformed CC with aluminum chloride as a coagulant with all other parameters being equal.

Optimal EC conditions are pH 8, current of 5 A, and temperature at 313k, which delivered 7,450

mg/L of aluminum.

Younker et al. (2011) compared CC and EC on the treatment of synthetic produced water symbolizing water produced from offshore oil production in the Canadian Atlantic. It was stated that CC by inorganic metal salts is a common treatment technology since most contaminants have a negative surface charge and are stabilized by electrostatic repulsion. Metal salts form positively charged species in water that will destabilize colloids allowing for aggregation and floc formation. EC is defined as an electrolytic process where sacrificial anodes are corroded to produce metal cationic species to induce coagulation. EC allows for fewer chemicals to be used and reduced waste volume compared to CC.

The synthetic water was made up of 25 mg/L of crude oil, 10 µL/L of surfactant (Triton X-100) in a brine solution of 1g/L of sea salt with freshwater, and was blended for three minutes. A dissolved air flotation (DAF) jar tester was used to perform CC at four concentrations (20, 40, 60, and 80 mg/L) of ferric chloride at pH of 5 and 8. EC was also used in place of CC for coagulant dosing with all other procedures remaining the same. An iron anode was used along with a stainless steel cathode. The dose of iron delivered from EC was calculated to be similar to the CC dose. Zeta potential, turbidity and COD were measured to compare treatment effectiveness.

As a control COD removal was measured using only a DAF and was found to be 23%. For CC, the highest COD removal of 70% was recorded at 80 mg/L of ferric chloride dosage and a pH of 8. The highest COD removal for samples with pH of 5 was 69%, which had a ferric chloride dose of 40 mg/L. These results indicated charge neutralization is an important mechanism for

18

COD removal. EC treatment produced a COD removal of 74% at pH 5 and an iron dose of 20.6 mg/L, which equates to 60 mg/L of ferric chloride. With the same iron dose and a pH of 8, only 48% of COD was removed. It was found that flocs became heavier and less likely to float as coagulant dose increased for both treatment types. Also, EC tended to have higher turbidity, likely due to the orange discoloration of the water from the iron electrode, deeming turbidity not an ideal water quality parameter for this study. Conclusions from the study were that EC and CC were comparable for COD removal and high conductivity means lower solution resistance between electrodes, which leads to lower energy usage.

The objectives of this research are:

1. Characterize flowback and produced water quality
2. For water of different quality, run chemical and electrocoagulation treatment tests
3. Identify and characterize limitations of coagulation processes related to water quality conditions

Key Results and Tasks

1. Obtain water samples from various wells across varying time periods
2. Perform analysis on raw water to determine water quality
3. Treat waters samples with chemical and electro coagulation to determine treatment effectiveness
4. Perform analysis on treated samples to determine final water quality
5. Compare results for chemical and electro coagulation to each other and to water quality of each sample.

Chapter 3

A Comparison of Electrocoagulation and Chemical Coagulation Treatment On Frac Flowback and Produced Water

Introduction

Water produced during oil and gas development is the largest waste product in the industry. Each year approximately 250 million barrels of water are produced daily around the world as a result of oil and gas extraction (Younker et al. 2011).   Approximately 27% (0.76 million gallons, 2.88 million liters) will flow back to the surface during the first 30 days (flowback), and approximately 71% (1.99 million gallons, 7.57 million liters) over the lifetime (25-30 years) of the well (Goodwin et al. 2013). Many waters produced with oil and gas development are more saline than seawater (35,000 mg/L), especially in North America, where TDS ranges from 1,000 mg/L to 400,000 mg/L (Cardoso et al. 2012). This high TDS water is typically disposed of in deep underground injection wells or evaporation ponds across the United States. Water that returns to the surface can be categorized into three main categories: flowback, transition water, and produced water. Flowback is defined as hydraulic fracturing fluid returning to the surface and typically occurs in the first 30 days (Bai et al. 2013a). This water is influenced mostly by the fracturing fluids used and typically has increased organic and solids content, but a lower TDS compared to produced water. After roughly 30 days, water returning to the surface is considered transition water, as it moves from flowback to produced water and contains characteristics of both. There is no true definition of the time period for this transition. Produced water is water

that returns to the surface and is influenced mostly by the formation from which it was extracted. Produced water typically has lower solids and higher TDS compared to flowback.

The volume of water returning to the surface creates a recycle/reuse opportunity for oil and gas production companies. A reuse model can reduce fresh water demand in already water-starved regions, such as Northeastern Colorado or the western United States in general. Produced water is typically handled in one of three manners: deep-well injection, surface discharge, or recycle/reuse (Cardoso et al. 2012). Significant treatment (solids and TDS removal) would be required to recycle these waters for irrigation, agriculture, or surface discharge. The high cost associated with TDS removal is causing producers to use disposal as the main method for handling flowback and produced water. Currently, roughly 90% of flowback and produced water in the United States is being injected into deep disposal wells (GAO 2012). However, treatment of flowback and produced water for reuse as fracturing fluid development does not require extensive TDS removal. Treatment methods do exist and have become readily available recently, however many companies are reluctant to recycle produced water due to inconsistencies, unreliability, and costs associated.

Treatment for hydraulic fracturing fluid reuse typically consists of removal of solids, some inorganic ions, and organic compounds. Historically, CC has been the preferred treatment method, which involves the addition of positively charged metal salts and polymers, typically aluminum or iron, to induce CF. The mechanism for CF is through charge neutralization of negatively charged particles, which are initially stable and hydrophilic. The colloids are de-stabilized, and they subsequently aggregate or flocculate into particles that can be settled or

filtered out of solution (Cardoso et al. 2012). EC is another form of treatment, which has been used sparingly but seems to be gaining popularity more recently. EC involves running electric current across metal plates (typically iron or aluminum) submerged in a solution. The metals oxidize at the anode to form metal hydroxides in situ, which act as the coagulant to destabilize charged hydrophilic particles and allow for flocculation and solid-liquid separation (Emamjomeh et al. 2008).

The objectives of this research are to characterize flowback and produced water quality, treat varying water qualities with both chemical and electro coagulation, and finally to identify and characterize limitations of the coagulation process related to water quality conditions.

Materials and Methods

Sample Location and Collection

Sample wells were chosen based on the length of time since the flowback process was initiated after hydraulic fracturing, fracturing fluid used, spatial variation, and flow rate (figure 2). All wells sampled were hydraulically fractured with one of two fracturing fluids. Frac fluid I is a guar derivative based gel with a pH of 10.2. The other, frac fluid II, is a cellulose-derivative based gel with a pH of 5.0. Samples were collected on days 1, 2, 17, 27, 70, 90, 153, 161, and 183 after flowback began, in clean 5-gallon buckets with secure lids and stored at room temperature until treatment was performed. Treatment was completed seven days after sample collection. A 250 mL aliquot was collected for analysis prior to treatment in a prewashed

polyethylene bottle to be analyzed as the raw sample. Treated samples were delivered to

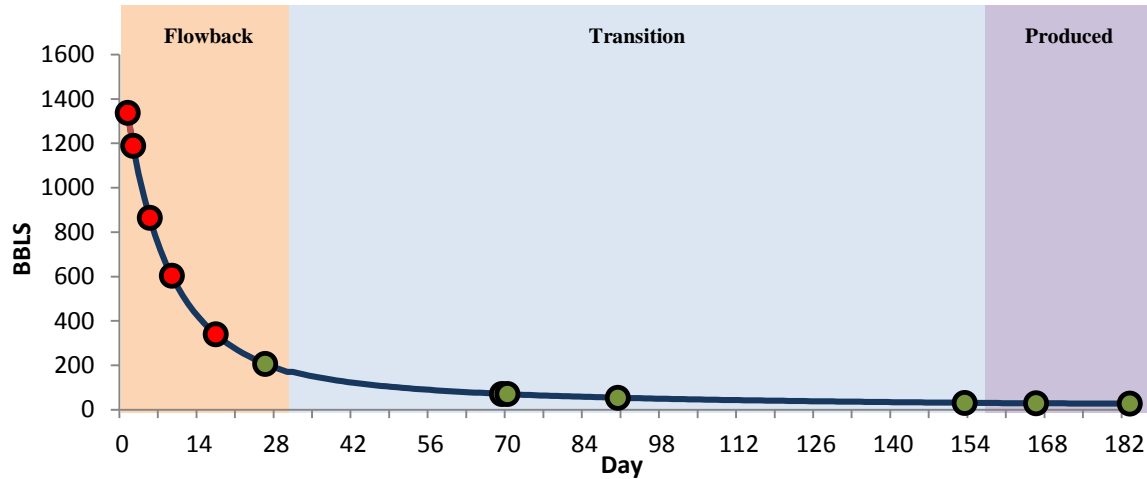eAnalytics Laboratory (Loveland, CO) on the same day treatment was performed.

Figure 2. Water production decline curve. Dots represent day of treated samples with red showing unsuccessful treatment and green showing successful treatment. Decline curve was produced from equations discovered by Bing Bai in 2012. The three water type classifications were determined by a change in the decline curve equations.

Electrocoagulation

The EC cell consisted of eight aluminum plates and eight iron plates spaced 1 cm apart

(Appendix H). Positive and negative electrodes were located on the top (Appendix P). The

treatment sample size was 4 liters. Water was pumped through the system for approximately one

minute before the electrodes were powered on in order to purge the cell of any trapped air. Once

the EC cell was powered on, 18 seconds of equilibrium time was used before current and voltage

were measured. At this point the effluent valve, on the EC bench, was opened to allow treated

water to flow into a clean 5-gallon bucket. At a flow rate of 1.8 gallons per minute (GPM) (6.81

liters per minute), there were 35 seconds of treatment time per batch cycle. The treated water was

set

aside for 20-30 minutes of flocculation and settling time. Water was decanted off the top while solids remained settled at the bottom of the bucket. The decanted water was then softened using sodium hydroxide (50% w/w, BDH) to a pH of 10.2 and filtered through a 2.5 µm paper filter (Whatman, Maidstone and Kent UK). The pH of the filtrate was then lowered to 7 with hydrochloric acid (37%, BDH, Randor, PA). A sample of the final product was sent to eAnalytics Laboratory (Loveland, CO) for analysis. After each use, hot tap water was flushed through the entire system for three minutes to clean the cell. Figure 3 provides a schematic of the EC process.

