

THESIS

CHARACTERIZATION AND COMPARISON OF FLOWBACK/PRODUCED WATER OF
FRESH WATER TO RECYCLED WATER STIMULATED WELLS AND THE
SUBSEQUENT EVALUATION OF THE INFLUENCE OF INORGANIC IONS ON
FRACTURING FLUID VISCOSITY

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ABSTRACT

CHARACTERIZATION AND COMPARISON OF FLOWBACK/PRODUCED WATER OF FRESH WATER TO RECYCLED WATER STIMULATED WELLS AND THE SUBSEQUENT EVALUATION OF THE INFLUENCE OF INORGANIC IONS ON FRACTURING FLUID VISCOSITY

As the Oil and Gas Industry begins to recycle flowback and produced waters, new challenges arise in using recycled water as a base fluid (fluid for hydrating gel) for future hydraulic fracturing operations. By understanding water qualities at all steps of the water life cycle in recycled operations, it is possible to improve treatment effectiveness and efficiency as well as make informed decisions on future fracturing fluid designs.

This thesis contains two studies. The first study looks to determine water qualities, their differences and similarities, among multiple wells in the same Basin. These wells were fractured using a variety of techniques such as varied recycled to fresh water blends and fluid designs. The collection and water quality analysis of roughly 150 samples from seven wells on two different sites showed that there is little difference in water quality between wells fractured with recycled water (recycled wells) and wells fractured with fresh water (fresh wells). The study does not find noticeable differences in dissolved ionic concentrations between fresh and recycled wells. However, recycled wells located on the first site show emulsified oils in flowback. This can be observed with increased total organic carbon loadings of 12,170mg/l for day three flowback of one recycled well in comparison to 3,268mg/L for day three flowback of a fresh well. Treatment

effectiveness was also correlated with emulsified oil concentrations and as their concentrations decreased, so did the coagulant dose required for optimum treatment. Spatial variation was observed between the two sites. Although the concentration of varying inorganics between the two locations was observable, temporal trends were consistent between wells.

The second study provides data that can be used in decision making for future fracturing fluid design and development. By observing the effect individual ions and ion combinations have on fracturing fluid stability, operational limits were determined for two fracturing fluids employed by operators in the DJ Basin. Theoretical mechanisms of action were determined for the factors that influence fracturing fluid stability. Specific cations compete for crosslink sites on the gel polymer through shielding or by competitively complexing with active sites that the added crosslinker would normally complex with, resulting in a less stable fluid. Hydrogen bonds can sometimes form bonds at active sites and make a weak crosslink. At lower concentrations calcium and magnesium can replace these weaker crosslinks with stronger bonds, creating a more stable fluid.

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1. INTRODUCTION

America has experienced a boom in the natural gas industry with the revolutionizing methods of directional drilling and hydraulic fracturing. More and more wells are being drilled in an increased number of states. Increased drilling and production has brought an economic boost to America's energy sector, but with it, are amplified strains on freshwater supplies. An immense input of water is required to complete the fracturing process (a frac). In addition to this, a large percentage of fracturing water returns to the surface as flowback and formation water returns to the surface as produced water. Both waters are compromised in quality when compared to fresh water and are typically disposed of, or require treatment before reuse.

Proper management of these waters can allow for reuse and thereby lower industry's water demand. Through reuse, flowback/produced waters can be used as a resource as opposed to being treated as waste water. In 2012, over 100 federal research studies looked into effective management, reuse, and treatment of produced waters over the previous 10 years (GAO 2012). But in order to use these waters, their qualities and characteristics need to be understood. It is important to determine flowback/produced water quality variations over time and how they differ from well to well, which can affect treatment decisions. It is also imperative to understand how these varying water qualities impact new well executions, as recycling efforts increase throughout the country.

The work presented in this thesis is the result of collaboration between Colorado State University Center for Energy and Water Sustainability, Noble Energy Inc., and Halliburton. Extensive sampling trips to active oil and gas sites as well as fracturing fluid testing in Halliburton's water quality lab were required to complete this thesis. Analytical lab work took

place for every sample collected, resulting in extensive water quality characterization both temporally and spatially. In addition to Chapter 2's literature review, this body of work is comprised of two separate papers. Chapter 3 contains a summary report that describes the observed water quality variability between two Noble Energy well sites in the DJ Basin. This paper was sent to Noble Energy Inc. Chapter 4 contains a summary report that was created from collaboration between Colorado State University, Noble Energy Inc. and Halliburton. Chapter 4 describes the impacts of flowback/produced waters' inorganic ions on the stability of hydraulic fracturing fluid. Chapter 5 provides a summary of conclusions from the two papers, Chapter 6 provides a discussion of future work, and Chapter 7 includes all references. Additional information pertaining to Chapters 2 and 3 can be found in the Appendices.

2. LITERATURE REVIEW

2.1 Petroleum Industry and its Activities

Because of the revolutionary process of directional drilling, compounded with the resurgence of hydraulic fracturing, America's petroleum industry has shifted its focus towards unconventional resources such as shale formations, drastically increasing its crude and natural gas production in the last ten years. Previously uneconomical petroleum resources are now viable as long extensive formations and can be accessed with a few multi-well pads instead of an extended network of vertical wells (API 2009).

In 2005, the total rate of crude production in the United States was 4,489 thousand barrels per day. Now, in 2015, the rate has increased to 8,610 thousand barrels per day (EIA 2015a). The same is true for natural gas, rising to a monthly average of 4,669 billion cubic feet per month of combined wet and dry gas in 2015 (EIA 2015b). It is estimated that by 2017, the United States will transition into becoming a net exporter of natural gas, partially due to the fact that natural gas consumption is forecasted to grow at a modest rate of 0.3% per year through 2040 (EIA 2015c). The United States Geological Survey estimated in 2013 that the total mean undiscovered gas resources in the U.S. is 1,149 trillion cubic feet of gas as shown in Figure 2.1 (USGS 2013).

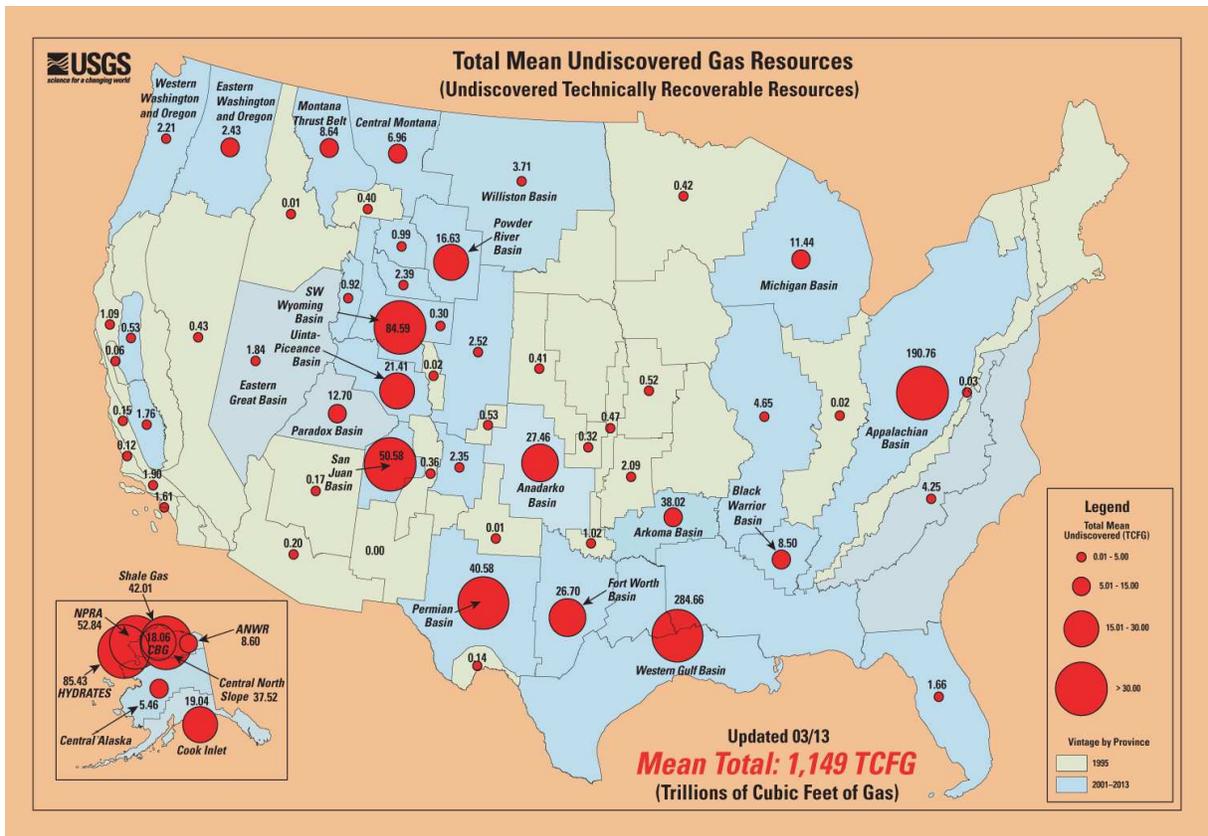


Figure 2.1: Total Mean Undiscovered Gas Resources in the U.S.

Currently, United States market demands for petroleum resources have stayed strong with a consumption of total petroleum liquids almost doubling that of domestic production. On average, 50% of American households use natural gas to heat their homes. This can be much higher in states with developed natural gas infrastructures such as Colorado with 75% of homes heated by natural gas (EIA 2009).

Extensive shale plays exist across the entire U.S. can be seen in Figure 2.2 (EIA 2015d). The figure shows the location of major plays in the lower 48 states. Oil and Gas Shale plays are considered unconventional. The unconventional category contains coal bed methane, shale gas, and tight gas sands. This study takes place in the Denver-Julesburg (DJ) Basin in Colorado. The Niobrara play shown in the figure is one of the most common shale plays operators obtain

resources from in the DJ Basin. The EIA has tracked the number of producing gas wells by state through 2013 and Colorado had 32,468 active gas wells out of a U.S. total of 484,994. (EIA 2015e)

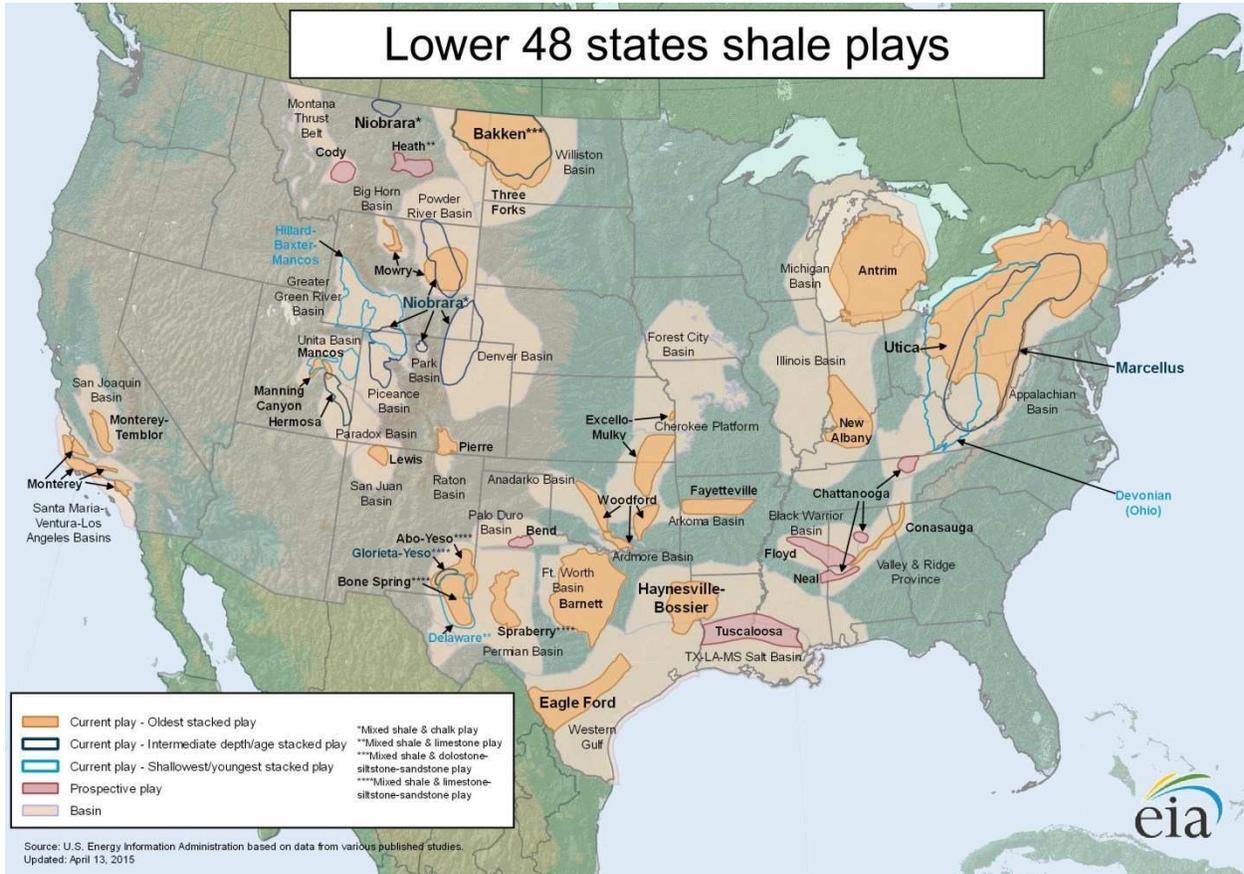


Figure 2.2: Shale Oil and Gas Plays in the Lower 48 States

2.1.1. Well Execution

Drilling a horizontal or vertical well consists of many iterative steps. In specific intervals during the drilling process, the drilling pipe is removed and steel pipe casings are put into place. These casings are not directly against the walls of the drilled hole, but instead leave a small annular space. Once the casing is put into place, a plug is put at the bottom of the hole, with a

cement mixture on top, followed by another plug. On top of that plug, a displacement fluid is used to push the recently poured cement throughout all of the desired annular space (API 2009).

For horizontal drilling, the well can be drilled out at a two to three degree angle over thousands of feet until the well runs horizontally through the producing formation. Once the well has been drilled, cased, and cemented, stages of casing where the formation exists can be perforated to allow for formational stimulation techniques such as hydraulic fracturing (API 2009). The number of stages per well varies depending on the total length of the well, design decisions made by the operator, and formational variables. The total number of stages can reach over forty (Goodwin, et al. 2013).

2.1.2. Fracturing Fluid and its Development

Before hydraulic fracturing, the permeability of a shale formation can be as low as 10^{-12} Darcy (Huang, et al. 2012). The hydraulic fracturing process allows oil and gas recovery in reservoirs with low permeability, such as shale or tight sands, and as a result is the most used stimulation technique in unconventional resources (Haghshena, Nasr-El-Din 2014). By increasing permeability, hydrocarbons previously trapped in the formation can now flow to the surface.

When hydraulic fracturing occurs, a fracturing fluid is pumped down the well, and the pressure exerted by the fluid opens, or widens, the naturally occurring fractures in the formation. By opening up the fractures, the flow of petroleum resources from the fracture increases. This can be shown in the cubic law for laminar flow of fluids through open fractures. The law shows that the petroleum resources flowrate is equal to the cube of the fracture aperture, or width of the aperture. In other terms, the ultimate goal of hydraulic fracturing is to open the aperture enough to achieve an economical flow of resources from the formation (Witherspoon, et al. 1980).

The first stage of hydraulic fracturing is called the Pad. This stage involves pumping large quantities of water into the well to propagate fractures into the formation. In the second stage, before pumping is stopped, a proppant such as sand is added to the fluid. This proppant keeps the fractures open even after pumping has ended. This results in a maintained level of acceptable formational permeability. Once the proppant has been delivered to the formation, a flushing stage occurs whereby any excess proppant is removed from the well.

With some wells reaching over 8,000ft in horizontal length, the proppant needs a way to be successfully delivered to the formation. A fracturing fluid is required to transport the proppant from the surface to the formation. Two common types of fluids exist, slickwater and gel fluids. Slickwater fluids are designed around water as the means for achieving formational fractures. Because of this, they usually contain minimal fluid additives such as biocide, scale inhibitor, and friction reducers (Rimassa, et al. 2009).