Raw Sample — EC Treatment — pH = 10.2 (NaOH) — 2.5 µm filter — pH = 7 (HCl) → Treated Sample
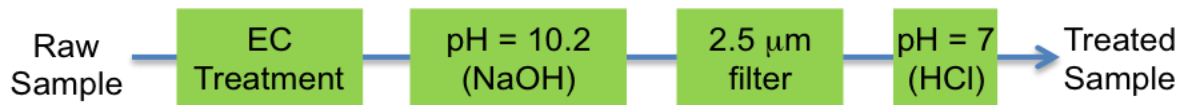
Figure 3. Flow chart for electrocoagulation treatment.

Faraday's Law (equation 1) was used to determine the dosage of aluminum and iron that were delivered during each treatment.

$$m = \left(\frac{It}{F}\right) * \left(\frac{M}{z}\right) \qquad (1)$$

where:

m = mass of the substance liberated at an electrode in grams, I = electrical current in amps, t = time in seconds current is applied, F = Farady's constant, 96485 C mol^{-1}, M = molar mass of the substance, and z = valency number of ions of the substance.

Chemical Coagulation

Four liters of raw produced water was treated with a "floc blend" to induce CF of contaminants. For this research, aluminum chlorohydrate (ACH) provided by Mulit-Chem (Houston, TX) and

poly-aluminum chloride (PACl) provided by Thatcher (Salt Lake City, UT) were used as chemicals in the floc blend, which consisted of a 1:1 ratio of ACH and PAC. Each 4 L sample was treated with 5 parts per thousand (20 mL) of floc blend. The actual coagulant dose per treatment is approximately 449 mg/L as aluminum. Once the floc blend was added, the solution was mixed manually using a stirring stick for approximately 30 seconds. There were 20-30 minutes of flocculation and settling time allowed before the water was decanted off the top. The decanted water was softened with sodium hydroxide (50%, BDH chemicals, Randor, PA) to a pH of 10.2 and filtered through a 2.5μm paper filter (Whatman, Maidstone, Kent, UK). The pH of the filtrate was lowered to 7 using hydrochloric acid (37%, BDH, Randor, PA). A sample of the final product was sent to eAnalytics Laboratory (Loveland, CO) for analysis. Figure 4 provides a schematic for the CC process.
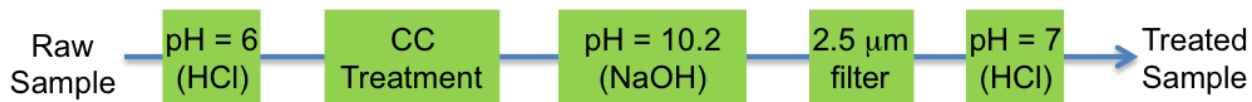
Figure 4. Flow chart for chemical coagulation treatment.

Water Quality Analysis

Analyses for TOC, COD, turbidity, TSS, and pH were conducted at the Colorado State University water laboratory. eAnalytics Laboratory (Loveland, CO) was used for analysis of total metals, anions, carbohydrates, total petroleum hydrocarbons(TPH), volatile organic carbon (VOCs), semi-volatile carbon (SVOCs), bicarbonate and sulfate.

Total metals were measured using EPA method 6010C and Varian Liberty ICP-AES. Anions

were measured using EPA 300.0. Bicarbonate was measured using EPA 310. EPA method

9253-titration was used for chloride and ASTM D 516 with Hach DR 890 for sulfate.

Carbohydrates were measured using an Anthrone colorimetric method, which involved digestion

of polysaccharides followed by measurement with a Hach (Loveland, CO) DRI 2500

Spectrophometer. For TPH analysis, EPA methods 8260/8015C were followed to measure

gasoline range organics (GRO; C6-C10), diesel range organics (DRO; C10-C28), and oil range

organics (ORO; C28-C36).   Volatile organic compounds (VOCs) were determined using EPA

method 8260C and semi-volatile organic compounds (SVOCs) were measured using EPA

method 8270D. The above organics were not initially considered for this study but are part of

another study involving the same water samples. Data regarding the above mentioned organics

are used only as support for hypothesis formulated from treatment results. TDS were calculated

by summing the concentration of total metals and anions, as well as a conversion from

conductivity. To calculate TDS from conductivity, the conductivity factor was multiplied by 670.

pH was measured using a Hach (Loveland, CO) HQ40d-multi pH meter. TSS were measured

using Standard Methods 2540 D. and dried at 105° C. Total organic carbon (TOC) was measured

using Standard Method 5130 B., High-Temperature combustion. Analysis of TOC was

performed with a Shimadzu TOC analyzer, which measured total carbon (TC) and inorganic

carbon (IC). The difference between TC and IC is TOC (TC-IC). COD was measured with a

Hach COD High Range Digestion Kit and colorimeter using EPA 5220 D., Closed Reflux,

Colorimetric Method. For analysis, 0.2 ml of sample was digested in potassium dichromate,

sulfuric acid, and mercury sulfate at 150° C for 2 hours, cooled and measured in a Hach

(Loveland, CO) DRI 2500 Spectrophometer. Turbidity was measured with Hach Laboratory

Turbidimeter (Loveland, CO) model 2100N following Standard Method 2130.

Results/Discussion

Raw Water Quality

Water quality of flowback and produced water changed significantly over time. For example, aluminum concentration in the early flowback was 2.34 ($\sigma = 1.08$) mg/L on days 1 and 2, and then peaked on day 17 at 4.41 mg/L before declining to an average concentration of 1.12 mg/L through day 183 (figure 5). Additionally, iron concentration increased over time, as concentrations on days 1, 27, and 161 are 20.2, 52.4, and 189 mg/L, respectively (table 1). Similarly, calcium, magnesium, barium, strontium, boron, and sodium nearly doubled from days 1 and 2 to day 27 and again at day 70. Chloride and sodium trended upward, unlike sulfate and bicarbonate, which started out much higher on days 1 and 2 then declined significantly on day 27 through 183. The pH of all samples ranged between 7.6 on day 2 and 6.3 on day 153. TOC began at 2,349 mg/L and decreased over time to 843 mg/L at day 183, except for a spike at day 17 to 3,242. This is thought to be due to increased volume of hydrocarbons present. Unlike TOC, turbidity, conductivity, and TDS increased over time. COD and TSS fluctuated through the sampling period and did not provide any trend. The changes in water quality over time suggest a transformation from flowback of fracturing fluids to produced water that is more heavily influenced by the formation. This makes sense as it is thought the formation would produce higher concentrations of iron, calcium, and magnesium with less concentration of aluminum and organics used in the fracturing process. The aluminum concentration is higher early due to the fracturing fluids, which rely on some aluminum to help cross-link the gel. TDS is a reliable measure of how water quality changes over time. Early flowback had an average

27

TDS concentration of 11,171 mg/L and the produced water from days 153, 161, and 183 had an average concentration of 36,500 mg/L. Many other water quality characteristics change over time and can be seen in table 1. Standard deviation was calculated across the population for all constituents, where there was a wide range of water quality values creating a large standard deviation. This is reflective of the constantly changing water quality.
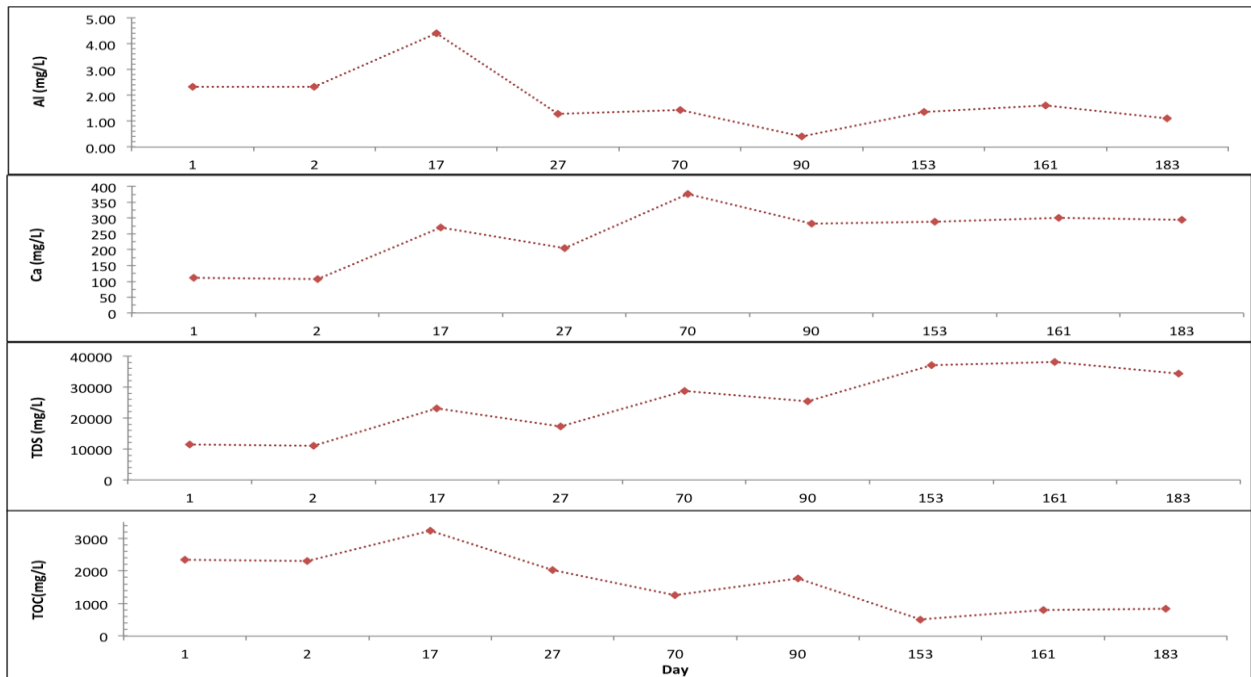

Figure 5. Concentration of aluminum, calcium, TDS, and TOC in raw water samples before treatment.

Table 1. Raw water quality characteristics and standard deviation across the entire population. ** refers to the inability to measure TSS for the 90 day sample as there was not enough sample remaining to perform analysis.

WQ Parameter	Days of Flowback									Std Dev(σ)
	1	2	17	27	70	90	153	161	183	
Iron (mg/L)	20.2	23.7	32.0	52.4	103	154	63.8	189	160	61.2
Magnesium (mg/L)	16.4	16.5	23.8	30.6	52.9	45.7	50.1	54.8	48.8	15.0
Barium (mg/L)	3.08	3.40	6.60	6.57	12.1	23.1	15.0	30.6	30.5	10.4
Strontium (mg/L)	12.7	13.6	21.2	28.0	48.9	44.4	49.5	52.7	51.4	15.9
Boron (mg/L)	12.3	11.6	14.2	17.5	24.7	21.0	23.0	13.3	20.4	4.64
Potassium (mg/L)	77.1	112	36.8	105	135	272	249	1032	163	288
Sodium (mg/L)	3932	3677	8245	5039	9874	9676	13624	13895	12549	3792
Chloride (mg/L)	5815	5730	13260	11100	17428	14340	22209	21613	20647	5977
Sulfate (mg/L)	274	243	10.0	49.9	33.3	9.80	24.3	89.9	0.05	98.1
Bicarbonate (mg/L)	1101	1026	1190	732	728	589	372	898	391	280
pH	7.06	7.63	7.35	7.13	6.83	6.72	6.32	6.59	6.59	0.39
COD (mg/L)	7770	15550	12700	8400	8830	5220	6800	11630	4800	3369
Turbidity (NTU)	2199	2498	3187	875	1252	1115	852	1984	3440	922
TSS (mg/L)	307	505	4861	333	620	**	537	535	280	1465
Conductivity (mS/cm)	9.05	7.54	23.4	38.0	19.0	15.5	37.1	42.5	43.6	13.5

Treatment Efficiency

For the purposes of this research, a successful treatment was defined as having a final turbidity

of ≤30 NTU. This is an arbitrary value and was based partly on current industry practices as

well as CF observations. There is currently no official industry standard for successful treatment

of flowback and produced water. The changing water quality seemed to correlate to treatment

effectiveness for both EC and CC. Early flowback proved to be more difficult to treat with the

methods used in this study. However, as time increased, treatment became more effective for

both treatment processes. Neither EC nor CC was successful on days 1, 2, and 17 (figure 6).

However, at day 27 both treatments were successful in meeting the 30 NTU threshold on all

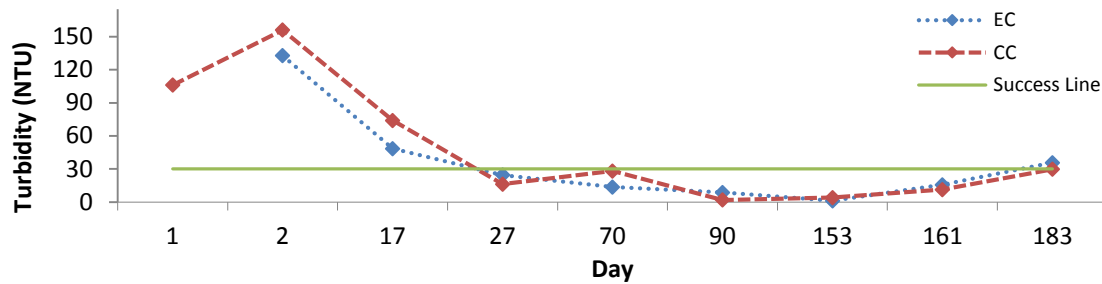samples except for EC on day 183, which had a turbidity of 35 NTU.

Figure 6. Final turbidity for EC and CC treatment. Turbidity for EC on day 1 was not included as it was considered an error. The success line marks the 30 NTU threshold.

Noticeable raw water characteristics that seemed to correlate to treatment effectiveness are TOC and TDS. Interference in treatment could be due to high levels of TOC present from the organics used in creation of fracturing fluid, low ionic strength causing an increased electric double layer (EDL), or a combination of the two.

Effect of Organics

TOC concentration on day 1 and 2 was 2,349 and 2,309 mg/L, followed by an increase on day 17 to 3,242 mg/L (figure 7). The increase at day 17 was likely due to visible hydrocarbons present in the sample as there was inefficient separation at the well pad before analysis was performed. TOC began a downward trend at day 27 with a concentration of 2,027 mg/L where the first successful treatment occurred, and continued to decline to an average of 1,037 mg/L on days 70 to 183. In the early flowback, destabilization of negatively charged particles occurs initially, as observed with pin-floc formation after CC treatment was applied (figure 7). However, the floc would not aggregate, as was observed in the successful treatments, where large floc formed quickly, aggregated, and settled out. In this case, the charge neutralization process could have been reversed due to the negatively charged organic matter adsorbing to the surface of the newly formed metal oxides. This may have caused colloids to gain a net negative charge and

30

restabilize, ultimately remaining suspended in solution (figure 8). This hypothesis is supported by previous research suggesting the hydrophobic organic molecules adsorb to the surface of the recently produced aluminum hydroxide particles, which prevents agglomeration (Carlson 2000, Tipping and Cooke 1982). These suspended colloids are now stable and will prevent any sweep flocculation.
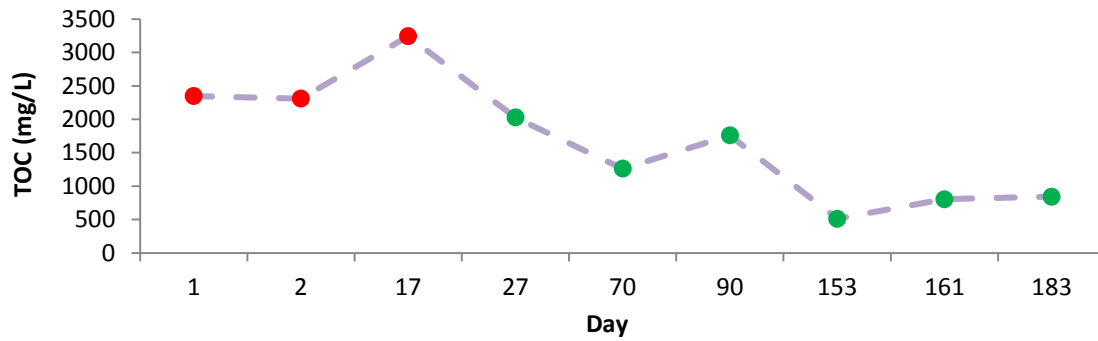

Figure 7. Concentration of TOC in untreated flowback and produced water. Red dots indicate an unsuccessful treatment, while green dots represent a successful treatment.

Charge Neutralization/Colloid Destabilization
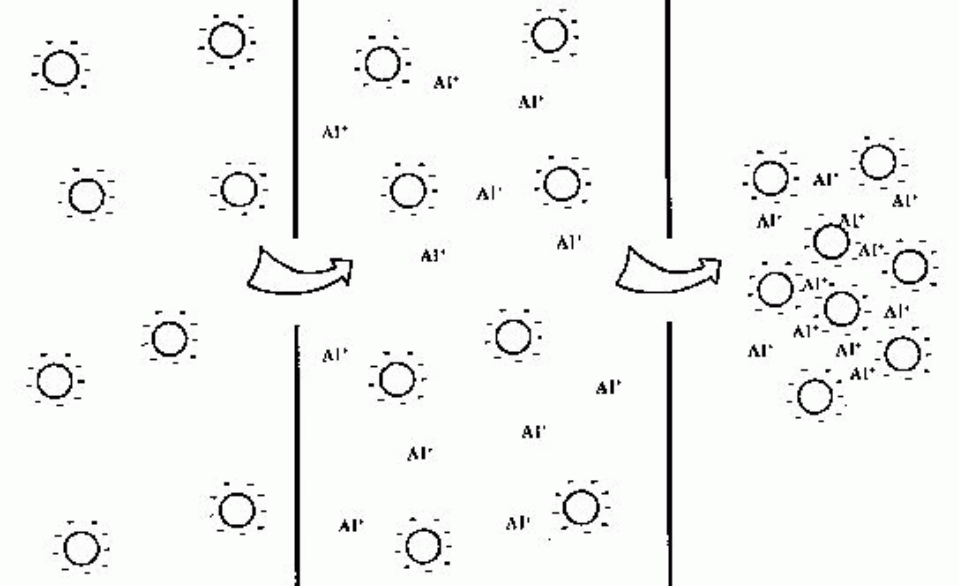
Figure 8. Example of charge neutralization and colloid destabilization. Courtesy of Tramfloc. Inc.

coagulant added

coagulant forms precipitate, trapping impurities

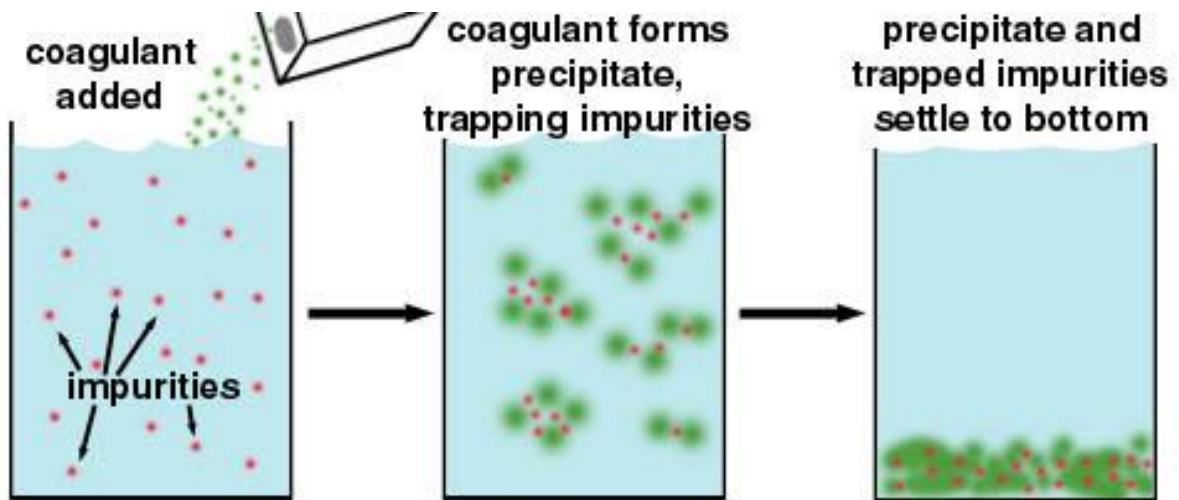precipitate and trapped impurities settle to bottom

impurities

Figure 9. Example of how coagulation occurs. Courtesy of Virginia's Community Colleges.