This study primarily focuses on gel based fracturing fluid design (gel fracs), due to their prevalent use by both Noble Inc. and Halliburton in the D.J. Basin. Gel fracs utilize guar, guar derivatives, cellulose, or synthetically derived polymers to increase the apparent viscosity of the fracturing fluid. This increased viscosity allows for more effective transportation of the proppant to the formation as well as increased fracture propagation (Modeland, et al. 2012). In gel fracs, the fluids ability to carry proppant is through its viscosity, which is dependent on the strength and amount of crosslink of the added gel (De Kruijf, et al. 1993). While other additives may assist in maintaining fluid stability, gel and crosslinkers are inherent to the chemical backbone that gives fracturing fluid its viscosity.

Lei and Clark (2004) describe the basic molecular interactions of fracturing fluid gels. Gels dissolve in a solvent, where polymer chains unravel and form bonds with one another, increasing

the fluids viscosity as the concentration of gel increases. At lower concentrations, interaction between polymer chains actually decreases viscosity, but once gel concentrations reach a critical point, crosslinking effectiveness allows for a considerable rise in fluid viscosity. The gels ability to hydrate can be pH dependent but varies between gels. Between polymer chains, crosslinks exist as covalent. Due to the nature of covalent bonding, crosslinks will constantly be made and broken as the gel is exerted to shears in pumping and in the formation.

The addition of crosslinkers, such as a zirconium chelate, can increase fluid viscosity as well as decrease the amount of gel used, thereby reducing fluid costs. By lowering gel concentrations, formational damage risks can also be lessened, as lower gel concentrations are easier to clean out of formations in the flushing stage (Lei, Clark 2004). Crosslinker behavior varies depending on the specific additive, but in general allows for a three dimensional structure to form by bonding across multiple polymers chains. Metallic crosslinkers such as zirconate or titanate form irreversible bonds with polymers.

An optimized gel fluid will maintain a viscosity until it has completed fracture propagation and proppant delivery. After this point, the gel should begin to break down, which lowers viscosity, allowing it be removed during the flushing stage. In addition to formational temperatures, pressures, and shears exerted on the fluid, breaker additives such as oxidizers, enzymes, or acids assist in the breakdown of gel fracs (Brannon, Ault 1991). If the fluid breaks down too soon, the proppant settling rate may increase and the proppant may not reach its desired location. If the fluid breaks down too late, formational damage may occur and production could be negatively impacted.

Other additives assist in the goal of a successful frac but may not contribute to the viscosity of the fracturing fluid. Buffers control the pH of fracturing fluid, resulting in water chemistry

that allows for effective dissolving and interaction of polymer chains. Friction reducers lower pumping costs by reducing the friction of the fracturing fluid. Biocides kill bacteria that may be present, reducing the chance of hydrogen sulfide creation, a safety concern. Other bacteria may foul the well or possibly the greater formation, negatively impacting production. Clay stabilizers prevent clay swelling, which can reduce formation damage and improve production (Gidley, et al. 1989).

2.2 The role of water in unconventional plays

Throughout new well execution, water is used. Drilling requires fluid to remove drill cuttings, lubricate the drill, and provide mud to stabilize the well. A study by the Joint Institute for Strategic Energy Analysis (Logan, et al. 2012) shows that the average amount of water used per frac per well is 3.3million gallons. Another report by Goodwin et al. (2013) found that in the DJ Basin, a linear correlation between water quantity and the number of stages resulting in .15million gallons of water per stage of a well. An extended horizontal well with forty five stages results in almost 7million gallons of water used for a single well. Water management costs have been estimated to account for 15% of the wells overall cost (Slutz, et al. 2012). 97% of Colorado Oil and Gas wells in 2011 were drilled in high or extremely high water stressed regions as defined by Ceres (Freyman 2014).As more and more wells are executed, industry's proper management of water resources becomes more crucial.

2.2.1 Return Water and its Characteristics

Depending on the source formation and how hydraulic fracturing was conducted by the operator, a large amount of water used for well stimulation can return to the surface. This initial water is classified as flowback. Although definitions vary, flowback is most readily defined by a time period in the field. For many field operations, flowback is all water that returns to the

surface until the well begins producing enough oil to be turned onto production lines. Typically this flowback is separated using temporary separators once the percent oil in the flowback is high enough. Once switched over to production, comingled oil, gas, and water are separated from each other using permanent separators either on site or nearby the producing well. This water is defined as produced water.

When defined by water quality, flowback more closely represents the water that was used in the frac. When compared to produced water, flowback water quality variation between wells lends itself more to the frac design than geologic factors. It typically has a lower total dissolved solids (TDS) concentration than the water that naturally occurs in the formation. Flowback water also contains the broken down gels and other additives used in the frac. Over time, the flowback water begins to more represent the water quality of the formational water and becomes produced water.

Produced water has higher TDS than flowback, and more hydrocarbons present in the water. Water quality variability can be seen within a formation between wells. A study by Li (2013) showed TDS variability in produced water across the northern Wattenberg field between wells. Monovalent and divalent anions and cations are present in produced water, with sodium and chloride accounting for the majority of TDS. Heavy metals, such as copper, lead, and mercury, can be present in produced water, but are found at much lower concentrations than many other ions. The amount of oil that is present in produced water is dependent on the type of oil, the pH, temperature, and salinity of the produced water, as well as the effectiveness of an operator's separation processes once the water returns to the surface (Fakhru'l-Razi, et al. 2009). A study by Alley et al. (2011) performed a meta-analysis, citing four sources to determine a typical range of produced water qualities from varying plays in the United States.

Table 2.1: Aggregated Natural Gas Produced Water Quality Values (as Cited by Alley et al. 2011-all values in mg/l unless otherwise stated)

Constituents	Min	Max	Constituents	Min	Max
pH	3.1	7	Cl	1400	190000
Conductivity(μ S/cm)	4200	586000	Cr	0.002	0.231
Alkalinity	0	285	Cu	0.02	5
Sulfate	1	47	Fe	No Data	1100
Oil and Grease	2.3	60	K	0.458	669.9
Al	0.4	83	Li	0.038	64
As	0.002	11	Mg	0.9	4300
B	No Data	58	Mn	0.45	6.5
Ba	0.091	17	Na	520	120000
Br	0.038	349	Ni	0.002	0.303
Ca	No Data	51300	Sr	0.084	917
Cd	0.02	1.21	Zn	0.02	5

Studies have determined water qualities for various wells across shale plays and found varying water characteristics. Most of these studies are not comprehensive in that they lack temporal resolution on the changing water qualities over the lifetime of the well. Sick (2014) has shown that water quality changes over the course of the first month for a newly executed well. Other studies compare produced water qualities between multiple states or plays, but do not look into variations from well to well within a field.

The quantity of produced water that returns to the surface depends on a number of factors as cited by Fakhru'l-Razi et al. (2009). These variables all show that produced water quantity is inherent to production volumes of oil and gas. Reservoir rocks are saturated with both petroleum hydrocarbons and saline water that occupy its pore space. This saline water is comingled with fossil fuels, and contains solids and dissolved solids from the reservoir rock (Reynolds, Kiker 2003).

2.2.2 Recycling/Reusing Produced Water and Flowback

Flowback and produced waters can be managed in a number of ways. The first method is to view the water as a waste and dispose of it. Evaporation pools are no longer legal practice in many areas, so injection is one of the only disposal methods, resulting in 90% of all produced water being injected in 2012 (GAO 2012). Waste waters that are associated with oil and gas production are disposed of in a class II disposal wells. These wells are regulated under the EPA's Safe drinking water act. The average cost of disposal fees can range from USD 0.75 to USD 1.00 per barrel (Lebas, et al. 2013). However, total disposal costs on a per barrel basis can vary, due to differences in trucking distances. When nearby disposal wells are closed due to safety concerns such as increases in seismic activity, trucking costs can increase as distances required to haul water become further (Passut 2015).

Due to the impaired quality of flowback and produced water, direct surface discharge of raw water is not an option. The EPA regulates surface discharge under the Safe Drinking Water Act by setting limits on contaminants that may come into contact with drinking water. Surface discharge requires advanced treatments such as reverse osmosis (RO) for salt removal but is typically avoided if possible due to the high costs associated with advanced treatments (Pearce 2008).

Another option in lieu of disposal is reusing flowback and produced water for new fracs. This does present new operational challenges, as the flowback from wells fractured with recycled water have poorer water quality than those of fresh wells. The more impaired water quality can present issues for further recycling as additional fracturing fluid residues can interfere with treatment and fracturing fluid stability (Rimassa, et al. 2009). However, not only does recycling

water show an operator's commitment to the community and environment, it also presents the possibility of increasing well production.

2.2.3 Treatment of Flowback and Produced Water.

Typical treatment for flowback and produced water includes both chemical addition and physical separation. These treatment methods look to remove residual oil in the produced water, residual fracturing fluid in the flowback, colloidal particles, hardness to reduce scaling risks, bacteria present in the water through disinfection, and potentially ions that may need lower concentrations to align with reuse goals.

Treatment options for both flowback and produced water have been studied, and performed in the field by a number of researchers and companies (Bryant, Haggstrom 2012). Oil removal can be a physical process of simply utilizing oil and water density differences or can be adsorbed to substances such as activated carbon or organoclay (Doyle, Brown 2000). Flowback also presents new challenges in water treatment as residual gels and surfactants can interfere with treatment efficacy. Surfactant addition provides a number of purposes, with one example being increased recovery by reducing oil-water interfacial tension (Hiraski 2008). Residual surfactants can stabilize emulsified oils by reducing oil-water interfacial tension, creating removal difficulties (Deng, et al. 2005). These difficulties are typically faced in coagulation, flocculation, and settling, which looks do destabilize hydrophilic colloidal particles, allowing for settling and removal.

Some studies have shown the benefits of adding a preoxidant to the chemical precipitation process to assist in the removal of fracturing fluid (Sick 2014). Other coagulation processes such as electrocoagulation have shown successful organic removal which could help in treating residual fracturing fluids (Ma, Wang 2006). Inorganic metals such as iron or aluminum can be

used for coagulation and have shown to be effective in removing solids in produced water (Zhou, et al. 2000). In addition to settling, microfiltration can provide mechanical separation of solids, ultrafiltration can remove macro molecules, and RO can deliver effective ion removal (Madaeni 1999).

Treatment costs vary between technologies and design. Fakhru’l-Razi, et al. (2011) aggregated produced water technology treatment costs. Table 2.2 shows some cost results from the study. It is important to note that not all treatment methods observed by the study are legally applicable methods in many states. Another study (Arthur, et al. 2005) shows costs as high as \$2.7/bbl for the RO treatment process alone, not including any pretreatment.

Table 2.2: Treatment Methods and their Associated Cost per Barrel of Treated Water.

Method	Estimated Cost (\$/bbl)	Method	Estimated Cost (\$/bbl)
Surface Discharge	0.01–0.08	Freeze-thaw evaporation	2.65–5.00
Secondary Recovery	0.05–1.25	Evaporation pits + flowlines	1.00–1.75
Shallow Reinjection	0.10–1.33	Constructed wetland	0.001–2.00
Evaporation pits	0.01–0.80	Electrodialysis	0.02–0.64
Commercial water hauling	0.01–5.50	Induced air flotation for de-oiling	0.05
Disposal Wells	0.05–2.65	Anoxic/aerobic granular activated carbon	0.083

Many times, waters are not treated to discharge standards. An option which is becoming more and more used in industry is to recycle the water for fracs on new wells. Flowback and produced water may still need to be treated and diluted with fresh water for new fracs if its salt concentrations are still too high (GAO 2012). However, many current operators use anecdotal evidence as to acceptable treatment levels and dilution rates. Other operators are adverse to added risks in new well execution and treat their water to fresh water quality. These reasons,

along with operational constraints such as transportation, treatment capacities, and storage, result in only a portion of the flowback and produced water being recycled. Figure 2.3 from Goodwin (2012) shows the lifecycle of water for typical oil and gas operations.

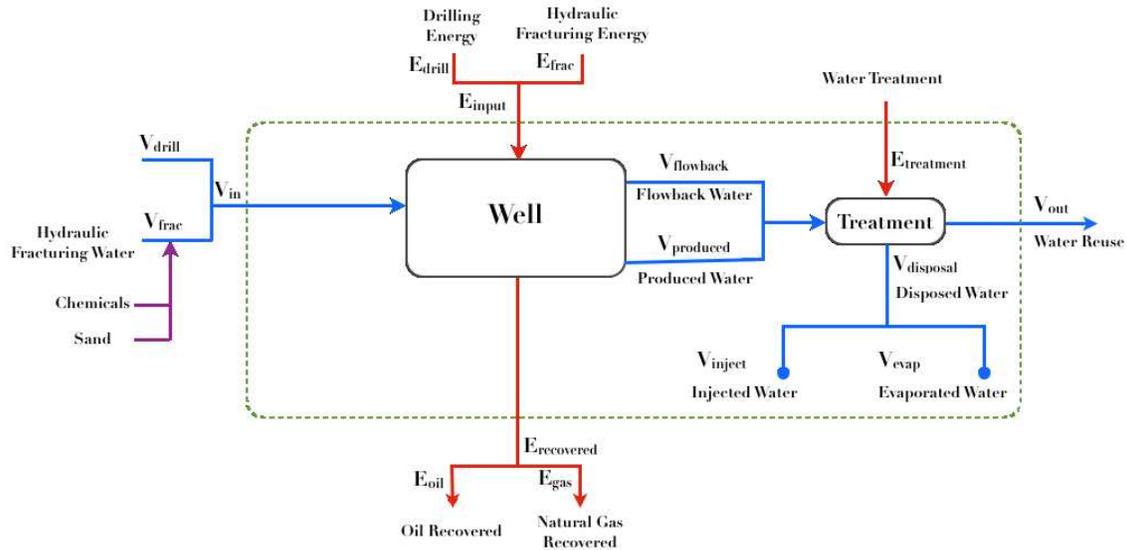


Figure 2.3: Lifecycle of water with respect to well execution and production

In the figure, once water is treated, it can either be disposed of or reused for more fracs. Although the figure only depicts water volumes, water quality is very important not only for reuse, but in designing efficient and effective treatment. By understanding the water quality characteristics of raw flowback and produced water, treatment can be optimized. For example, Sick (2014) determined organic loading from flowback interfered with proper coagulation, flocculation, and settling. Produced water and flowback come from many sources and can display a wide spectrum of water quality, even in the same basin or well site. If these variations occur and are not understood, then treatment may be oversized or unable to process highly compromised waters. Because of this, the water quality of recycled water needs to be fully monitored and understood. When reusing water for fracs, knowing water quality is important in

frac design of the well. It can help determine starting requirements for recycled water, such as maximum TDS concentrations, and can assist in designing efficient dilution ratios with fresh water.

2.3 Fracturing Fluid Limitations

When fracturing fluid is developed, the input water quality is taken into account. Numerous studies have shown the impact of using recycled water on the stability of fracturing fluid. (Fontenelle, et al. 2013, Lebas, et al. 2013, Li, et al. 2015, Haghshenas, et al. 2014). The stability of fracturing fluid is determined by taking rheological properties, typically measured using a viscometer. Fluid can be prepared in a lab by hydrating the polymer for 10 to 20 minutes, then adding fluid additives (Li, et al. 2015). Crosslinker is added last in order to allow additives to enter into the base fluid, otherwise, the 3D structure of crosslinker complexes would not allow for proper additive mixing. Once the fluid has been created its properties can be measured. Hydraulic fracturing research typically employs the use of Fann 50-type viscometers that use high pressure and high temperature when shearing the fluid. These viscometers best model conditions fracturing fluid would be exposed to in the formation. At the temperature and pressure that best represents formation, steadily increasing shear is exerted on the fluid by an immersed bob.

A study by Khaled and Abdelbaki (2012) showed the rheological effects of the addition of salts to the base fluid. Khaled and Abdelbaki used carboxymethyl cellulose (CMC) for their gel additive and added both monovalent and divalent salts to fresh water to observe their impacts on the apparent viscosity of hydrated CMCs when a shear stress was present. The same study proposes a mechanism of action for monovalent salts reducing disentanglement of CMCs, thereby lowering the apparent viscosity of the fluid. Another study (Yang, et al. 2007) showed

the positive impact aluminum had on gel viscosities. Although these studies show the impacts using specific salts, they do not provide a full spectrum of inorganic ions present in flowback and produced water, nor do they provide any sort of effective operational limits for these salts.