While the majority of TOC present is thought to be polysaccharides from the fracturing fluid, humic substances from phytoplankton are also present (Wilkinson and Negre 1997). Humic substances can cause steric stabilization when adsorbed to particle surfaces. Steric stabilization is the prevention of particles from moving close enough together for dispersion forces to induce aggregation (Tipping and Cooke 1982), and typically occurs in solutions with high salt content (Dobias 1993). One solution to steric stabilization may be two-stage coagulation. Two-stage coagulation was found to be more effective at removing TOC in drinking water (Carlson 2000), and the same principles may apply here. This would involve an additional coagulation step after initial coagulation, which would allow any restabilized (steric stabilization) to then be destabilized and precipitated.

Analysis of organics was performed in an attempt to better understand the actual makeup of the 2,445 mg/L of TOC present. Results suggested that about half (50.7%) of the early flowback is made up of carbohydrates (polysaccharides), TPH accounts for 1.4%, and VOCs and SVOCs totaled 0.3% (figure 10). The makeup of the remaining 47.6% is currently unknown. More research is being completed to better understand this unknown portion, which could help determine what characteristics of TOC are causing interference in treatment.
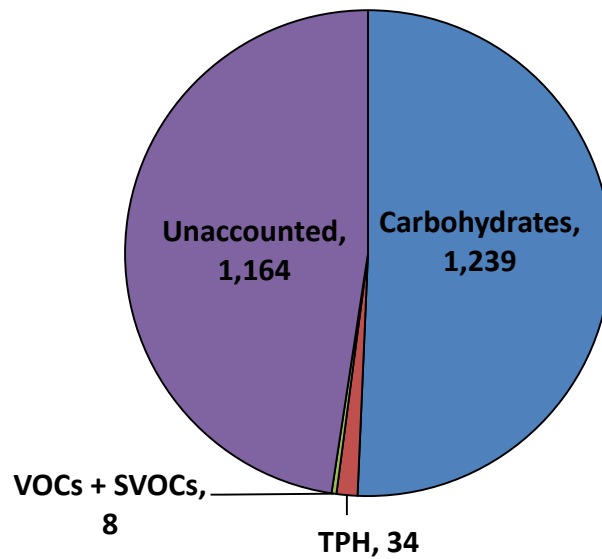
Figure 10. Pie chart showing breakdown of TOC for a 9-day early flowback sample. All values are in mg/L.

EC produced no floc formation in the early flowback samples, which suggests the coagulant dose may be too low to achieve particle destabilization (table 2). However, EC was successful after TOC levels dropped to or below 2,027 mg/L. CC was more effective at removing TOC with an average removal of 51% compared to EC with an average of 19% (Appendix D). Even with 51% removal, there is a considerable amount of TOC remaining after treatment (figure 11). The lowest final TOC concentration was 368 mg/L on day 151 with CC treatment (Appendix C). The average final TOC concentration for CC treatment was 800 mg/L and 1,288 mg/L for EC. Clearly, CC is more effective at removing TOC compared to EC, which is likely due to the increased coagulant dose. A greater coagulant dose allows for greater particle destabilization, which forms a great number of solids and increased sweep flocculation.

Table 2. Coagulant dose for each treatment. Values are based on Farday's Law.

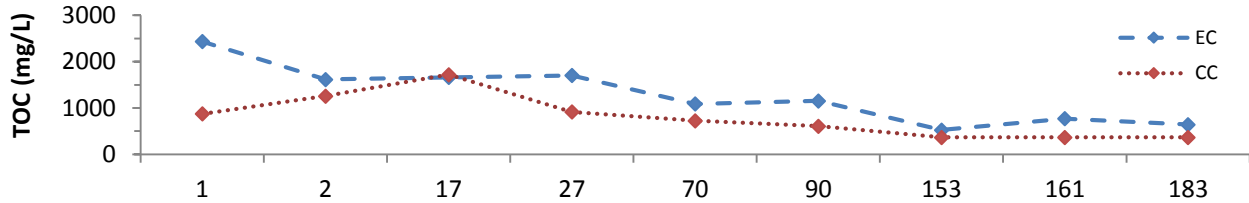| Dose	Day									Average
	1	2	17	27	70	90	153	161	183	
Fe EC (mg/L)	110	116	124	123	128	124	126	127	123	123
Al EC (mg/L)	35.6	37.5	40.1	39.7	41.2	40.1	40.5	41.0	39.7	39.5
Al CC (mg/L)	449	449	449	449	449	449	449	449	449	449

Figure 11. TOC concentration after treatment for both EC and CC.

Effects of TDS

Another possible explanation for the unsuccessful treatment of the early flowback is a low ionic strength. Ionic strength is a measure of the total concentration of ions in a solution. When ionic strength is low, the EDL around particles can extend farther into the solution compared to higher ionic strength solutions (figure 12). An EDL is the electrostatic potential surrounding a charged particle, which consists of a layer of counterions on the surface of a particle and a diffuse layer of ions forming a net charge around the particle (Crittenden et al. 2012). The solution surrounding the surface contains an excess of counterions and a shortage of coions that would equalize the surface charge. The counterions are distributed spatially due to thermal agitation, creating a diffuse ionic cloud. The surface charge and the ionic cloud form a diffusive electrical

35

double layer (Dobias 1993). The EDL can extend up to 300 Å into a solution (Kruyt 1952), which is farther than the 10 Å van der Waals attractive forces can extend (Crittenden et al. 2012). This electrostatic repulsion between the EDL of particles drives them apart while van der Waals forces attempts to bring them together (Holt et al. 2002). This is further described by the Deryaguin and Landau, Verwey and Overbeek (DLVO) theory (Deryaguin and Landau 1941, Verwey and Overbeek1948). In the DLVO theory, van der Waals force is greater, typically at large and very small distances allowing repulsive forces to dominate at intermediate distances from the surface. Increasing concentration of electrolytes, which support flocculation and coagulation, can decrease repulsion (Dobias 1993). If the repulsive force of the EDL is greater than van der Waals force, particles will remain stable, preventing CF. The EDL is inversely proportional to ionic strength, so as ionic strength increases the EDL compresses.
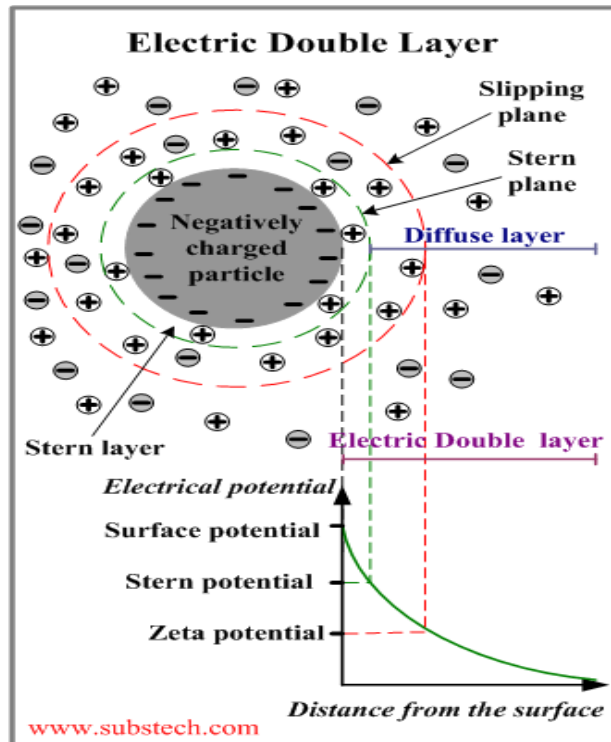

Figure 12. EDL in depth. Courtesy of Substech.

36

In days 1 and 2, the EDL thickness was 6.83 and 6.97 Å, while TDS concentration was 11,376 and 10,966 mg/L, respectively (figure 13). As TDS increased to 23,114 mg/L on day 17, the EDL thickness decreased to 4.78 Å. The increase in TDS is likely due to a greater influence of the formation on the water present through dissolution of salts, in solid form, present downhole (NY DEC SGEIS Information Requests 2010). Together, low ionic strength and TOC can prevent charge neutralization and flocculation, which seems to be the case on day 17. While the EDL decreased on day 17, TOC concentration increased by 40%. Day 27 had a higher average EDL thickness of 5.55 Å compared to day 17, but TOC concentration dropped significantly to 2,027 mg/L from 3,242 mg/L. All remaining samples had successful treatment and an average EDL thickness of 4.02 Å. Results suggest that ionic strength can impact particle aggregation or floc formation and a combination of TOC concentration and ionic strength are responsible for treatment effectiveness of early flowback.
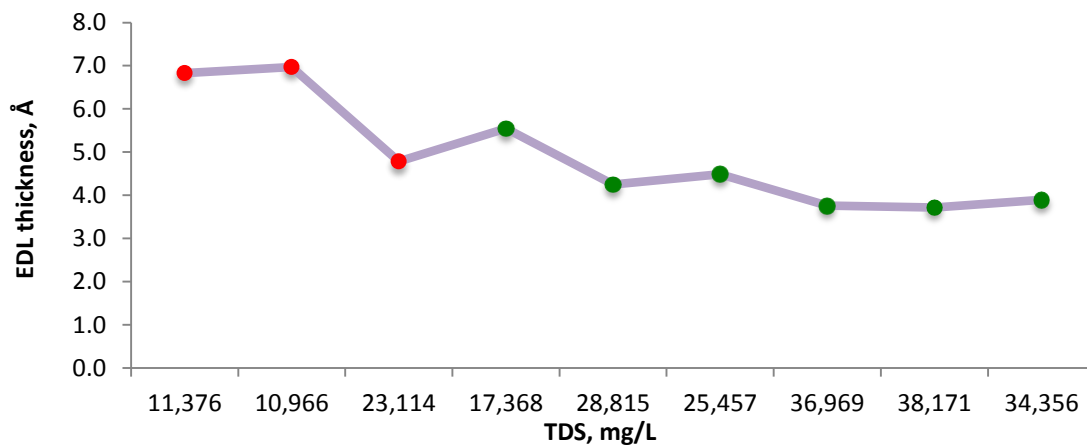

Figure 13. EDL thickness and TDS. Red dots indicate unsuccessful treatment and green dots represent successful treatment.

Inorganic Water Quality Characteristics

The main inorganic characteristics analyzed for treatment efficiency are tri-valent and di-valent cations, aluminum, iron, calcium, magnesium, barium, and strontium (Appendix A-C). Aluminum and iron are metals of concern to production and service companies due to their ability to affect the hydraulic fracturing process. Both aluminum and iron can cause over crosslinking of fracturing fluids, which dehydrates the gel used to carry proppant downhole. This may make aluminum a good surrogate to determine successful treatment for reuse. Service companies like to see aluminum concentration below 6 mg/L in water used to create fracturing fluids. Final concentration of aluminum was significantly over 6 mg/L in days 1, 2, and 17 with concentrations of 42, 33, and 20 mg/L, respectively for EC, and 42, 114, and 22 mg/L, respectively for CC (figure 13). Both treatments produced aluminum values below 6 mg/L at day 27 and beyond (figure 14). These results support the hypothesis that early flowback is more difficult to treat successfully. Iron follows a similar pattern, as concentration on days 1, 2, and 17 are significantly higher than final concentrations from day 27 to day 183. Calcium did not show any trend over time as concentration fluctuated randomly for both treatments. Higher concentrations of aluminum and iron in the early flowback also support the theory that TOC could be restabilizing particles after the coagulant is introduced.
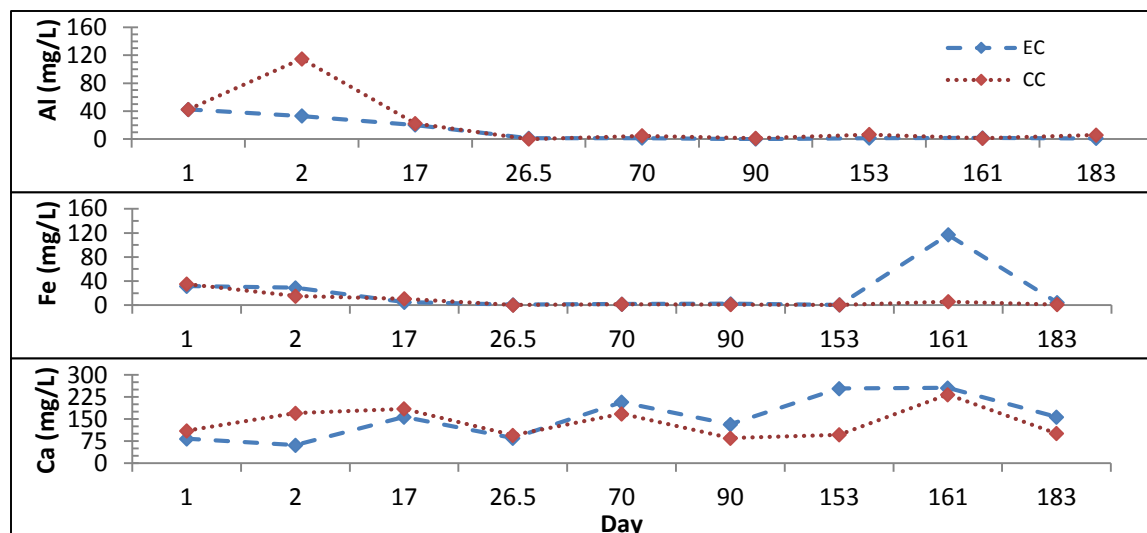
Figure 14. Concentration of aluminum, iron, and calcium after each treatment. Aluminum concentration for CC on day 2 and iron concentration on day 161 could be a result of systematic errors in the filtering process.

CC removes aluminum more effectively than EC on early flowback with an average removal of 87% compared to 18% for EC (Appendix C). However, neither treatment was able to reduce aluminum concentration to below 6 mg/L until day 27. CC averaged a 99% removal of aluminum while EC averaged 70%. In this case, CC was more effective at aluminum removal and EC was considered mostly ineffective. EC removed iron at a much higher rate than CC on the early flowback with an average of 84% compared to 8% for CC. Overall, EC removed 90% of the iron concentration and CC only 69%. EC treatment was more effective at removing calcium in the early flowback with a removal of 37% compared to 0% for CC. However, on days 27-183 CC became more efficient at removing calcium. For all samples, EC removed 37% and CC removed 34% of the calcium concentration. In order to determine which treatment is a better option a final water quality goal must be known and the specific parameters can be targeted. For a full list of removal percentages see Appendix D.

There may be raw water quality characteristics that can serve as indicators of treatment effectiveness. Possible indicators include TOC, TDS, and aluminum. Based on results and observations, TOC levels above 2,000 mg/L may suggest difficult treatment in which greater coagulant dose or some form of dilution could be required. TDS concentration could be an indicator of treatment effectiveness as it directly correlates to ionic strength, which may be causing interference in treatment. Aluminum could potentially serve as an indicator as well since final concentration of aluminum was significantly lower when treatment was successful. More research would need to be completed to obtain a specific concentration or acceptable range of concentrations that suggest whether treatment will be successful.

There are several aspects of this research that could be expanded in future work. First, CC treatment should be expanded to include other coagulants such as alum, ferric chloride, etc. It is possible that other coagulants could improve treatment of early flowback and reduce suspended particles. Also, the organics that make up the concentration of TOC should be explored in greater detail. It is likely that there is a subset of the total TOC concentration that is responsible for interference in treatments. Knowing which organics make up the difference between TOC concentrations of early flowback where treatment was unsuccessful and produced water where treatment was successful, would go a long way in determining how to optimize treatment in the early stages. For EC there are also areas that need to be expanded further to ensure a more complete understanding of the capabilities. One of those areas is the residence or treatment time regarding how long the produced water is treated within the EC cell. It is believed that a longer flow time through the EC cell would result in an increased coagulant dose, which may affect treatment efficiency. Another area that needs expansion is the composition of metal plates in the

EC cell. Using a cell entirely of aluminum, iron, other metal, or combination of other metals may also affect treatment effectiveness. Future work could also include both CC and EC could include an oxidation step prior to treatment for the early flowback as a step to reduce some of the organic matter. Finally, a treatment comparison of gel fracturing fluid versus slick fracturing fluid (no gelling agent) could help shed light on what actually caused interference in the treatment of early flowback.

Statistics

Statistical analysis was performed where available. For each TOC sample, standard deviation (table 3) and machine precision (table 4) was calculated. The standard deviation in table 3 was calculated by the Shimadzu TOC analyzer and was printed with the results. Each TOC sample was injected and measured three separate times and the standard deviation was calculated based on the three analyses.

Table 3. Standard deviation for all TOC analysis.

	Day							
	1	**2**	**27**	**70**	**90**	**153**	**161**	**183**
Standard Deviation-Raw	39.3	44.0	35.0	8.50	22.4	4.70	9.70	4.70
Standard Deviation-EC	12.8	23.8	33.5	12.3	33.6	7.60	9.60	0.00
Standard Deviation-CC	0.10	12.0	10.0	9.75	33.6	1.90	7.80	1.60

The Precision of the Shimadzu TOC analyzer was calculated to determine the accuracy of the machine for a single user and for the machine overall. The precision of the analyzer is impacted due to particulate matter and can range between5%-10% (Standard Methods 2012). Precision has been determined in a laboratory setting to be roughly 2 mg/L. Based on the equation for a single user,

$$S_o = 0.0027x + 0.29 \qquad (2)$$

and the equation for overall total precision,

$$S_t = 0.0044x + 1.49 \qquad (3)$$

where S_o = single-operator precision,

S_t = overall precision, and

x = TOC concentration, mg/L.

Since the precision of the machine is a function of the TOC concentration, it makes sense that as

the TOC values decrease the precision increases. Based on these precision values, on average

the TOC values should have a range of 6.3%.

Table 4. Precision of Shimadzu TOC Analyzer using equations from standard methods precision section.

| | | Day | | | | | | | |
		1	2	27	70	90	153	161	183
RAW	So	63.7	62.6	55.0	34.4	47.8	14.1	22.1	23.1
	St	105	103	90.7	57.1	79.0	24.0	37.0	38.6
EC	So	66.0	43.9	46.2	29.6	31.4	14.4	21.1	17.7
	St	109	72.6	76.4	49.3	52.2	24.5	35.4	29.8
CHEM	So	23.9	34.2	25.0	19.9	16.7	10.1	10.2	10.2
	St	40.0	56.7	41.8	33.4	28.3	17.5	17.6	17.6

Conclusion

There is a time component to water quality changes over the life of a well. Early flowback

typically has higher concentrations of aluminum, solids and TOC as it is influenced mostly by

the makeup of the fracturing fluid. At some point around the 30-day mark, a transition in water

quality begins. The water seems to be affected by the formation and has a greater influence on

water quality than does the fracturing fluid. TDS increases as the age of the well increases.