Other research has taken a systematic approach of developing new fracturing fluids for high TDS base waters. Rimassa et al. (2009) describes a process to optimize new fracturing fluid that is less sensitive to water quality and more compatible with flowback and produced water. This optimization involves varying additive selections as well as varying the concentrations of gel and crosslinker. As mentioned in the second report of this thesis, some fracturing fluids can be used with TDS values over 270,000mg/l (Acharya, et al. 2011). However, using high TDS fracturing fluid increases risks of scaling.

2.4 Research Objectives

The summary of objectives for the research contained in this thesis is as follows:

Objective 1. Determine the spatial and temporal variability of flowback and produced water qualities between wells in the same field. A selection of oil and gas wells owned by the same operator (Noble Energy Inc.) will allow for a 1 to 1 comparison of sampled water qualities of similarly executed wells. Samples will be collected over the course of several months to observe temporal changes. Water quality analysis will be performed on all samples to determine concentrations of various analytes. By observing similarities and differences between both locations, conclusions can be drawn on how varied the water quality characteristics are and their potential impact on recycling treatment efforts in the region. This objective can aid operators in determining important water quality parameters and at which resolution monitoring should take place.

Objective 2. **Understand how fracturing fluid and water reuse influences flowback and produced water quality.** Selecting wells on the same location that are fractured with different recycled dilutions can result in a better understanding of how flowback/produced water qualities may or may not differ for fresh fracs vs. recycled fracs. As in objective 1, samples will be collected over the course of several months to observe temporal changes. Water quality analysis will be performed on all samples to determine concentrations of various analytes. This objective also looks to compare and contrast observed water qualities between wells that have been fractured with different fracturing fluid compositions (varied additives and gels).

Objective 3. **Understand how the presence inorganic ions in flowback, produced, and treated water used for new hydraulic fracturing operations influences the stability of fracturing fluid.** For Objective 3, individual inorganic ions and ranges of their concentration in a base fluid will be selected using determined values from both Objectives 1 and 2 as well as information gathered in the literature review. Attempts to find isolated ionic effects on stability are determined by adding individual salts to the base fluid. Coactive effects are determined by creating combinations of ions in the base fluid. Operational limits will be determined for fluid stability using two fracturing fluid designs that are employed by operators in the DJ Basin. Through understanding the limits of these fracturing fluids, operators can modify treatment to meet specific and definable water quality goals, resulting in more efficient treatment design and lower costs.

The first study in this thesis looks to achieve Objectives 1 and 2, while the second study completes Objective 3. Both work towards understanding water qualities for flowback/produced water and also recycled water and how these qualities influence field operations. Currently, there

is a lack of research that examines spatial variability of water qualities within a single field. The knowledge of water qualities between shale plays or basins is well understood and can aid an operator in moving to another field, but this knowledge is at too large of a scale and does not impact daily operations.

Other research that relates to Objective 3 does not provide comprehensive ionic analysis for all ions that would be present in typical recycled water. This study also differs in the fact that ionic impacts are studied using a wide array of individual ions at varying concentrations. By doing so, a more complete understanding of mechanisms of action can be gleaned.

By utilizing conclusions from all objectives, treatment can be tailored to a specific influent raw water quality and for a specific end use quality. Operators can also determine if the starting raw water quality is too compromised (too high of an inorganic ion loading) to use in future fracs. This can allow an operator to selectively treat water and dispose of water that would prove problematic in treatment or fracturing fluid development. Informed water management decisions results in lower treatment costs for the operator. The lowering of costs per barrel of treated water makes recycling efforts more economical and in turn can increase recycling rates for waters which were once viewed as a waste.

3. NOBLE ENERGY INC. FLOWBACK AND PRODUCED WATER QUALITY COMPARISON STUDY

3.1 Introduction

The following report was submitted to Noble Energy Inc. (Noble) to share the findings from a two well pad study proposed by CSU and approved by Noble. The report has been modified to better match the formatting of the thesis. Proprietary information such as trade names of fracturing fluids, well locations, and formational data provided by Noble have been omitted. Other than these changes, the study appears as whole

Noble Energy, Inc. (Noble) currently stimulates wells with either fresh water or a blend of recycled and fresh water. Recycled water is most commonly blended at 7:1 and 5:1 ratios (fresh: recycled). Colorado State University (CSU) Center for Energy and Water Sustainability partnered with Noble to characterize and compare the flowback and produced water from several fresh and recycled wells from two sites, Crow Creek State and Chandler State. This report presents an account of all results from the two studies. The first section will summarize findings from the Crow Creek State study and the second section will summarize findings from the Chandler State study.

For the Crow Creek wells, 73 samples were collected from four separate wells (two primary wells, two secondary wells). Four time periods from Crow Creek were chosen for treatability experiments and all samples from both sites were analyzed for various water quality characteristics. The Chandler State study consists of three wells (all primary wells) and a total of 66 samples.

3.2 Goals

The primary goal of the study was to determine what differences, if any, there are in the water qualities between freshwater stimulated and recycled water stimulated wells. This study looked at the temporal water quality trends that included metals, solids, and organics. In addition to this, a treatability study took place to assess the secondary goal of understanding differences in treatability between wells. Other secondary goals include assessing differences in flowback water quality between 7:1 blends vs. 5:1 blends of recycled base water for stimulation.

Varying water qualities between fresh and recycled wells may be indicators to how the fracturing fluids behave with the formation down hole. Varying water qualities might also affect future water reuse in terms of treatment. Findings in this report can be used to help in the determination of appropriate blending ratios and preliminary treatment options available for flowback and produced water.

3.3 Description of Wells

All of the wells sampled from are located on the Crow Creek State (Crow Creek) East Pad and the Chandler State (Chandler) pad. Table 3.1 contains a description of the seven wells that CSU sampled from for the duration of the study.

Table 1.1: Well Description

Designation	Well Name	API #	True Vertical Depth (ft)	Base Water Volume (gal)	FracFluid Package	Key Date 1	Key Date 2	Key Date 3
Primary Recycled (7:1)	Crow Creek State AC36-73HN	05-123-37423-00-00	6685	2,371,163	Fluid-A	2/7/2014	2/20/2014	3/15/2014
Primary Fresh	Crow Creek State AC36-76-1HN	05-123-37420-00-00	6742	1,335,328	Fluid-A	2/6/2014	2/20/2014	3/15/2014
Secondary Fresh	Crow Creek State AC36-73-1HN	05-123-37422-00-00	6747	2,403,381	Fluid-A	2/6/2014	2/21/2014	3/18/2014
Secondary Recycled (5:1)	Crow Creek State AD31-79HN	05-123-37426-00-00	6674	2,301,153	Fluid-A	N/A	2/21/2014	3/18/2014
Primary Fresh	Chandler State D15-72-1HN	05-123-38322-00	6834	3,390,198	Fluid-B	No Preflow	7/11/2014	7/15/2014
Primary Recycled (7:1)	Chandler State D15-73-1HN	05-123-38323-00	6759	3,677,478	Fluid-B	No Preflow	7/11/2014	7/14/2014
Primary Recycled (5:1)	Chandler State D15 74-1HN	05-123-38321-00	6840	3,154,662	Fluid-B	No Preflow	7/11/2014	7/14/2014

Key date 1 refers to the first 24 hour sample collection period. During this time, the wells were opened to flow for 24 hours before coil cleanout. Due to logistical issues, the Chandler State wells were not preflowed before coil cleanout. Key date 2 refers to the second collection period when the wells were opened post production tubing. Key date 3 occurred once samples were no longer collected at the wellhead and instead collected from the permanent oil water separators (separators). However for Crow Creek, the wells were flowing to separators before Key Date 3. Table 3.2 shows the amount of recycled water per well, based on the base water volumes and the blending ratios.

Table 3.2: Water Quantity Summaries

Well Name	Ratio	Amount of Recycled Water (gal)	Amount of Fresh Water (gal)
Crow Creek State AC36-73HN	7:1	296,395	2,074,767
Crow Creek State AC36-76-1HN	Fresh	0	1,335,328
Crow Creek State AC36-73-1HN	Fresh	0	2,403,381
Crow Creek State AD31-79HN	5:1	383,526	1,917,628
Chandler State D15-72-1HN	Fresh	0	3,390,198
Chandler State D15-73-1HN	7:1	459,684	3,217,794
Chandler State D15 74-1HN	5:1	525,777	2,628,885

3.4 Crow Creek Study

The following section presents Crow Creek State specific well information, methodologies, analysis, and results.

For Crow Creek, each well was fractured with exactly the same frac package. This includes sand, gel, cross linkers, breakers, surfactants, scale inhibitors, friction reducers, and additives. The only difference between the wells are whether fresh water or a recycled blend is used. Although the fracturing ingredients are the same, the loadings of each ingredient vary from well to well. Loading data is not available, but the variation is assumed to be negligible. Table 3.3 is an example of the fracturing fluid composition taken from fracfocus.org.

Table 3.3: Fracturing Fluid Composition- Crow Creek

Trade Name	Purpose	Ingredients
Fresh Water or Recycled water blend	Base Fluid	Water
Sand	Proppant	Crystalline silica, quartz
WG-39	Gelling Agent	Polysaccharide
BA-20 BUFFERING Agent	Buffer	Ammonium acetate
		Acetic Acid
CL-23 CROSSLINKER	Crosslinker	Zirconium
		Acetate Lactate oxo
		Ammonium complexes
		Ammonium Chloride
OilPerm A	Non-Ionic Surfactant	Ethanol
		Heavy aromatic petroleum
		Naptha
		Napthalene
		Poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omegahydroxy-, branched
		1,2,4 Trimethylbenzene
OilPerm B	Surfactant	Terpenes and Terpenoids
		sweet orange-oil
		Isopropanol
CL-41	Crosslinker	Inorganic salt
		Lactic acid
OPTIFLO-III DELAYED RELEASE BREAKER	Breaker	Ammonium persulfate
		Crystalline silica, quartz
VICON NF BREAKER	Breaker	Sodium chloride
		Chlorous acid, sodium salt
DVE4O004	Scale Inhibitor	Ethylene Glycol
Cla-Web TM	Additive	Ammonium salt
SP BREAKER	Breaker	Sodium persulfate
FR-66	Friction Reducer	Hydrotreated light petroleum distillate

Crow Creeks wellheads are oriented from west to east on the Crow Creek East Pad. Table 3.4 shows the pad layout with respect to well order.

Table3.4: Wellhead location- Crow Creek

West									East
AC36-76-1HN	AC36-75HN	AC36-75-1HN	AC36-74HN	AC36-74-1HN	AC36-73HN	AC36-73-1HN	AC36-72HN	AC36-72-1HN	AD31-79HN

3.4.1 Crow Creek Methodology

3.4.1.1 Collection Procedure

Samples were collected from each primary well during every visit to the pad. Secondary wells were treated as duplicates (79HN for recycled and 73HN for fresh) and only sampled 5-6 times for the duration of the study. For the first 24 hour period during key date 1, samples were collected every 8 hours. For the first 24 hours of key date 2, samples were collected every 8 hours from either the wellhead or from the manifold before key date 3. Table 3.5 shows an example collection schedule for well 76-1HN.

Table 3.5: 76-1HN Sampling Schedule- Crow Creek

Sample Date	Sample Time	Days from start of flowback	Sample Date	Sample Time	Days from start of flowback
2/7/14	7:15am	0	3/1/14	8:15pm	7
2/7/14	3:10pm	0.3	3/2/14	11:20am	8
2/7/14	10:30pm	0.7	3/4/14	n/a	10
2/20/14	10:30am	1	3/5/14	n/a	11
2/20/14	6:30pm	1.5	3/6/14	n/a	12
2/21/14	3:00am	2	3/7/14	n/a	13
2/21/14	10:40am	2.3	3/8/14	n/a	14
2/21/14	8:10pm	2.7	3/9/14	n/a	15
2/25/14	8:15pm	3	3/12/14	n/a	18
2/26/14	8:00am	3.5	3/15/14	n/a	21
2/26/14	8:30pm	4	3/18/14	n/a	24
2/27/14	8:20am	4.5	3/24/14	n/a	30
2/27/14	8:30pm	5	3/31/14	n/a	37
2/28/14	10:00am	5.5	4/17/14	n/a	54
2/28/14	8:20pm	6			

The Days column denotes how many days the well has been flowing back since pre coil tubing. Between key date 1 and 2, the wells were shut in. The wells were also shut in between 2/21 and 2/25. The Days column reflects the shut in times and does not change during periods of no flow.

When samples were collected from the wellhead, roughly five gallons were collected into a clean plastic carboy. The carboys then sat for 15 minutes to allow for oil water separation. Samples were decanted off of the bottom of the carboy into 250mL bottles for later analysis. 40mL VOAs were also filled at each sampling time for volatile organic compounds and total

petroleum hydrocarbons. For the secondary treatment study, 5-gallon buckets were filled with the remaining water in the carboys.

Samples were collected from separators once it was determined to be no longer feasible to get samples from the wellhead. Allocation separators dedicated to a single well were used as opposed to a multi-well batch separator. Collection occurred, after separation, off of a 1/4inch ball valve downstream of the water dump. Clean 5-gallon buckets were also filled for the secondary treatment study.

3.4.1.2 Analysis Methods

CSU measured all water quality characteristics shown in Table 3.6. Total petroleum hydrocarbons and volatiles were measured by eAnalytics. Tables 3.6 and 3.7 include a description of all methods as well as the referenced EPA method number for CSU and eAnalytics analysis procedures. All other characteristics were measured by Nalco Champion. Table 3.8 shows all analytes measured by Nalco Champion and used in this study.

Table 3.6: Analytical Methods Performed by CSU

Parameter	Method Number	Description
pH	Hach PHC10105 gel-filled pH probe	A glass electrode is used to measure the emf of the sample against a reference solution and the measured emf is used to determine the hydrogen ion concentration based on a three-point standard curve generated using pH buffer solutions.
Conductivity	Hach CDC401 conductivity probe	A graphite, 4-pole conductivity probe is used to measure the electrical conductivity of the sample in mili-Siemens/cm
Total Organic Carbon (TOC)	Adapted from Standard Methods*, Method 5301 B	A Shimadzu TOC-VCSH analyzer is used to measure TOC as the difference between Total Carbon (TC) and Total Inorganic Carbon (TIC). In general, TC and TIC were both analyzed by oxidizing carbon to CO ₂ and measuring CO ₂ concentrations using a non-dispersive inferred detector. The TC oxidation includes a high temperature (680°C) combustion chamber with a platinum catalyst, allowing for more complete oxidation.
Dissolved Organic Carbon (DOC)	See above	Same as above, except that the sample is first filtered through a Whatman 934-AH glass microfiber filter (1.5 um equivalent pore size).
Total Carbohydrates	Total Carbohydrates Protocol UIUC 2004	Polysaccharides are hydrolyzed and monomers are dehydrated with sulfuric acid digestion. Anthrone is added and reacts with digested products to give a color change. Ultraviolet (UV) absorbance is measured using a HACH DR/4000 spectrophotometer at 578nm against a glucose standard curve.
Chemical Oxygen Demand (COD)	Hach Method 8000	COD is measured as the amount of O ₂ consumed in a sample heated for 2 hours with sulfuric acid and a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion (Cr ₂ O ₇ ²⁻) to green chromic ion (Cr ³⁺). The amount of Cr ³⁺ that is produced is then measured colorimetrically with a spectrophotometer at 620 nm.
Turbidity	EPA Method 180.1	Turbidity is measured using a Hach 2100 N turbidimeter to measure the light scattering potential (“cloudiness”) of each sample. Measurements were collected in nephelometric turbidity units (NTUs).
UV254	Adapted from Standard Methods*, Method 5910	The Ultraviolet (UV) absorbance is measured using a HACH DR/4000 spectrophotometer at 254 nm against organic-free water as an indicator of organic constituents in the sample. Results are automatically reported in absorbance per centimeter (cm ⁻¹).
Alkalinity	Standard Methods*, Method 2320 B	Alkalinity was measured as the amount of hydrochloric acid (HCl) added to a sample of a given size until the titration endpoint of pH 4.5 was achieved.
Gravimetric Solids Analysis: Gravimetric Solids Analysis: TS, TDS, TSS, TVS, VDS, VSS	Standard Methods*, Method 2540	Total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), total volatile solids (TVS), volatile dissolved solids (VDS), and volatile suspended solids (VSS) analyses are conducted via evaporation, drying, filtration, muffling, and weighing. TS, TDS, and TSS samples were dried at 105 °C; TVS, VDS, and VSS samples were muffled at 550 °C. Whatman 934-AH glass microfiber filters (1.5 um equivalent pore size) were used to filter samples.

*Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF **Table created by Sick (2014)

Table 3.7: Analytical Methods Performed by eAnalytics

Parameter	Method Number	Description
Metals: Al, Ba, B, Ca, Fe, K, Mg, Na, Si, Sr, Zr	EPA 6010C	Samples are acid digested to pH < 2 to dissolve all metals. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is then used to measure target metals.
Ammonia (NH ₄)	EPA 350.1	The sample is buffered at a pH of 9.5 and is distilled into a solution of boric acid. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue and measured colorimetrically.
Bicarbonate (HCO ₃)	EPA 310.1	An unaltered sample is titrated to an electrometrically determined end point of pH 4.5.
Bromide (Br)	EPA 300.0	A small volume of sample is introduced into an ion chromatograph (IC). The anions of interest are separated in the IC column and are measured against a standard curve with a conductivity detector.
Chloride (Cl)	EPA 9253	Sample is adjusted to pH 8.3 and titrated with a silver nitrate solution in the presence of a potassium chromate indicator. The end point is indicated by persistence of the orange-silver chromate color.
Sulfate (SO ₄)	ASTM D516	Sulfate ion is converted to barium sulfate suspension under controlled, stabilized conditions. The resulting turbidity is determined by a nephelometer, spectrophotometer, or photoelectric colorimeter and compared to a standard sulfate curve.
Oil Range Organics (ORO)	EPA 8015	Nonhalogenated organics in the range of C28 - C36 are extracted from the sample and introduced into a GC. Detection of analytes is achieved through a Flame Ionization Detector (FID).
Total Petroleum Hydrocarbons (TPH)	See Description	Sum of GRO, DRO, and ORO
BTEX (Benzene, Toluene, Ethylbenzene, Total Xylenes)	EPA 8260C	The volatile compounds are introduced into a gas chromatograph (GC). The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS). Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve.

*Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF **Tables 3.6 and 3.7 created by Sick (2014)

Table 3.8: Analysis Performed by Nalco Champion

Parameter
Conductivity
Metals: Al, Ba, B, Ca, Cu, Fe, Mg, Mn, Pb, Na, Si, Sr, Zn
Chlorine
Bicarbonate
Sulfate

*Nalco Champion measures metals using inductively coupled plasma optical emission spectrometry (ICP-OES). Samples are prepared by digesting to a pH less than 2 in order to dissolve all metals.

3.4.1.3 Water Treatment

Three samples from each primary well, representing early, mid, and late flowback were treated using a series of jar testing methods. The standard method ASTM D2035-13 was used as

a starting point, but was modified to produce optimal treatment results. These methods include dosing six identical 1L samples with a varying load of coagulant. A Phipps&Bird PB-900 programmable jar tester was used for the treatment study. The coagulants chosen for this study were aluminum chlorohydrate (ACH) and Ferric (III) chloride (Ferric). These two chemicals were chosen because they are commonly used coagulants in oilfield treatment trains. Turbidity, following the methods outlined in Table 3.6, was taken before and after treatment to determine treatment efficiency. Initially, rotational speed of the mixing paddles was optimized to create optimal settled flocculent and lowest turbidity of effluent. The determined mixing schedule is shown in Table 3.9.

Table 3.9: Jar Test Mixing Schedule

Mixing/Flocculation	
120 rpm	1 min
25 rpm	10min
12 rpm	10min
6 rpm	10min

Once mixing was stopped, samples were collected after 20 minutes of settling. It was determined, after multiple trial runs, that after 20 minutes, change to the optimal coagulant dose and final NTU was negligible. Samples were decanted from the top of each jar using a 10mL pipette. Optimal coagulant doses were chosen by the lowest NTU. Optimal doses were also chosen based on the criteria that the smallest dose required is optimal as long as an increase in coagulant does not result in meaningful turbidity removal.

3.4.2 Crow Creek Characterization

3.4.2.1 Crow Creek Characterization Results

The results section will first look at comparisons in water quality between the two primary wells, recycled vs. fresh. It will then move into the primary vs. secondary well data for both fresh and recycled wells. Figures 3.1 and 3.2 show a majority of the samples collected for the two primary wells 76-1 and 73.

Except for the very first 73 sample, both wells started out very clear with little oil. As the sampling progressed, the observable color turned to a dark yellow-brown. Higher emulsified oils could be seen in the later samples as well. For well 73, emulsified oils were seen as early as the final 16 hours of pre coil flow. For well 76-1 observable emulsified oils were not seen until around day 3. Even then, the amount of visible emulsified oils in 76-1 samples was far less than that of 73 samples throughout the sampling period. Since multiple months had passed for the early samples before pictures could be taken for Figures 3.1 and 3.2, some of the samples darkened. Figure 3.3 shows a picture of pre coil tubing samples on the day they were collected.

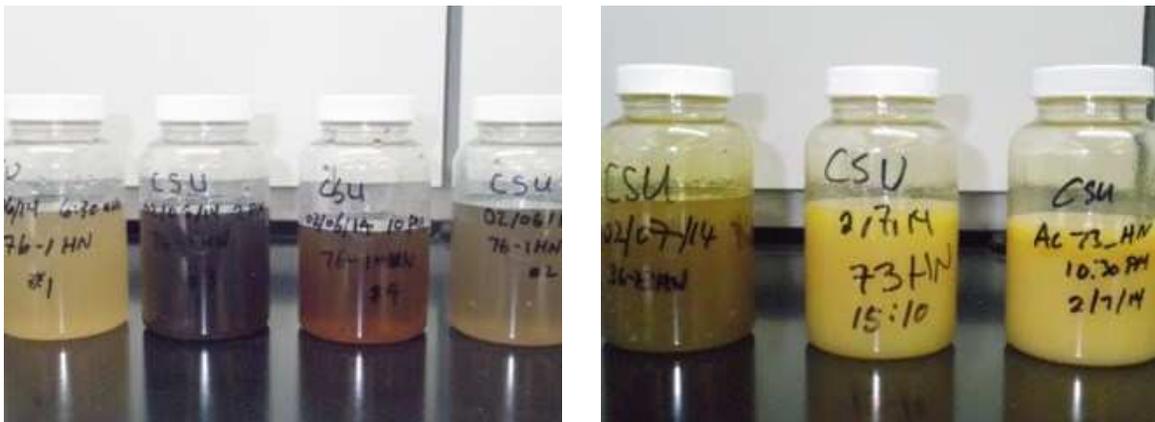


Figure 3.3: Pre Coil Tubing Samples 76-1 and 73- Crow Creek

In general, there were very few differences between the fresh and recycled well. The only notable difference was in the turbidity and the organics testing results. There was a high degree of variability for most water quality characteristics in the first 3-4 days of samples. Figures 3.4, 3.5, 3.6, and 3.7, show results of the analysis performed on all samples from both wells.

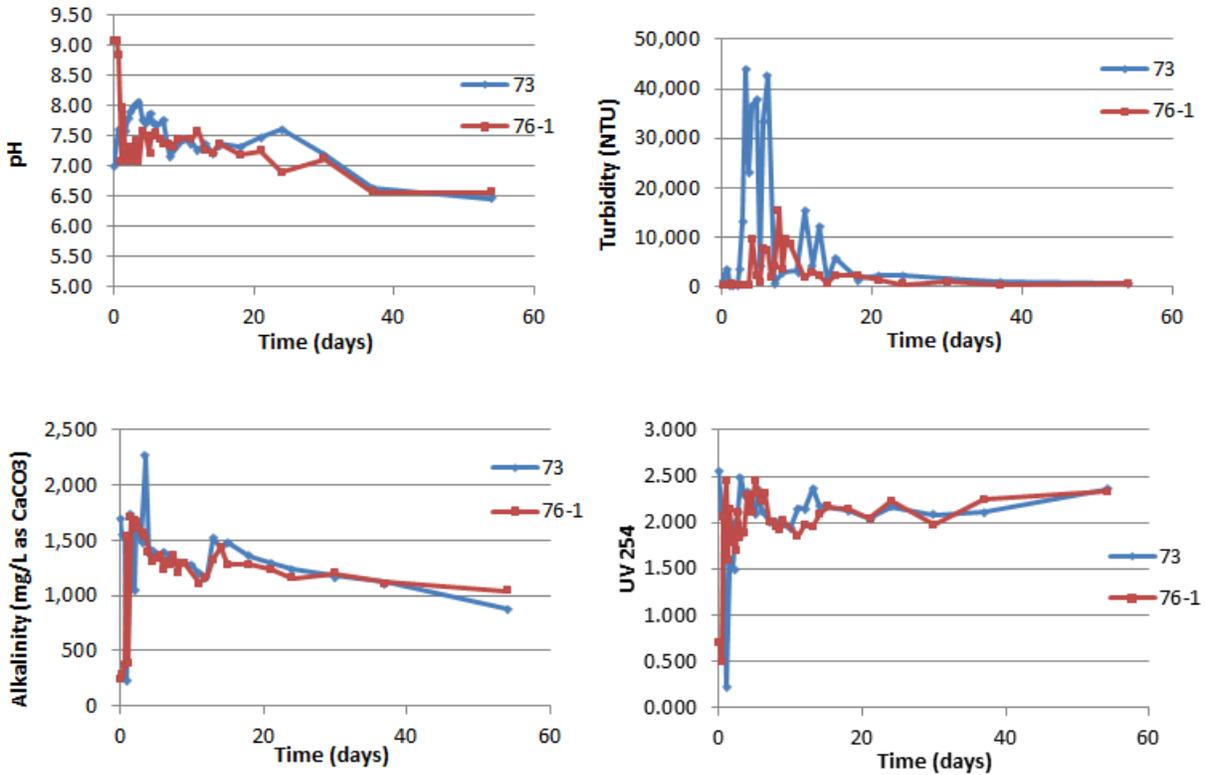


Figure 3.4: Selected Wet Chemistry Results Primary Wells- Crow Creek

It was observed that the pH was very similar between each well. 76-1 started at a pH of 9.05 and lowered to stay in a range close to 7 for 30 days until the pH dropped to a 6.5. 73 started at a pH of 7.1 and followed a similar temporal trend as the fresh well. Turbidity for 73 was much higher than that of 76-1 for the first 13 days, but approached a similar turbidity at day 20. The primary wells were very similar for alkalinity and UV254 absorbance. However, 76-1 had much lower alkalinity than the average for the first three days before key date 2. Figure 3.5 shows the summary results of the gravimetric analysis performed by CSU on all samples up to day 37.

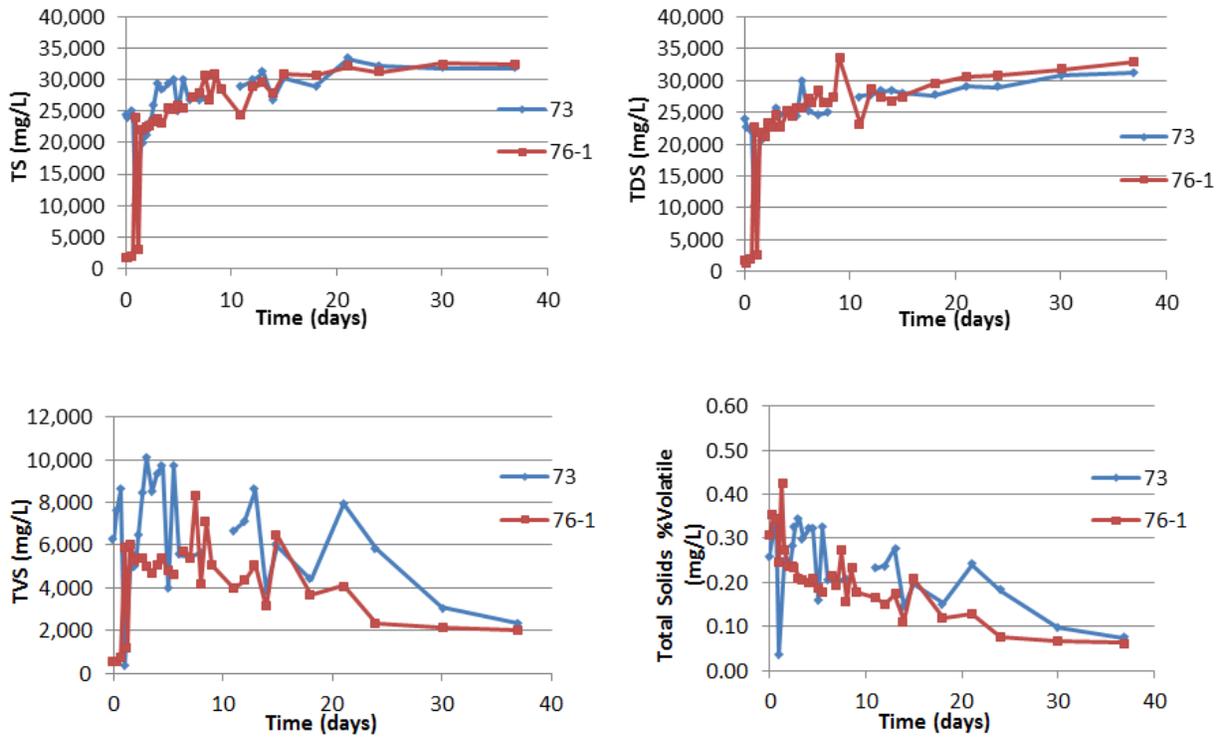


Figure 3.5: Selected Gravimetric Results Primary Wells- Crow Creek

Once again, both wells followed similar trends for all solids. 73 did exhibit slightly higher total volatile solids. Total volatile solids were normalized to total solids as %volatile. This is seen in the Total Solids % Volatile graph. Except for the first three days of sampling, 73 did show a slightly higher percentage of total solids as volatile. Figure 3.6 shows aluminum, calcium, magnesium, and chlorine concentrations in the samples.

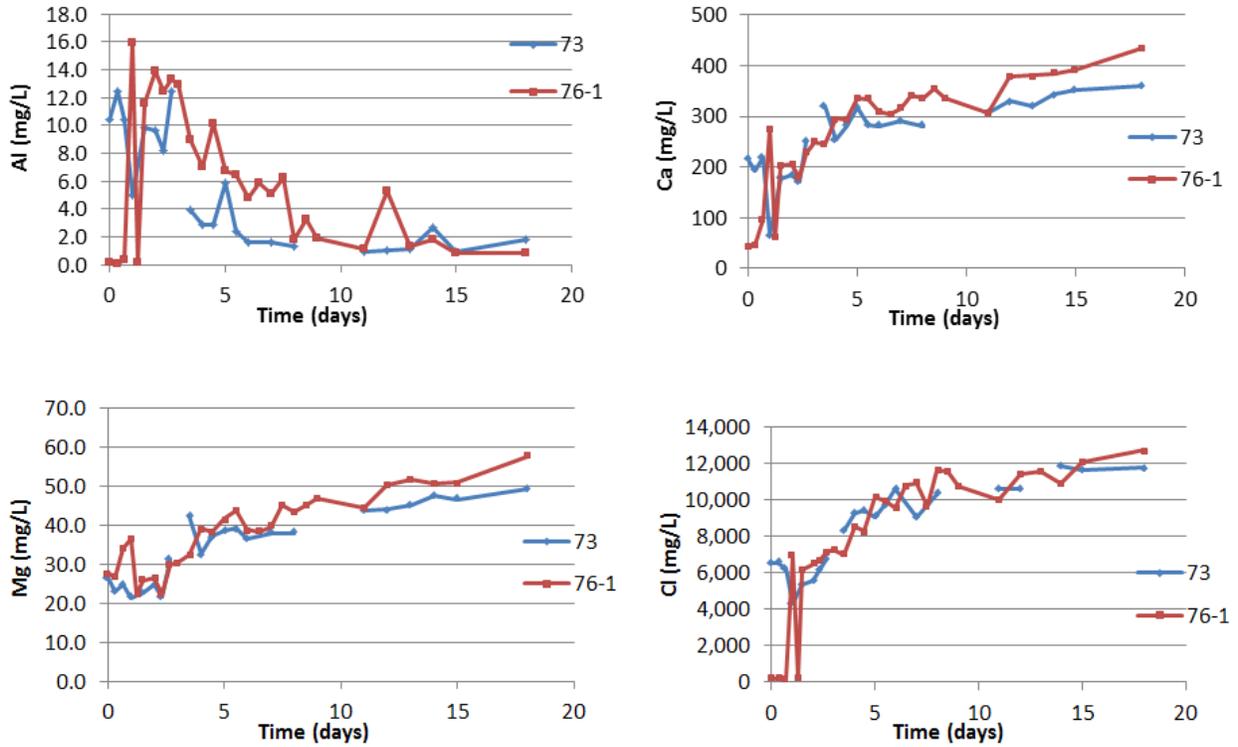


Figure 3.6: Al, Ca, Mg, Cl Results Primary Wells- Crow Creek

All metal concentrations were similar between both wells. However, CSU was only able to obtain up to 18 day samples from Nalco. As shown, aluminum follows a downward trend as calcium, magnesium, and chlorine all follow an upward trend as the water becomes more representative of the formation. Figure 3.7 depicts the organic results of the primary wells.

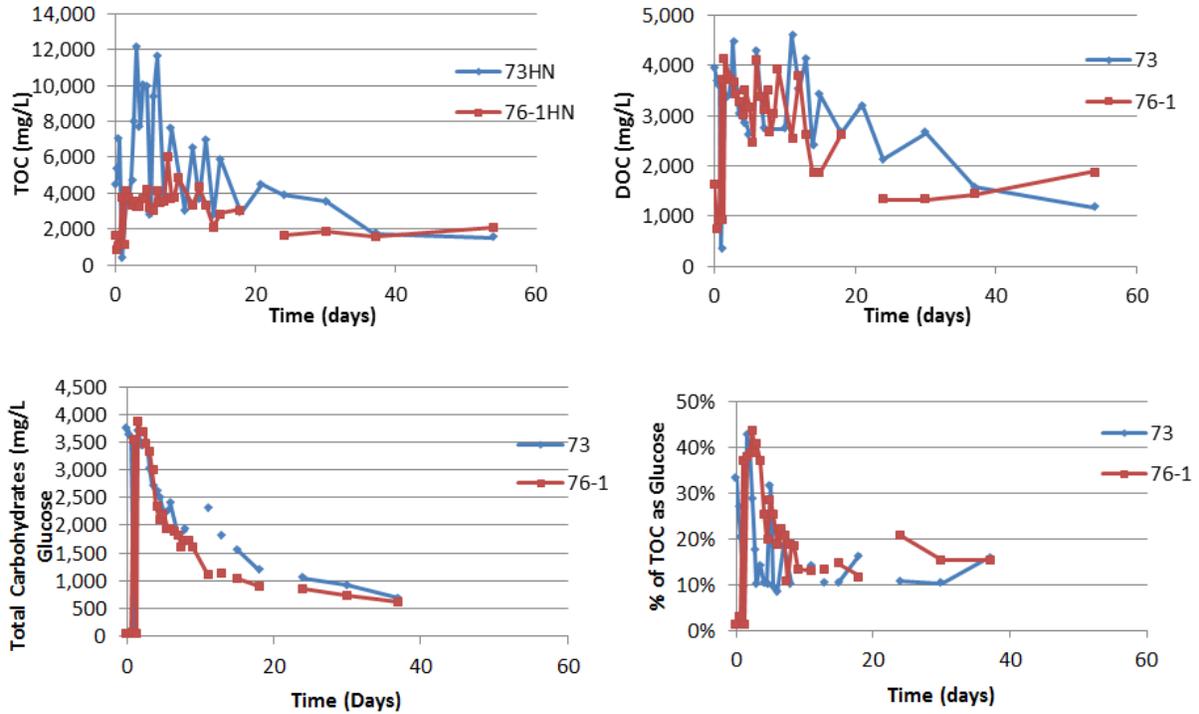


Figure 3.7: Organic Results Primary Wells- Crow Creek

As seen in the total organic carbon (TOC) results, the recycled well had much higher TOC concentrations. Well 76-1 stayed within the 4,000mg/l range and decreased to 2,000 by day 24. Well 73 varied with a maximum of 12,170mg/l TOC. Once the samples were filtered and dissolved organic carbon (DOC) was measured, it was seen that the samples were much more similar in concentrations. Both samples also followed a similar temporal trend in total carbohydrates. The % of TOC as Glucose graph took the glucose concentrations as carbon by weight (40% of glucose is carbon by weight) and found what percentage of TOC is composed of carbohydrates. It was seen that even though 76-1 had a lower total carbohydrate concentration on average, its carbohydrates represented a larger percentage of the total TOC. Figure 3.8 depicts selected results from the primary and secondary recycled wells.

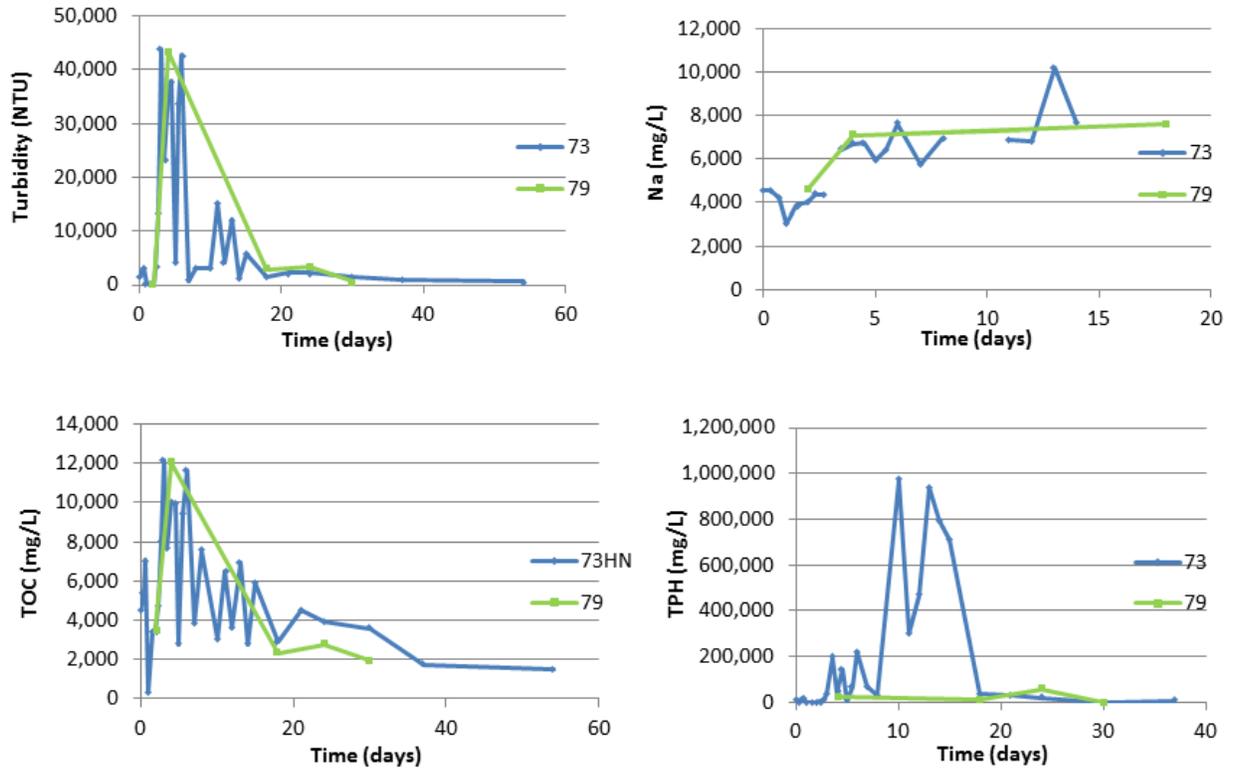


Figure 3.8: Selected Results Primary and Secondary Recycled- Crow Creek

The secondary recycled well only had five data points for turbidity, TOC, and TPH. For metals, only three data points exist for each well. It appears that the primary and secondary well are similar. When the TPH spiked from day 10 to day 18, samples were not collected for the secondary well. The TPH Figure 3.9 shows selected results from the primary and secondary fresh wells.

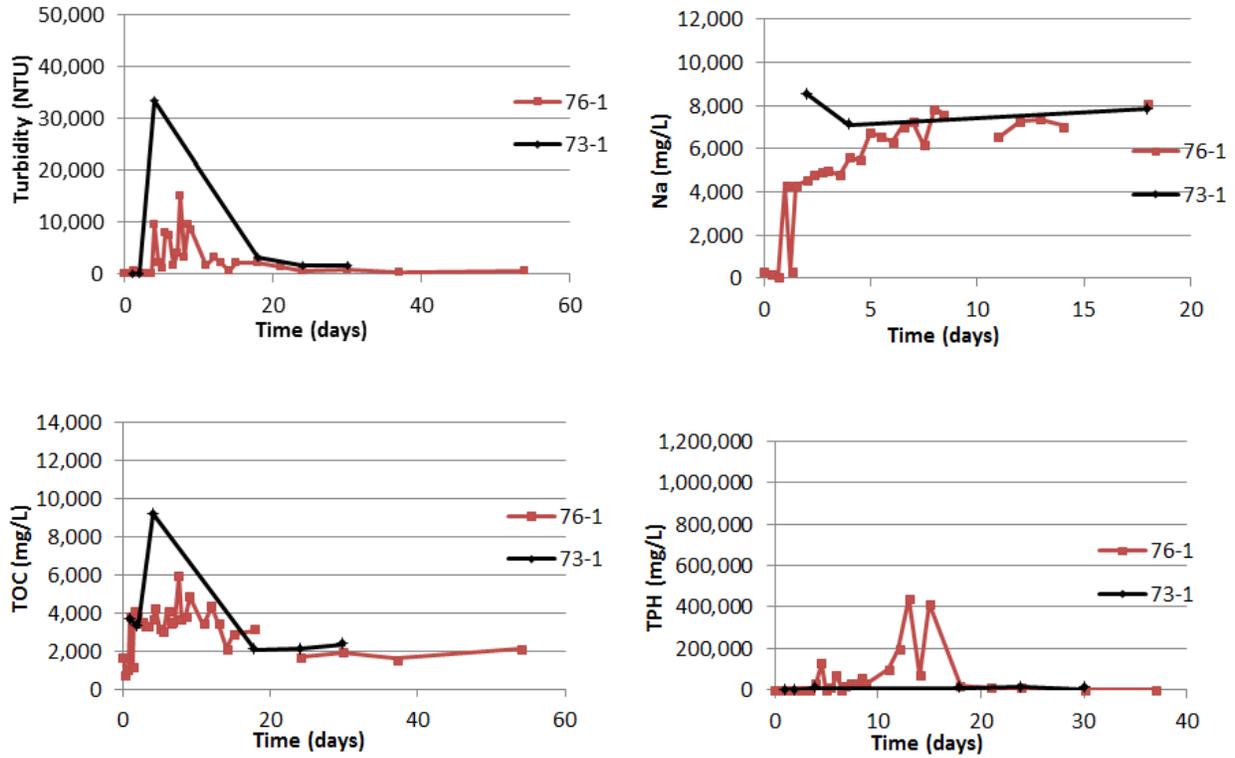


Figure 3.9: Selected Results Primary and Secondary Fresh- Crow Creek

The secondary fresh well had three data points for metals and six data points for all other water quality characteristics. It appears that there is a higher turbidity and TOC for the secondary well on day 4. Sodium concentrations also seem slightly higher than the primary well for day 2 and 3. TPH concentrations seem to be highly correlated for all six data points. Variability between secondary and primary wells will be discussed in the next section. Table A.1 (in *Appendix A: Water Quality Characteristics*) contains all averages and the range for each constituent tested for every well.

3.4.2.2 Crow Creek Characterization Discussion

As mentioned in the results section, there was a great amount of noise in the first 3-5 days of sampling for many water quality parameters. This noise is most likely contributed to the high variability in early flowback water quality. Early flowback is less of a homogenous mixture than later flowback as early flowback water comes out of the well that may not have fully interacted with the formation. Depending on the cumulative flow and how the well was stimulated, early flowback may contain finishing water (base water that has not reached the horizontal lateral and contains no fracturing chemicals), fracturing water that has not entered the formation, water that interacted with the formation for a very short period, or the formation water itself. This seems to be especially apparent in the pre coil water shown in Figure 3.3. Figure 3.3 depicts samples taken in only a 24 hour period. As the wells flow for a longer period of time, a more consistent water quality is established.

It appears that the recycled and fresh wells are very similar in water quality characteristics except for organics. Metals appear to be similar, but the quality of the metals data cannot be verified. CSU received lab results from Nalco Champion's lab, but was not able to obtain calibration curves or a proper documentation of methodology. Also, a lack of data past day 18 made it difficult to draw any late flowback conclusions on metals. Although the validity of the absolute values of metal concentrations is not conclusive, the relative concentrations between wells can be used for analysis. When looking at Table A.1, it appears that both wells have very similar concentrations for all metals in both averages as well as max and min concentrations.

Organic measurements include TOC, DOC, total carbohydrates, TPH, and BTEX. As shown in Figure 3.7 and Table A.1, TOC concentrations were much higher for the recycled well during the first thirty days. This can be explained with a number of observations. The first explanation is

that there seemed to be a higher level of emulsified oil in the recycled well samples. Even after 15 minutes of separation in the carboys, the water taken off of the bottom spout of the carboy had high levels of visually observable oil. Further evidence of this is shown in the DOC results. Once the oil was filtered out using a 1.5um filter, the dissolved organic carbon concentrations between wells were exactly the same.

The higher recycled well TOC concentrations also correlate directly to higher TVS concentrations in the solids analysis for the recycled well. Higher TOC concentrations due to higher levels of emulsified oils could mean that the recycled water allows the fracturing fluid to interact with the formation more readily than the freshwater base. This may be due to the fact that the recycled base water more closely matches the formation water in terms of TDS. The TOC concentrations lowered over time as the organics from the fracturing fluid subsided and the flowback began to take on more characteristics of the formation water. The fresh and recycled wells converged by day 40. This was also observed visually, as the samples began to look more and more alike, even after day 18.

Total carbohydrate concentrations for both wells were very similar; however the fresh well had slightly lower carbohydrate concentrations. As less and less of the flowback consisted of fracturing fluid, the carbohydrates dropped with time. Even though the fresh well had lower carbohydrates, it can be seen in Figure 3.7 that the % of TOC as carbohydrates was higher for the fresh well than the recycled well. This may further prove the point that a larger portion of the TOC for the recycled well was emulsified oils.

For the secondary wells, not enough resolution exists to draw substantial conclusions from the results. Issues prevented sample collection on certain dates, and lessons learned from mistakes in the Crow Creek study will be shared in the lessons

learned section. Figures 3.8 and 3.9 may be misleading for TPH results. It is entirely possible that the TPH spike seen in both the primary wells also occurs for the secondary wells. However, there was not enough resolution to capture the spike in the secondary wells. Also, the day four sample for the secondary fresh well seems to be much higher in many water quality characteristics. Early flowback variability may be contributing to this higher data point, but it is still higher than the max points for the primary well. It was observed that the oil water cut in this sample was not a clean cut. It is possible that a higher level of oil was present in this sample. However, it is also possible that the higher level of oil was due to emulsified oils. Overall, the secondary wells did seem to follow similar trends as their primary counterparts. The similarities and differences between the two secondary wells also followed the same similarities and differences between the primary wells.

One possible explanation for the TPH spike is in the methodology for TPH analysis and the state of oil in the primary well samples. From day 10 to day 15, the TPH concentration noticeably increased. eAnalytics ran TPH analysis on all samples for the duration of the study. The days that showed a spike in TPH were all processed as a single batch. The entire increased TPH trend was only during this time period. It is possible that there was a change in the flowback for both wells and that the oil water cut was not as clean as the days before day 10, and that on day 16, the cut became cleaner and it was easier to gravimetrically separate the crude from the flowback.