Treatment seems to correlate to the changing water quality, as treatment is less effective on the early flowback compared to produced water. TOC and low ionic strength may be the reason early flowback is more difficult to treat. Also, chemical coagulation is more effective than EC at removing TOC and aluminum in early flowback water compared to EC, while EC is more effective at removing iron. However, both treatments are effective after day 27. Aluminum removal could possibly serve as an indicator of treatment success as it correlates to observations during treatment, where it was visibly restabilized during unsuccessful treatments. 99% turbidity removal can be expected for either treatment after 27 days of flowback. More research should be completed in order to determine what raw water characteristics, if any, could serve as a surrogate to indicate treatment effectiveness. Also, a better understanding of the components that make up the TOC concentration in the samples could be instrumental in determining why treatment is more difficult for early flowback, and could uncover what is causing interference in treatment.

Chapter 4

Conclusion and Future Work

There is a time component to water quality changes over the life of a well. Early flowback typically has higher concentration of aluminum, solids, and TOC as it is influenced mostly by the makeup of the fracturing fluid. At some point around the 30-day mark, a transition in water quality begins. The formation or connate water seems to have a greater influence on water quality than does the fracturing fluid. Treatment seems to correlate to the changing water quality, as treatment is less effective on the early flowback compared to produced water. TOC and low ionic strength may be the reason early flowback is more difficult to treat. Also, chemical coagulation is more effective than EC at removing TOC and aluminum in early flowback water compared to EC, while EC is more effective at removing iron. However, both treatments are effective after day 27. Aluminum removal could possibly serve as an indicator of treatment success as it correlates to observations during treatment, where it was visibly restabilized during unsuccessful treatments. 99% turbidity removal can be expected for either treatment after 27 days of flowback. More research should be completed in order to determine what raw water characteristics, if any, could serve as a surrogate to indicate treatment effectiveness. Also, a better understanding of the components that make up the TOC concentration in the samples could be instrumental in determining why treatment is more difficult for early flowback, and could uncover what is causing interference in treatment.

There are several aspects of this research that could be expanded in future work. First, CC treatment should be expanded to include other coagulants such as alum, ferric chloride, etc. It is possible that other coagulants could improve treatment of early flowback and reduce suspended particles. Also, the organics that make up the concentration of TOC should be explored in greater detail. It is likely that there is a subset of the total TOC concentration that is responsible for interference in treatments. Knowing which organics make up the difference between TOC concentrations of early flowback where treatment was unsuccessful and produced water where treatment was successful, would go a long way in determining how to optimize treatment in the early stages.

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Appendices

Appendix A

Produced Water Well Name and Sample Date

Water Quality Parameter	16-69 (1 day)			16-69 (2 day)			16-69 (27 day)			16-69 (60 day)		
	Raw	EC	Chemical	Raw	EC	Chemical	Raw	EC	Chemical	Raw	EC	Chemical
Aluminum (mg/L)	1.27	42.7	NA	1.19	32.5	133	1.29	1.26	0.061	1.5	1.49	1.22
Iron (mg/L)	11	28.1	NA	15.1	22.8	11.5	52.4	0.85	0.32	102	2.81	1.36
Sodium (mg/L)	4822	5031	NA	4347	4158	4684	5039	3516	4984	10651	12853	14565
Calcium (mg/L)	94.7	55.7	NA	104	23	51	206	85.4	95.0	397	292	272
Magnesium (mg/L)	15	17	NA	17.7	15.7	7.62	30.6	24.8	11.5	53.3	46.9	41.3
Barium (mg/L)	2.88	1.84	NA	3.85	2.48	1.42	6.57	1.74	2.7	11.8	4.83	11.3
Strontium (mg/L)	12.4	6.87	NA	14.5	6.36	6.16	28.0	13.9	17.2	48.8	36.3	46.6
Potassium (mg/L)	87.5	92	NA	164	162	163	105	104	97.4	132	111	132
Chloride (mg/L)	6840	7140	NA	6720	6310	7320	11100	10920	11100	16815	21095	18680
Sulphate (mg/L)	159	199	NA	173	86.5	49.9	49.9	56.2	19.4	34.2	22.8	1.66
Boron (mg/L)	12.5	13.1	NA	12.9	10.3	9.21	17.5	16.2	13.3	23.5	28	24.5
Bicarbonate (mg/L)	1116	1008	NA	1020	1104	540	732	506	228	842	476	104
Calculated TDS (Metals)	13174	13635	NA	12593	11934	12977	17368	15246	16569	29112	34970	33880
pH	7.73	7.13	NA	7.61	8.22	7.32	7.53	7.78	6.45	6.75	7.55	6.95
COD (mg/L)	874	846	NA	1100	656	383	840	477	283	1120	541	306
TOC (mg/L)	1985	1844	NA	1958	1469	1062	1537	1362	750	1286	1102	697
UV254	4.35	7.14	NA	4.16	3.97	3.46	7.976	1.995	0.965	9.1	1.67	1.39
TSS (mg/L)	160	23.3	NA	150	1023	893	333	117	83.3	775	0	5
Turbidity (NTU)	679	1446	NA	526	236	262	875	24.5	16.2	3944	22.4	39.4
Conductivity (mS/cm)	19.7	20.4	NA	20.4	19.3	NA	30.3	29.4	30.8	38	38.2	39.4
Calculated TDS (COND)	13790	14280	NA	14280	13510	NA	21210	20580	21560	26600	26740	27580
TDS DIFFERENCE	616	645	NA	1687	1576	NA	3842	5334	4991	-2512	-8230	-6300

Appendix B

Water Quality Parameter	Produced Water Well Name and Sample Date								
	16-68 (1 day)			16-68 (2 day)			16-68 (70 day)		
	Raw	EC	Chemical	Raw	EC	Chemical	Raw	EC	Chemical
Aluminum (mg/L)	3.4	42.3	42.3	3.48	33.5	96.5	1.37	1.21	8.02
Iron (mg/L)	29.4	35.2	35.2	32.3	35.1	19.1	104	1.18	2.18
Sodium (mg/L)	3042	3257	3257	3007	3110	4460	9097	7962	9437
Calcium (mg/L)	126	110	110	110	99.2	119	354	123	63.6
Magnesium (mg/L)	17.8	17.9	17.9	15.2	14.9	17.3	52.4	31	4.74
Barium (mg/L)	3.27	3.34	3.34	2.94	2.92	2.72	12.3	5.57	1.91
Strontium (mg/L)	13	11.6	11.6	12.6	10.8	13.3	48.9	21.4	12.8
Potassium (mg/L)	66.6	64.8	64.8	59.6	57.5	71.5	137	114	116
Chloride (mg/L)	4790	5100	6290	4740	4810	6840	18040	16810	18620
Sulphate (mg/L)	389	316	137	313	158	97.2	32.4	20.2	22.8
Boron (mg/L)	12	9.56	7.88	10.3	7.95	8.21	25.9	22.1	18.8
Bicarbonate (mg/L)	1086	1082	480	1032	988	597	613	367	365
Calculated TDS (Metals)	9578	10050	10457	9338	9328	12342	28518	25479	28673
pH	6.59	7.97	6.72	6.59	7.97	6.72	6.9	8.04	7.25
COD (mg/L)	680	500	360	2010	642	561	645	461	427
TOC (mg/L)	2040	1974	1159	1829	679.2	428.6	1217	1056	781
UV254	1360	1500	1080	4.39	4.43	2.87	9.412	1.408	1.668
TSS (mg/L)	453	1170	293	860	960	1087	465	15	180
Turbidity (NTU)	48.4	65.8	106	27.3	29.5	50	2096	4.92	16.9
Conductivity (mS/cm)	16.5	17.7	15.8	9.76	9.76	18.5	37.5	34.4	39
Calculated TDS (COND)	11550	12390	11060	6832	6832	12950	26250	24080	27300
TDS DIFFERENCE	1972	2340	603	-2506	-2496	608	-2268	-1399	-1373

Appendix C

Produced Water Well Name and Sample Date

Water Quality Parameter	24-62 (90 days)			06-63 (153 days)			14-66 (161 days)			14-63 (183 days)		
	Raw	EC	Chemical	Raw	EC	Chemical	Raw	EC	Chemical	Raw	EC	Chemical
Aluminum (mg/L)	0.403	0.1	1.13	1.37	1.48	6.39	1.6	1.6	1.3	1.1	1.07	5.71
Iron (mg/L)	154	2.52	1.1	63.8	0.68	0.67	189	117	5.85	160	4.60	1.13
Sodium (mg/L)	9676	9500	9717	13624	12604	14382	13895	12002	12614	12349	9762	7964
Calcium (mg/L)	282	132	85.4	288	254	96.5	301	256	233	294	157	101
Magnesium (mg/L)	45.7	38.1	20.3	50.1	46.2	18.7	54.8	48.4	36.6	48.8	30.3	12
Barium (mg/L)	23.1	5.12	7.81	15	13.6	9.43	30.6	17.2	21.5	30.5	10.6	9.25
Strontium (mg/L)	44.4	26.3	23.3	49.5	43.2	27.2	52.7	43.5	40.6	51.4	29.7	20.2
Potassium (mg/L)	272	264	281	249	236	215	1032	889	740	163	124	85.1
Chloride (mg/L)	14340	14868	14768	22209	18918	29164	21613	18489	17762	20647	15180	12042
Sulphate (mg/L)	9.8	23.2	4.6	24.3	6.12	7.29	89.9	139	0.50	0.05	0.05	0.05
Boron (mg/L)	21	14.5	8.65	23	13.2	9.55	13.3	9.74	6.38	20.4	12.2	7.26
Bicarbonate (mg/L)	589	418	207	372	518	253	898	588	264	391	324	84
Calculated TDS (Metals)	25457	25292	25125	36969	32654	44190	38174	32603	31727	34559	25636	20333
pH	6.72	7.34	7.02	6.32	7.41	7.13	6.59	6.25	6.97	6.59	7.97	6.72
COD (mg/L)	522	447	287	680	500	360	1163	290	191	0	Over	0
TOC (mg/L)	2007	1152	609.3	512	523	364	806	770	367	843	643	367
UV254	NA	NA	NA	NA	NA	NA	0.27	0.273	0.249	NA	NA	NA
TSS (mg/L)	NA	NA	NA	280	70	175	537	147	160	535	66	1015
Turbidity (NTU)	1115	8.64	1.92	852	1.18	3.97	1984	15.6	1125	3440	35.6	29.7
Conductivity (mS/cm)	15.45	11.14	11.88	37.1	23.8	NA	42.5	42.3	38.2	43.6	8.26	NA
Calculated TDS (COND)	10351.5	7463.8	7959.6	24857	15946	NA	28475	28341	25594	29212	5534.2	NA
TDS DIFFERENCE	15106	17828	17166	12112	16708	NA	9699	4262	6133	5147	20102	NA

Appendix D

Raw

Day	TOC (mg/L)	STD DEV	Turbidity (NTU)	TSS (mg/L)	COD (mg/L)
1	2349	3.65	582	307	7770
2	2308	2.95	400	505	15550
17	3242	NA	3187	4861	12700
27	2027	3.6	875	333	8400
70	1263	0.65	3020	620	8830
90	1761	2.24	1115	NA	5220
153	512	0.47	852	537	6800
161	806	0.97	1984	535	11630
183	843	0.47	3440	280	4800

Electrocoagulation

Day	TOC (mg/L)	STD DEV	TOC Removal (%)	Turbidity (NTU)	Turbidity Removal (%)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)
1	2434	2.2	-3.6	756	-30.0	597	-94.7	6730	13.4
2	1617	1.45	30.0	133	66.8	992	-96.3	6490	58.3
17	1661	NA	48.8	48.5	98.5	2736	43.7	5480	56.9
27	1702	1.8	16.0	24.5	97.2	117	64.9	4770	43.2
70	1087	0.95	14.0	13.7	99.5	7.50	98.8	5010	43.3
90	1152	3.36	34.6	8.64	99.2	NA	NA	144	97.2
153	523	0.76	-2.1	1.18	99.9	960	-78.8	265	96.1
161	770	0.96	4.5	15.6	99.2	15	97.2	751	93.5
183	643	0	23.7	35.6	99.0	1170	-318	456	90.5

Chemical Coagulatoin

Day	TOC (mg/L)	STD DEV	TOC Removal (%)	Turbidity (NTU)	Turbidity Removal (%)	TSS (mg/L)	TSS Removal (%)	COD (mg/L)	COD Removal (%)
1	874	0.1	62.8	106	81.8	293	4.40	3600	53.7
2	1256	0.85	45.6	156	61.0	990	-96.0	4720	69.6
17	1721	NA	46.9	74	97.7	237	95.1	4137	67.4
27	916	0.6	54.8	16.2	98.1	83.3	75.0	2830	66.3
70	725	0.9	42.6	28.2	99.1	92.5	85.1	3665	58.5
90	609	3.36	65.4	1.92	99.8	NA	NA	450	91.4
153	364	0.19	28.9	3.97	99.5	160	70.2	471	93.1
161	367	0.78	54.5	11.3	99.4	1015	-89.7	836	92.8
183	367	0.16	56.5	29.7	99.1	175	37.5	604	87.4

Figure 15. Picture of 70 day water samples with raw produced water on the left (1), a raw filtered sample (2) and a final CC on the right (10)

Appendix F
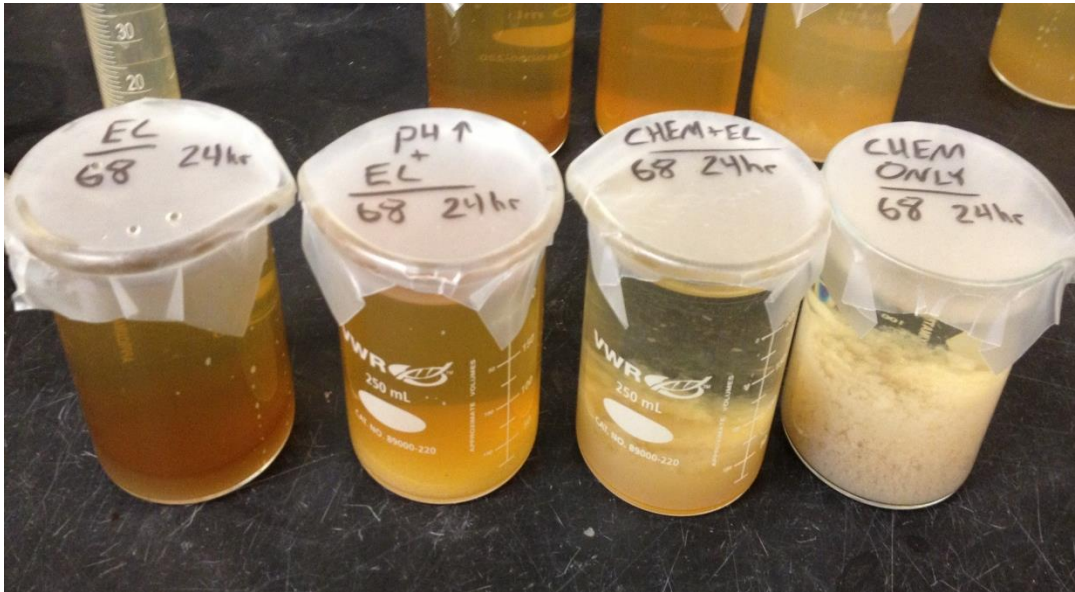
Figure 16. Picture of a 1 hour sample after each treatment. EC treatment is on the far left and CC is on the far right.The middle two samples were not considered in the thesis.
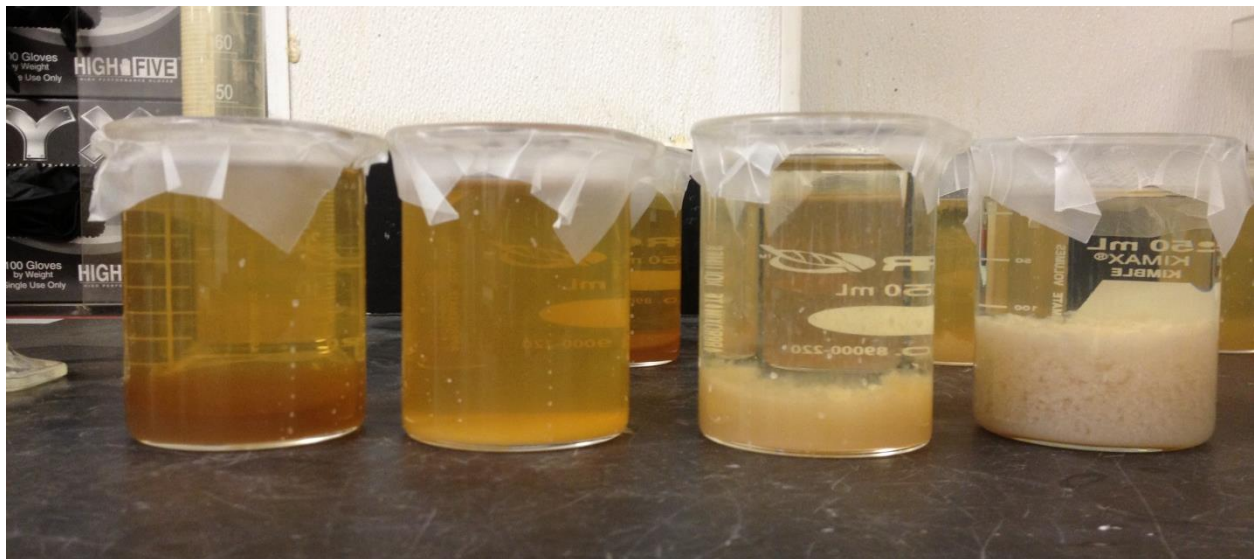
Figure 17. A side view of 1 day flowback after treatment. EC treatment is on the far left and CC is on the far right. The middle two samples were not considered for this Thesis.

Figure 18. Example of the EC cell and plates before use. In this case, all plates are aluminum. However, in the experiment, a combination of aluminum and iron plates were used.

Figure 19. Picture of the actual EC cell and plates used for this Thesis. The plates on the right are aluminum and the plates on the left are iron.