It is also possible that the method for collecting a sample from the VOAs for TPH analysis contributed to the results. Due to the high levels of oil in the sample, eAnalytics was instructed to shake the VOAs and then pull sample from the middle of the VOA. It is

possible that either shaking did not occur on the 10-15 day batch of samples, or samples were pulled off the top of the vial, where the majority of the oil resides. This is most likely the case, as day 10 for well 73 contained almost 1,000,000mg/L TPH, meaning that the sample consisted entirely of oil. Figure 3.10 shows the TPH results with days 10-15 removed to allow for a more appropriate scale.

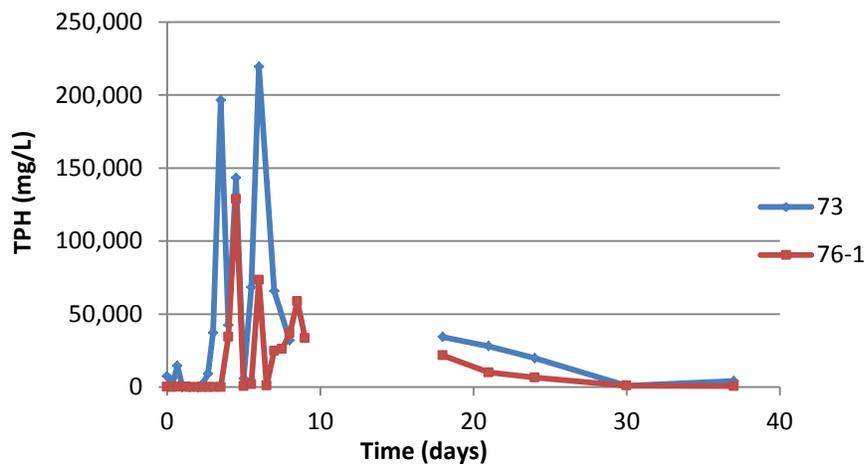


Figure 3.10: TPH with Omitted Anomalies

3.4.3 Crow Creek Treatment

3.4.3.1 Crow Creek Treatment Results

Figure 3.11 shows the initial results of aluminum chlorohydrate (ACH) vs Ferric (III) chloride (ferric). The graph represents turbidity readings of treated samples with different doses of the two coagulants. The ferric treated water appears to have slightly lower NTU values at all doses.

76-1 Day 21: ACH vs Ferric

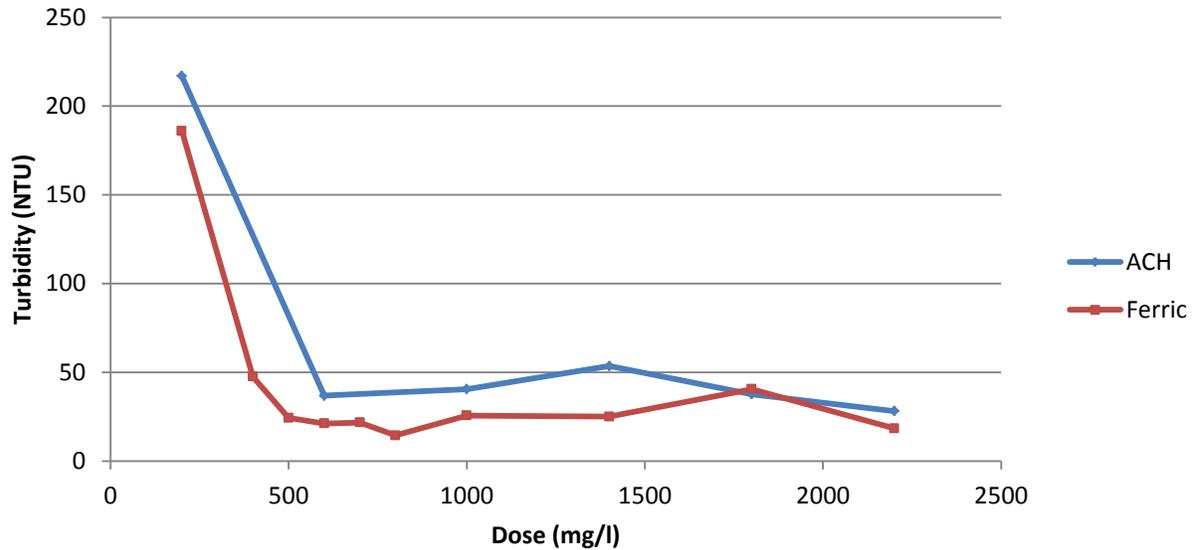


Figure 3.11: ACH vs. Ferric 76-1 Treated Water NTU: Day 21

Figures 13 and 14 show a visual comparison in the jar tests between ACH and Ferric. Each jar represents a different dose of either ACH or Ferric. A sludge blanket can be seen at the bottom of each jar. In Figure 12, the sludge blanket for most doses is over 50% of the volume. Visual observation showed a loose floc that was not conducive to settling. Figure 13 shows the results of using ferric on the same flowback sample. The sludge formed took up roughly 25% of the volume depending on the dose. Visual observation also showed the floc to be much denser than the ACH treated water.



Figure 3.12: 76-1 ACH Treatment Result: Day 21



Figure 3.13: 76-1 Ferric Treatment Result: Day 21

Figure 3.14 shows the final result of the jar tests for the two primary wells. The y-axis represents the optimum dose of a coagulant to achieve optimum turbidity removal. As expected from previous studies, the earlier flowback required larger doses of

coagulant. It is apparent that ACH requires a much larger dose than ferric to achieve an optimum dose. This is especially true in the earlier samples. It is also apparent that the difference between the optimum ferric dose required to treat the fresh and the recycled wells is negligible. There is a more noticeable difference in the optimum ACH required to treat the two primary wells.

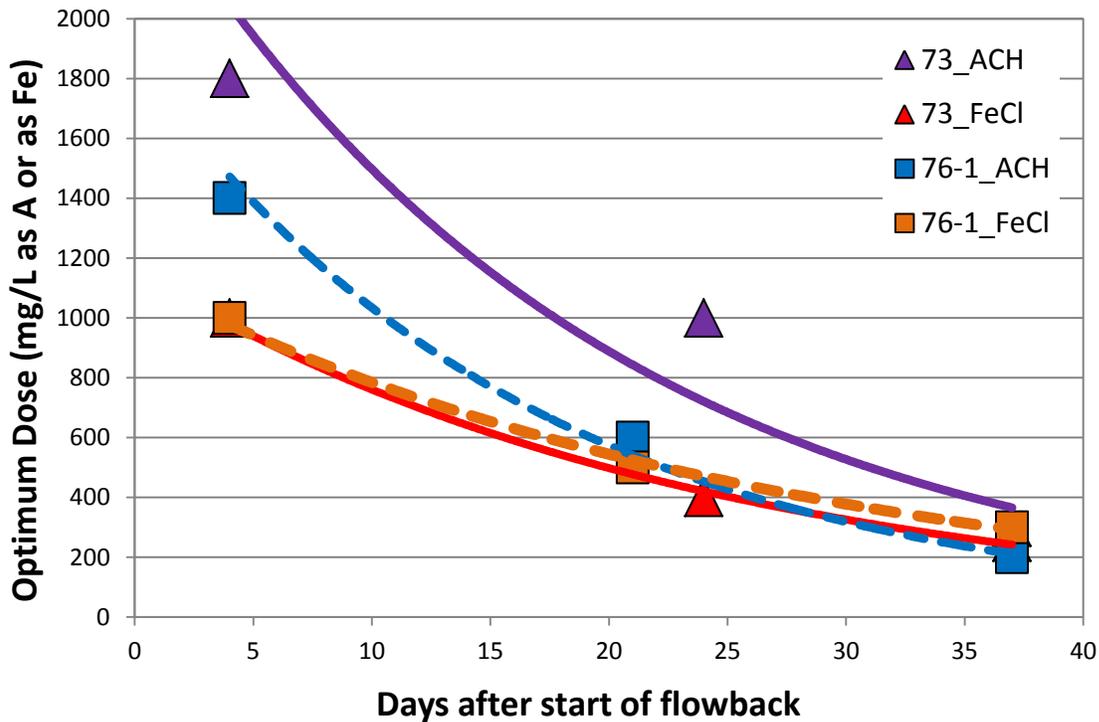


Figure 3.14: Treatment Optimum Dose Results

3.4.3.2 Crow Creek Treatment Discussion

Based on Figure 3.14 and the visual observations of the jar tests, Ferric is the better choice in coagulation of flowback from the primary wells. Even though ferric is a better choice than ACH, 1,000mg/l as ferric is an extremely high dose to treat large quantities of water. It is suspected that a larger dose is required due to interference from fracturing fluid gels in the early

flowback. There is a direct relation between optimum coagulant dose required and organic loading. As TOC concentration lower with time, the optimum dose required lowers. It is important to note that the optimum doses in the treatment portion of this study are not recommended doses for treatment. They are only used to compare relative doses between the two primary wells.

It is clear that when using ferric, the difference in treatment feasibility between recycled and fresh wells is negligible. However, ACH was able to treat fresh well flowback with a lower dose than recycled well flowback. It is possible that ACH is more susceptible to interference from emulsified oils than ferric. This could be visually observed with the pin floc that was present in ACH treated samples.

3.4.4 Crow Creek Lessons Learned

Over the course of the sampling campaign, many insights were gained for the improvement of sample collection and analysis. It has been determined that the level of noise during the first five days makes the need for a high resolution of samples insignificant. The same water quality conclusions could have been drawn with once per day samples for the first week as opposed to four times per day.

By reducing resolution, it will be possible to expand the scope of parameters tested for. There will also be more time to analyze the data and address issues in an immediate fashion. The lack of timeliness in analyzing the data was seen with metals concentrations. For future work, more involvement needs to take place in the chain of custody, methods, and results from third party labs to prevent the generation of unsubstantiated data. Either this needs to occur, or a more trusted laboratory with transparent and accurate analysis methods should be used.

By having a more timely feedback loop of sampling to data generation to analysis, anomalies or unusual trends in the data could be more closely looked at. By the time the TPH data had been graphed and it was noticed to be inconsistent with expected trends, it was too late to run more samples to eAnalytics since TPH is a very time sensitive parameter. Another benefit to reducing resolution on the primary wells is it frees up time to increase the resolution on secondary wells or increase the sample population, resulting in stronger datasets.

It is also much more convenient for CSU to collect samples on site and directly bring them back to the CSU lab for analysis. By limiting the sampling to once per day for the first week, there will be no need for an onsite trailer. By eliminating the onsite trailer, onsite titrations for dissolved gasses will not be possible. However, the results of the dissolved gases data were inconclusive due to unavoidable variation in colorimetric titrations between samplers. Issues arise with colorimetric titrations because of the high level of oils in the samples resulting in color interference, allowing for over or under titration. Similarly, conductivity measurements were interfered due to high oil levels in the sample. Since TDS is measured using a gravimetric technique, the need to measure conductivity is reduced and can be eliminated in future sampling if it presents issues. For future sampling, field oxidation reduction potential (ORP) measurements should be taken as well as lab ORP. ORP is a useful metric in treatability studies and can give insight on the current speciation of certain ions in solution.

3.5 Chandler State Study

The following section presents Chandler State specific well information, methodologies, analysis, and results.

The Chandler State wells were all fractured with a Fluid-B Fracturing package. This differs from the Fluid-A package that was used on all of the Crow Creek wells. Table 3.10 outlines some of the major differences between the two fracturing fluids.

Table 3.10: Fracturing Fluid Design

Fracturing Fluid	Gel	Cross Linked pH	Anecdotal Kinetics
Fluid-A	Cellulose	8	Cleans up quickly in well
Fluid-B	Guar	9	Takes Longer to no longer be present in flowback

As seen in Table 3.10, the Fluid-B uses a guar based gel, where Fluid-A uses a cellulose based gel. In addition to different gels, the starting pH's for these two packages vary, with Fluid-A at pH 8 and Fluid-B at pH 9.

For Chandler State, each well was fractured with exactly the same frac package. The only difference between the wells is whether fresh water or a recycled blend was used. Although the fracturing ingredients are the same, the loadings of each ingredient vary from well to well. Loading data is not available, but the variation is assumed to be negligible.

3.5.1 Chandler State Methodology

3.5.1.1 Collection Procedure

Using the lessons learned from the Crow Creek Study, the temporal resolution of collected samples was decreased. As shown in Table 3.10, key date 1 was skipped for the Chandler State wells. There was no preflow before coil tubing on the Chandler State wells. Hence, Table 3.10

depicts the sample collection schedule for the study and starts on day 1 instead of day 0 like the Crow Creek Wells.

Table 2.10: Chandler State Sampling Schedule

Sample Date	Days from Start of Flowback	Sample Date	Days from Start of Flowback
7/11/14	1	7/27/14	17
7/12/14	2.0	7/30/14	20
7/13/14	3.0	8/2/14	23
7/14/14	Shut in	8/5/14	26
7/15/14	5.0	8/8/14	29
7/16/14	6.0	8/15/14	36
7/17/14	7	2/12/1900	43
7/18/14	8.0	9/5/2014	57
7/19/14	9.0	9/19/2014	71
7/20/14	10	10/19/2014	101
7/21/14	11.0	11/18/2014	131
7/22/14	12.0	12/18/2014	161
7/23/14	13	1/17/2015	191
7/24/14	14.0	2/16/2015	221

In order to improve the reproducibility of sampling procedures, samples were collected from separators as soon as possible. Samples were collected from temporary separators on day 2 and permanent separators starting day 5. This was deemed a reasonable approach because each well was assigned to a single separator, removing the uncertainty of comingled wells.

Samples were collected from the water side sight glass from each separator. Because the separators effectively removed all free oil, samples were poured directly into clean 1L and 250mL plastic bottles for analysis. Section 3.5.1.2 explains the analysis differences between the Crow Creek and Chandler studies.

3.5.1.2 Chandler Analysis Methods

From the lessons learned in the Crow Creek Study, changes were made to the analysis methods as well as the analytes tested. CSU completed all of the studies outlined in Table 3.6, except for COD. The COD methodology employed was determined to be unreliable at high chloride levels due to chloride interference. It was also determined that the TOC and carbohydrate tests provided enough data to make the COD tests irrelevant. Refer to Tables 3.6 and 3.7 for information on specific analysis methodologies.

eAnalytics was used for all metals testing, removing the need for Nalco Champions for laboratory tests. Table 3.11 shows the metals tests eAnalytics ran for each sample. BTEX was removed from testing procedures as well.

Table 3.11: Analysis Performed by eAnalytics

Ions	Al, B, Ba, Br, Ca, Fe, K, Mg, Na, Si, Sr, Zn, Cl, NH ₄ , HCO ₃ , SO ₄
Organics	TPH: DRO, GRO, ORO

3.5.2 Chandler State Characterization

3.5.2.1 Chandler State Characterization Results

The results section will first look at comparisons in water quality between the three wells on the site. During collection, it was noted that there was little to no free or emulsified oil in the water samples throughout the study. There was no discernable observational difference between the three wells, as all samples looked very similar. The turbidity results in Figure 3.15 reflect this. 72-1 is shown in blue and represents the fresh water fractured well. 73-1 is shown in green and represents the 7:1 recycled well. 74-1 is shown in red and represents the 5:1 recycled well.

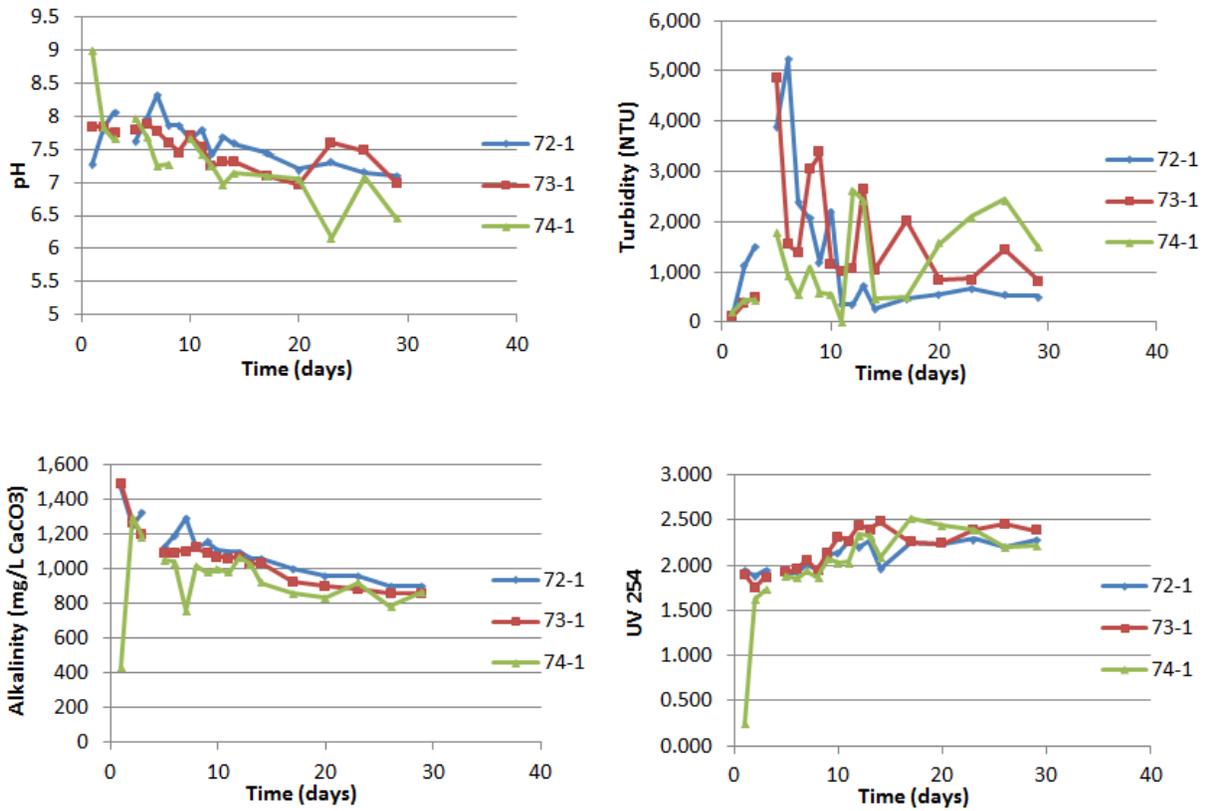


Figure 3.15: Selected Wet Chemistry Results- Chandler

The wet chemistry results for all three wells were all similar. By day 2, pH values for all three wells were within the 7-8 range and followed a downward trend towards 6-7 by day 30. For turbidity, all three wells saw a spike in turbidity on day 5. The fresh water and 7:1 wells have similar turbidity data. Little difference is seen between the wells for Alkalinity and UV 254 absorbance as well.

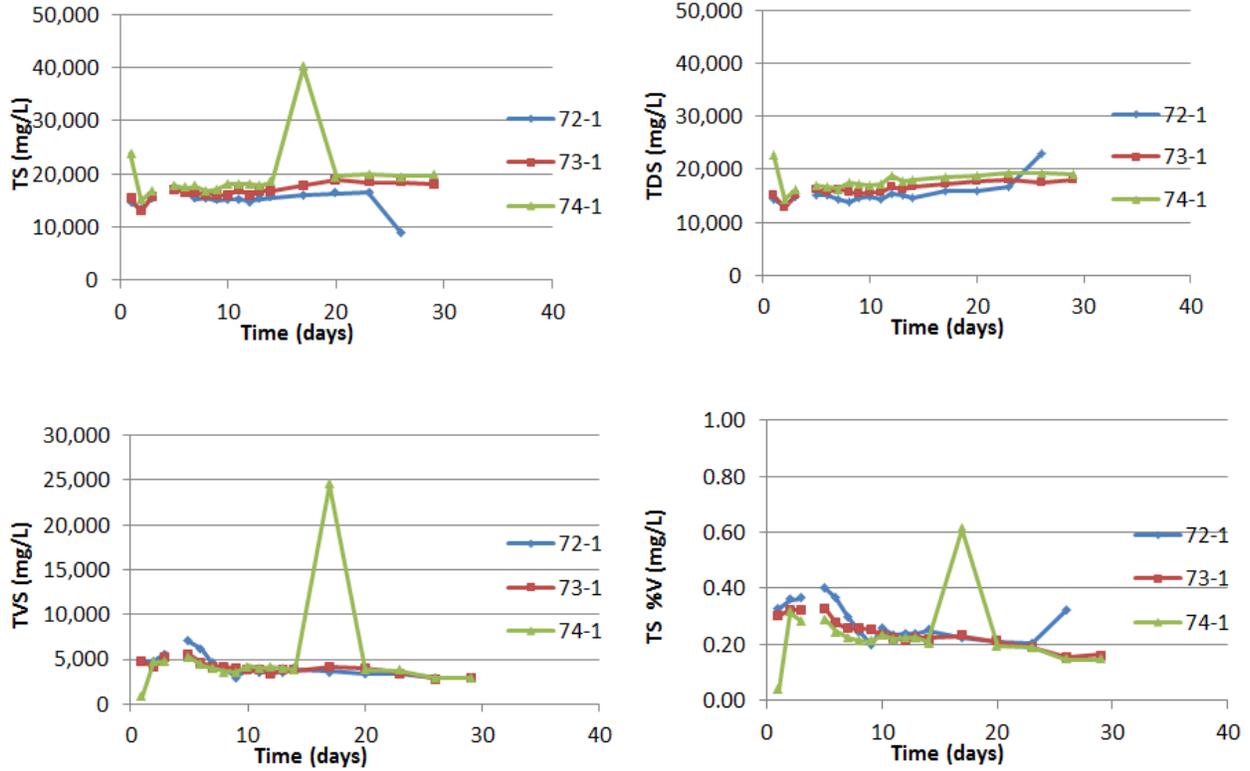


Figure3.16: Selected Gravimetric Results- Chandler

The gravimetric results show all three wells having similar solids concentrations. (The day 17 spike for 74-1 was most likely due to laboratory error. The total solids and total dissolved solids all follow a slight upward trend. The total volatile solids and percent total solids as volatile follow a slight downward trend.

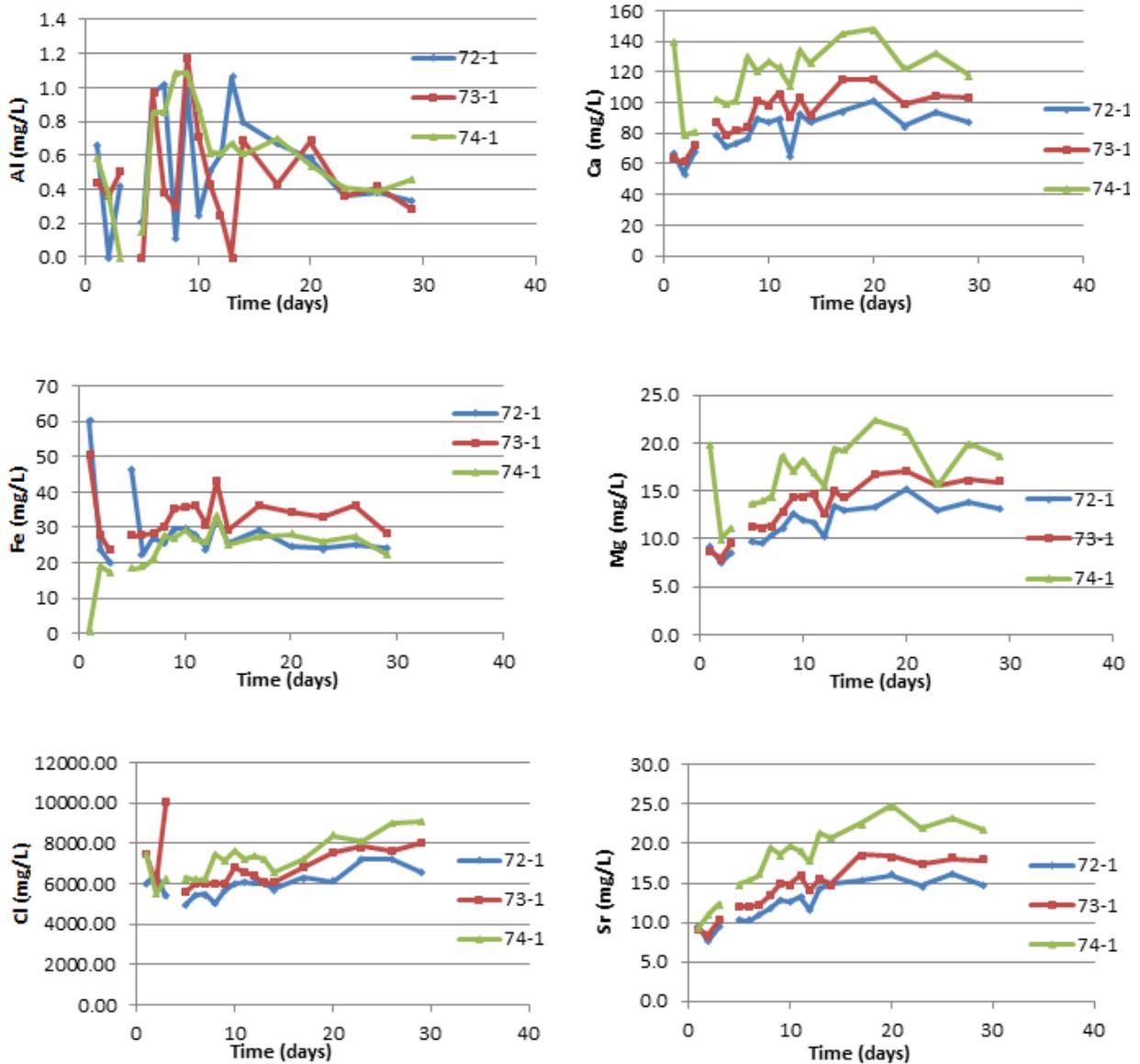


Figure 3.17: Selected Metals Results- Chandler

There was no discernable difference between all three wells for aluminum and iron concentrations. However, it appears that the fresh well had lowered divalent cation concentrations for metals such as strontium, magnesium, and calcium. The 5:1 recycled well showed the highest divalent cation concentrations with the 7:1 well resulting in the second highest divalent cation concentration. Chlorine concentrations also showed a similar trend, with

the 5:1 well showing the highest concentration and the fresh water showing the lowest concentration.

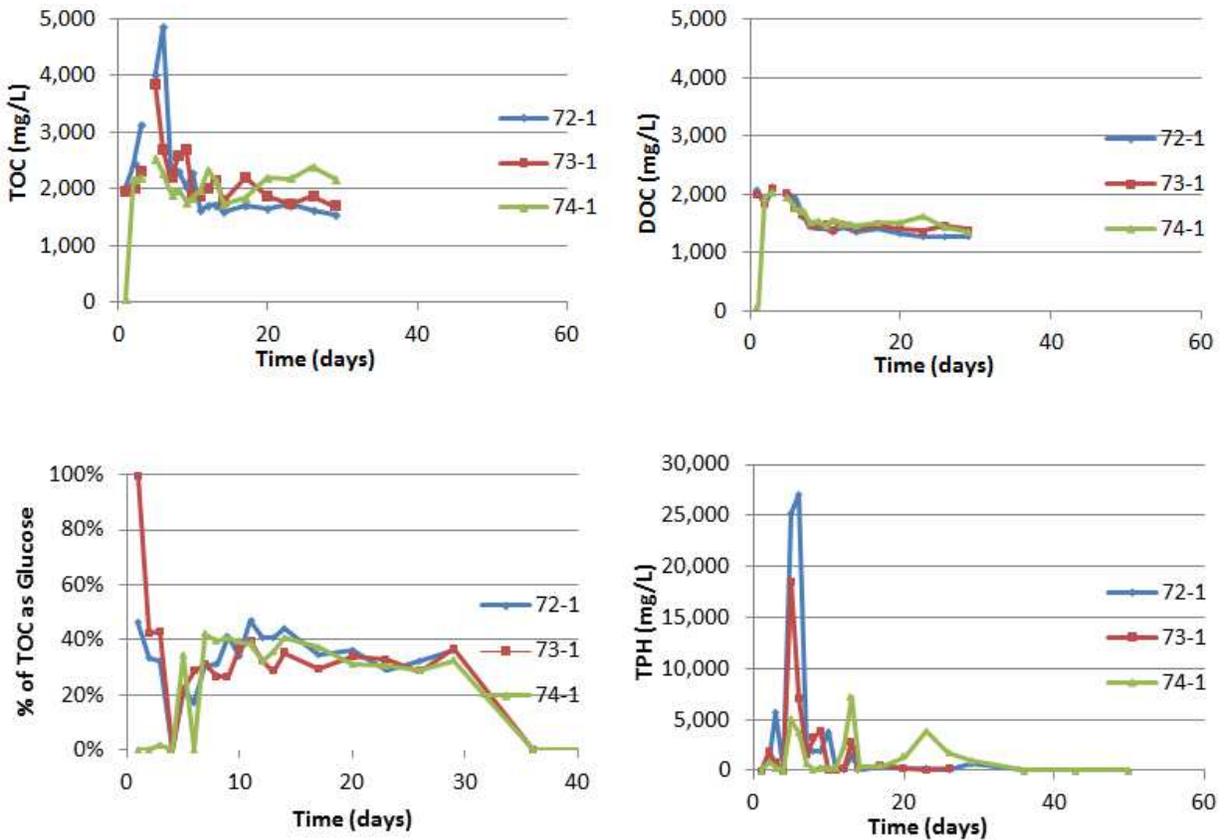


Figure 3.18: Selected Organic Results- Chandler

The organic results show that all three wells were very similar in their organic characteristics. The TOC and TPH had a spike in concentration on day 5 and 6 for the fresh and 7:1 wells. On day 5 and 6, the fresh well had the highest TOC concentration, but by day 8, the recycled wells had the same or higher TOC concentrations. Overall, the organic concentrations shown were highly correlated between all three wells.

3.5.2.2 Crow Creek and Chandler State Results Comparison

Selected results from the Crow Creek and Chandler studies are compared in the following figures. The fresh wells were paired from each site and the 7:1 wells were paired from each site.

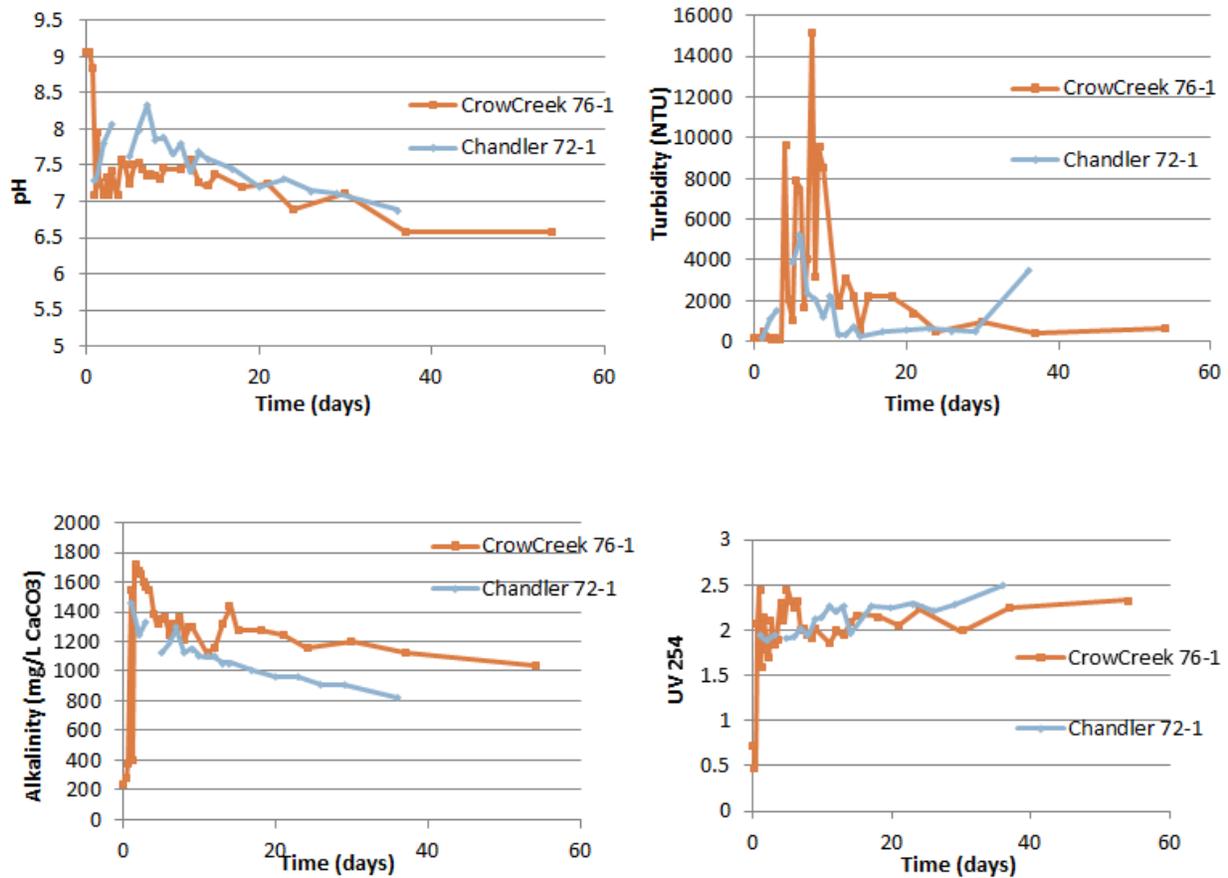


Figure 3.19: Selected Wet Chemistry Results: Fresh Water Comparison

The wet chemistry results between the fresh wells follow similar trends. Differences to note include a divergence in alkalinity, with the Chandler State decreasing more rapidly than Crow Creek. It is also apparent that the initial turbidity spike in the Chandler well is not as high as the turbidity in the Crow Creek well. Observationally, this can be seen in the reduced emulsified oil concentrations, even in the fresh wells, for Chandler state.