Appendix H
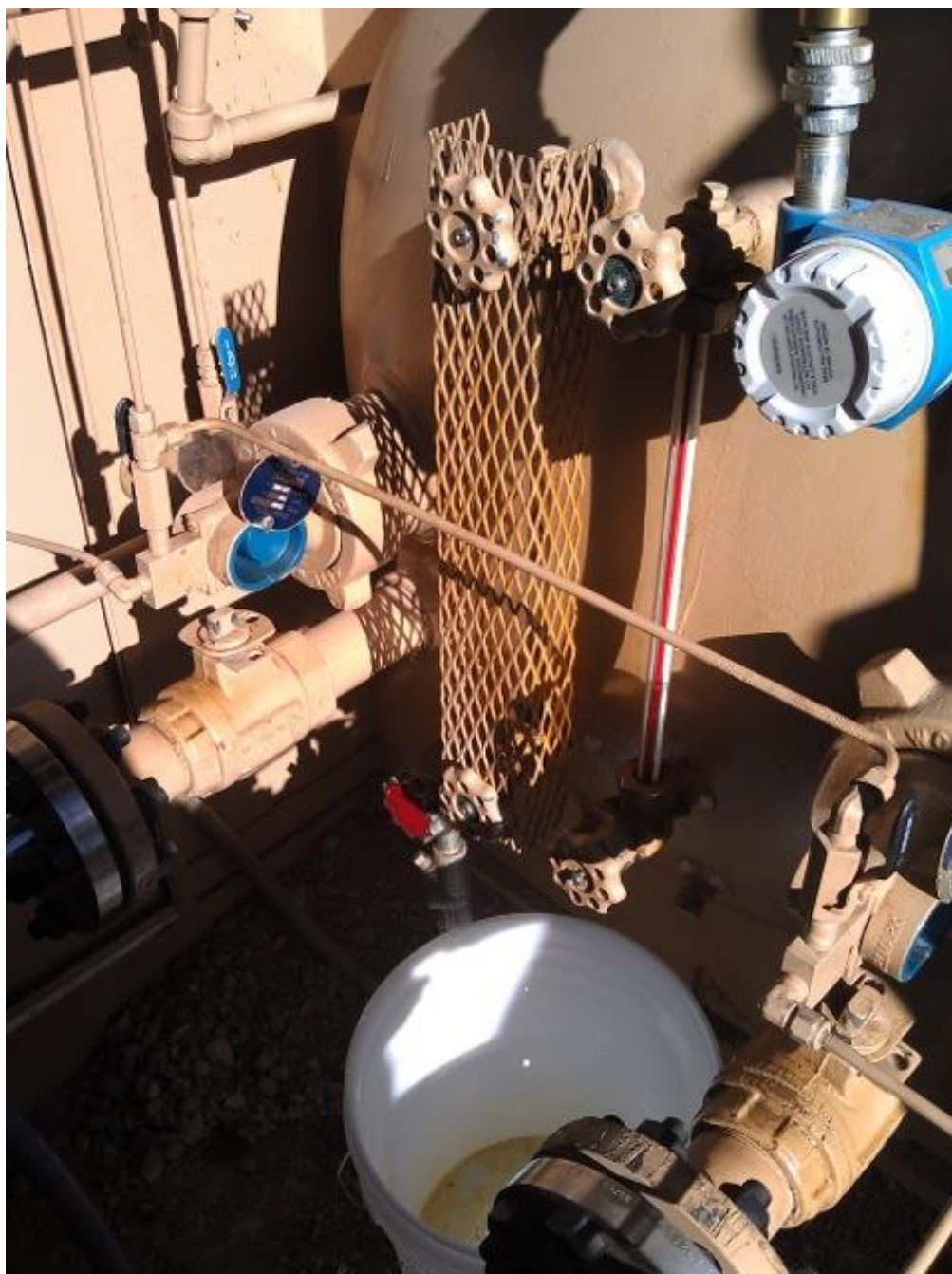
Figure 20. Oil/Water separator where water samples were taken. Water valve is on the left.

Appendix I
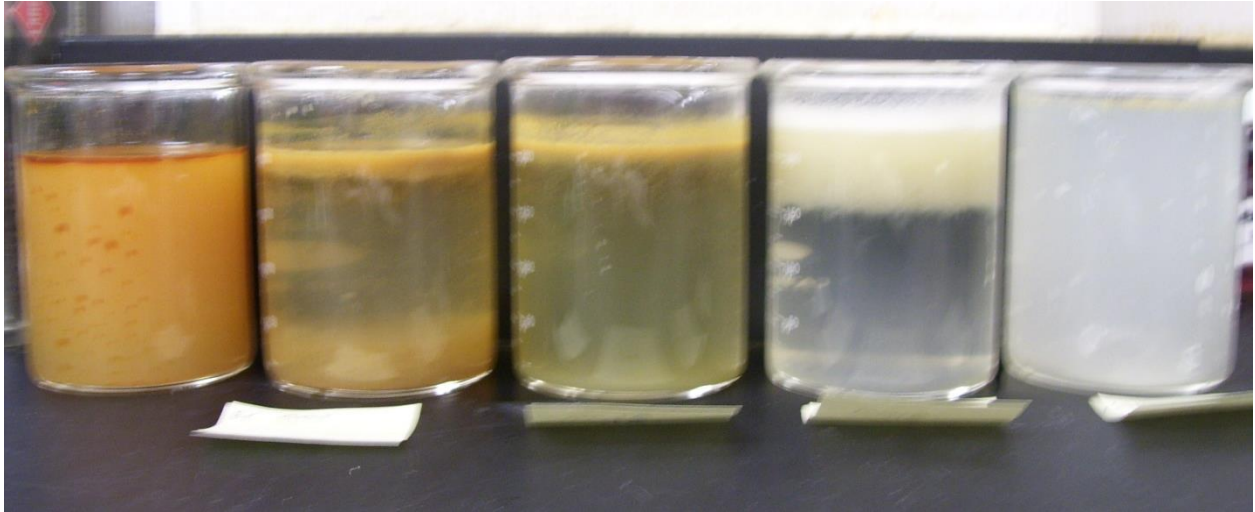
Figure 21. Day 90 samples immediately after treatment and before final softening process.

Figure22. Day 90 raw and post treatment samples. The raw sample is on the far left with EC directly to the right. The CC sample is on the far right. The two samples in the middle were not used for analysis in the Thesis.

Figure 232. Day 151 samples immediately after treatment and before the final softening step. The raw sample is on the far left with EC directly to the right. CC is on the far right. The additional two samples were not used for analysis.
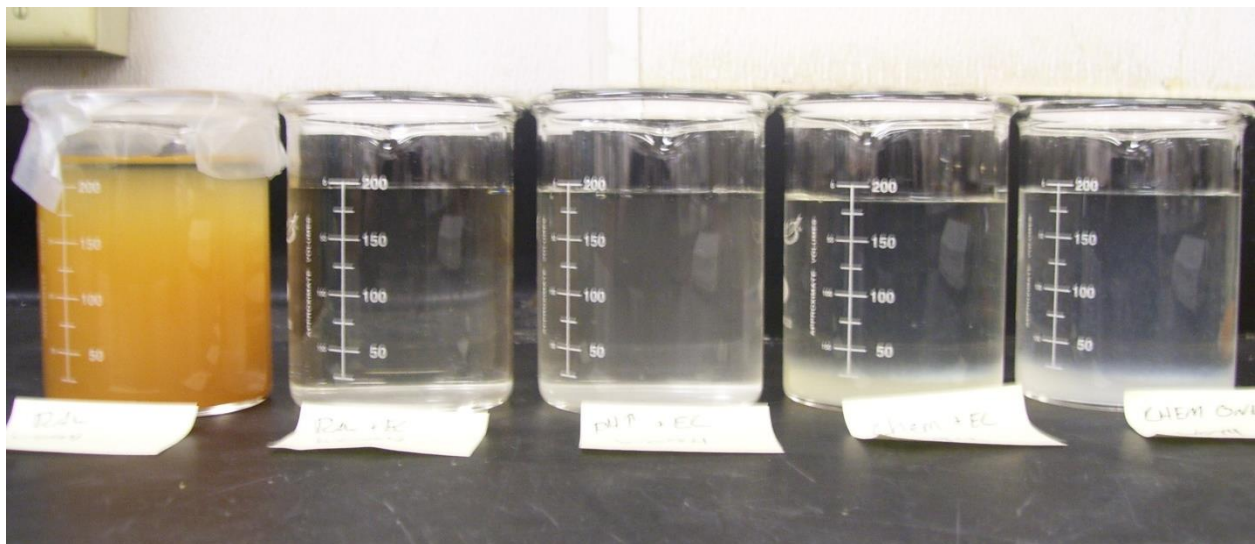
Figure 24. Final day 151 samples after treatment and softening compared to the raw sample. The raw sample is on the far right with the EC sample directly to the right. The CC sample is on the far right. The additional samples were not used for analysis.

Appendix K

HALLIBURTON
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JTT – Flowback Treatment Evaluation Notes

Sample Well Name_____ Sample Collection Date_____ Sample #_____

Post EC Treatment				
Chemical	pH initial (before addition)	pH adjusted	mL used	Sample Size
50% NaOH				
22˚ Bé HCl				

Post pH to 9.5 + EC Treatment				
Chemical	pH initial (before addition)	pH adjusted	mL used	Sample Size
50% NaOH				
22˚ Bé HCl				

Post Chemical Pretreatment + EC Treatment				
Chemical	pH initial (before addition)	pH adjusted	mL used	Sample Size
50% NaOH				
22˚ Bé HCl				

Post Chemical Treatment				
Chemical	pH initial (before addition)	pH adjusted	mL used	Sample Size
50% NaOH				
22˚ Bé HCl				

Sample Checklist:

☐ Raw – Unfiltered*
☐ Raw – Filtered
☐ Post EC only (Pre-pH swing)
☐ Post EC – Final
☐ pH to 9.5 pre-treatment
☐ pH to 9.5 + EC only (Pre-pH swing)
☐ pH to 9.5 + EC – Final
☐ Chemical treatment only (Pre-pH swing)
☐ Chemical treatment + EC (Pre-pH swing)
☐ Chemical treatment + EC – Final
☐ Chemical treatment – Final
*All samples are filtered under vacuum prior to collection unless marked with asterisk.

Tech's name _____ Treatment Date_____

Figure 25. Example of data sheet used to record data during testing.

Appendix L

Figure 26. Example of mobile field EC unit deployed by Halliburton. Picture is courtesy of Halliburton.

Figure 27. Inside view of the mobile EC trailer. Courtesy of Halliburton.

Appendix M

Figure 28. Water Tectonics EC brochure page 1.

Appendix N

Figure 29. Water Tectonics EC technology brochure page 2.

Appendix O

Figure 30. Top view of bench scale EC unit used for this thesis.

Figure 31. Close up of the top of the EC cell. Electrodes, purge adaptor, and influent water valve attached.

Figure 32. Underside view of EC bench unit. Effluent of EC cell on left, raw water sample in the white bucket on the left, treated water sample flows to the right bucket.