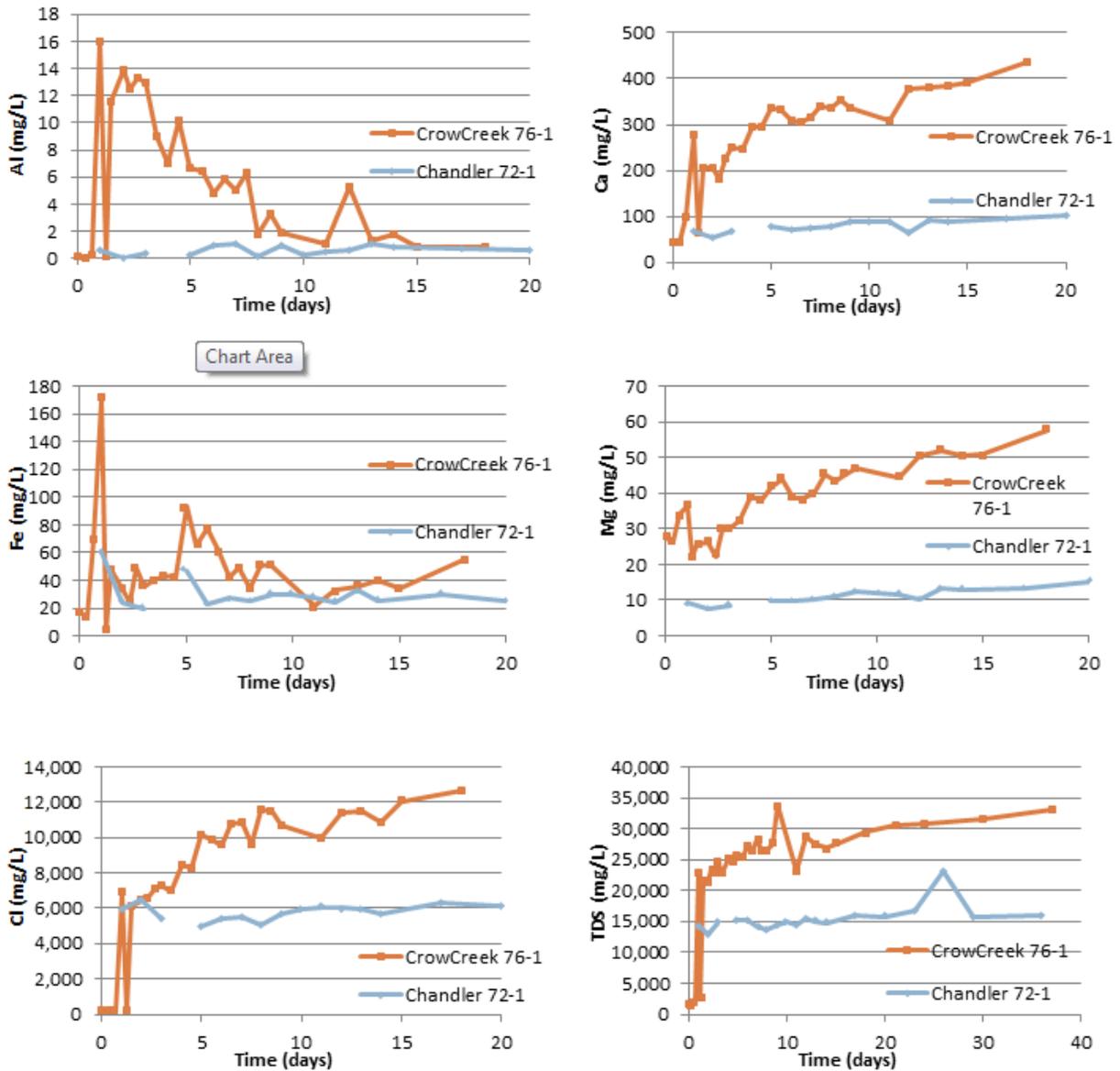


Figure 3.20: Selected Metals Results: Fresh Water Comparison

The Chandler State results show a much lower concentration for all metals. This can be seen in the TDS concentration, which is on average 10,000mg/L lower than the Crow Creek Concentrations. Temporally, the concentrations for divalent cations and chlorine do not increase as rapidly for Chandler as for Crow Creek.

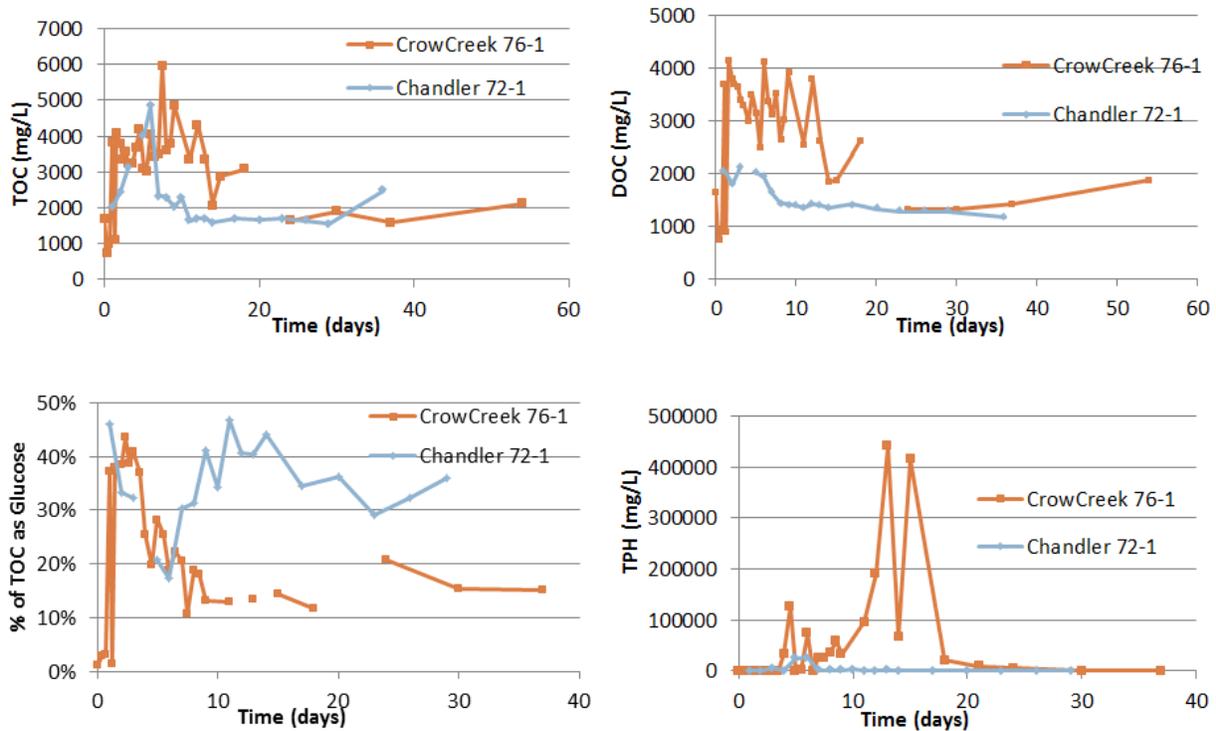


Figure 3.21: Selected Organics Results: Fresh Water Comparison

Overall, organic concentrations for the Chandler fresh wells are lower than that of the Crow Creek well. TOC and DOC follow similar temporal trends, but have lower concentrations than the Crow Creek well, with initial DOC concentrations around 2,000mg/L lower. %TOC as glucose is higher in the Chandler well, however the total glucose concentration is not higher, only the percentage of glucose with respect to the total carbon present.

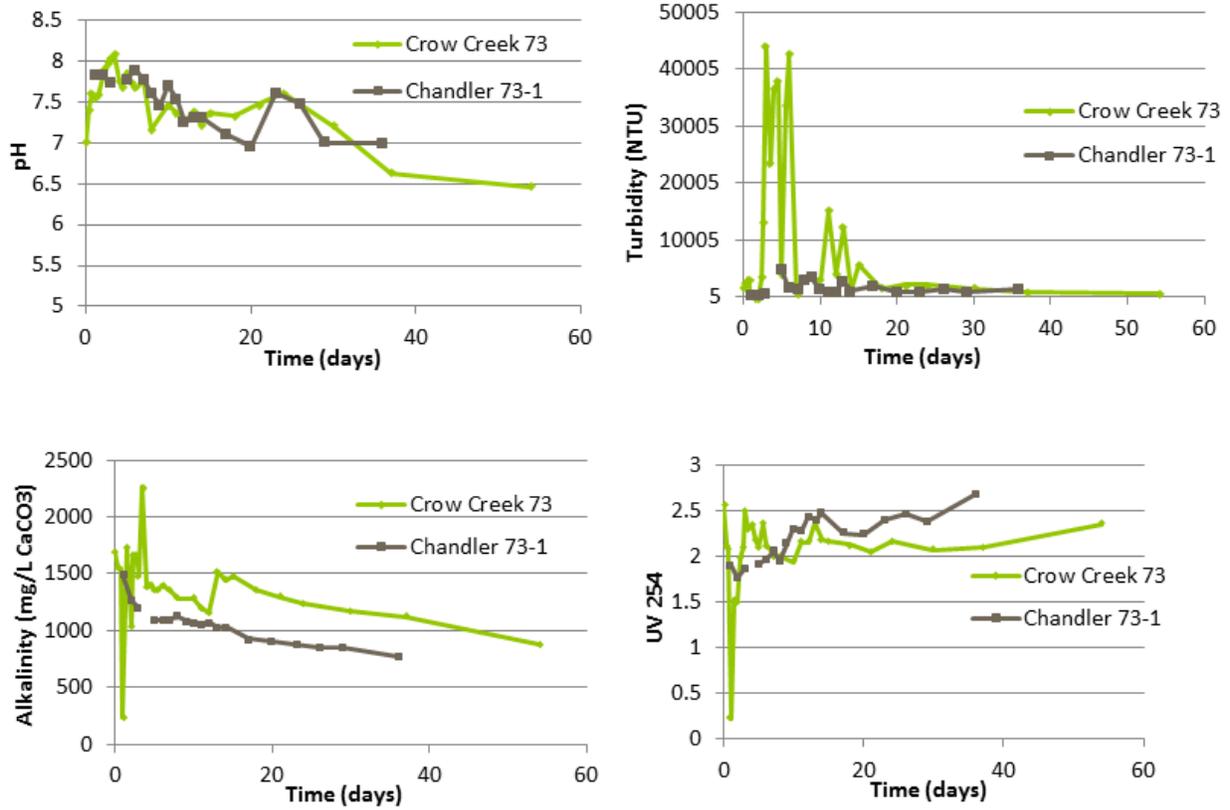


Figure 3.22: Selected Wet Chemistry: Recycled Comparison

The recycled wells had similar results as the fresh wells. Lowered alkalinity and turbidity, but similar temporal trends exist for all wet chemistry results.

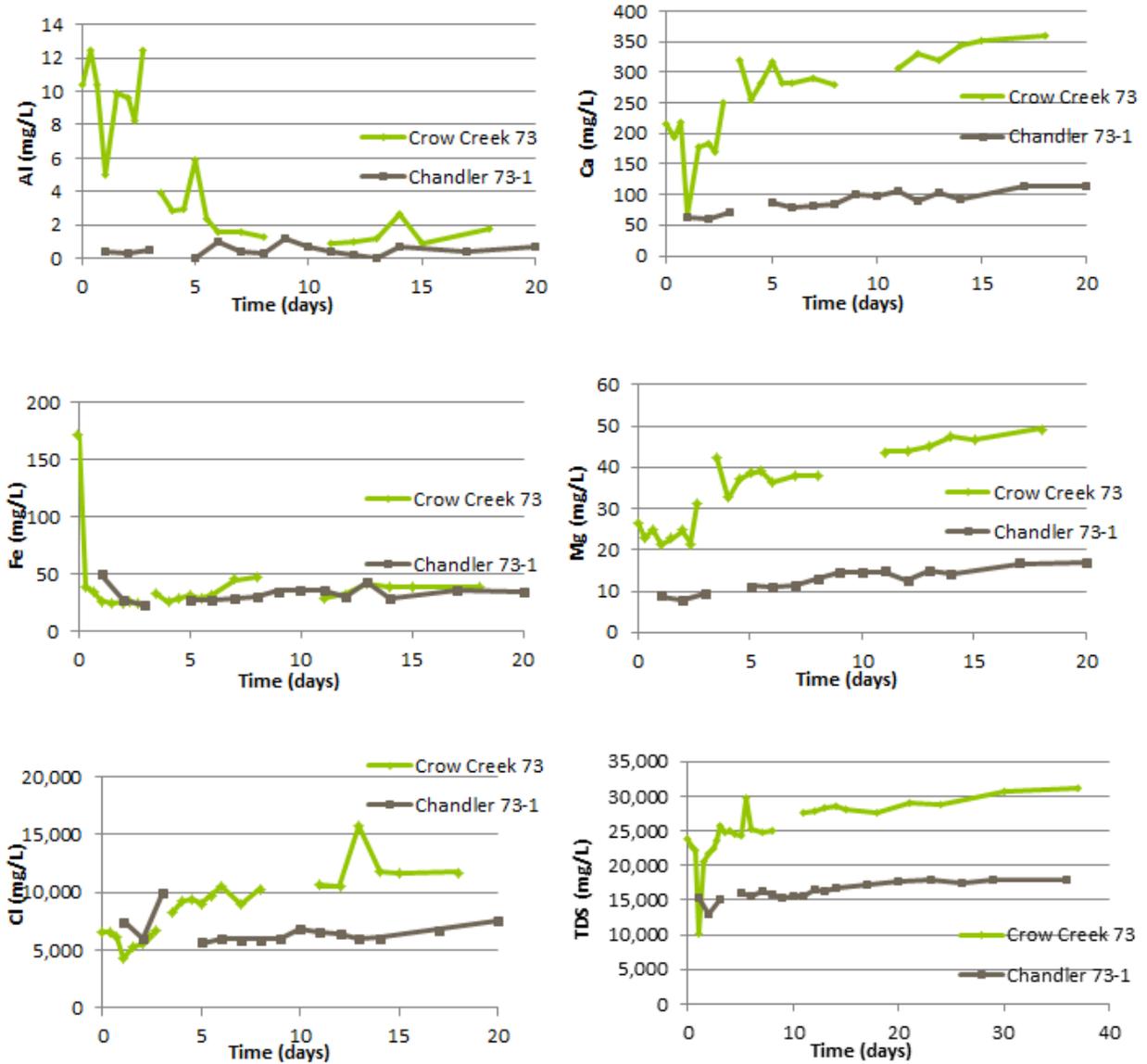


Figure 3.23: Selected Metals Results: Recycled Comparison

The recycled wells had the same results as the fresh wells, with Chandler having lowered metals concentrations and a lower TDS by about 10,000mg/L. Iron concentrations were similar and initial chlorine concentrations were similar, but diverged as time from start of flowback increased.

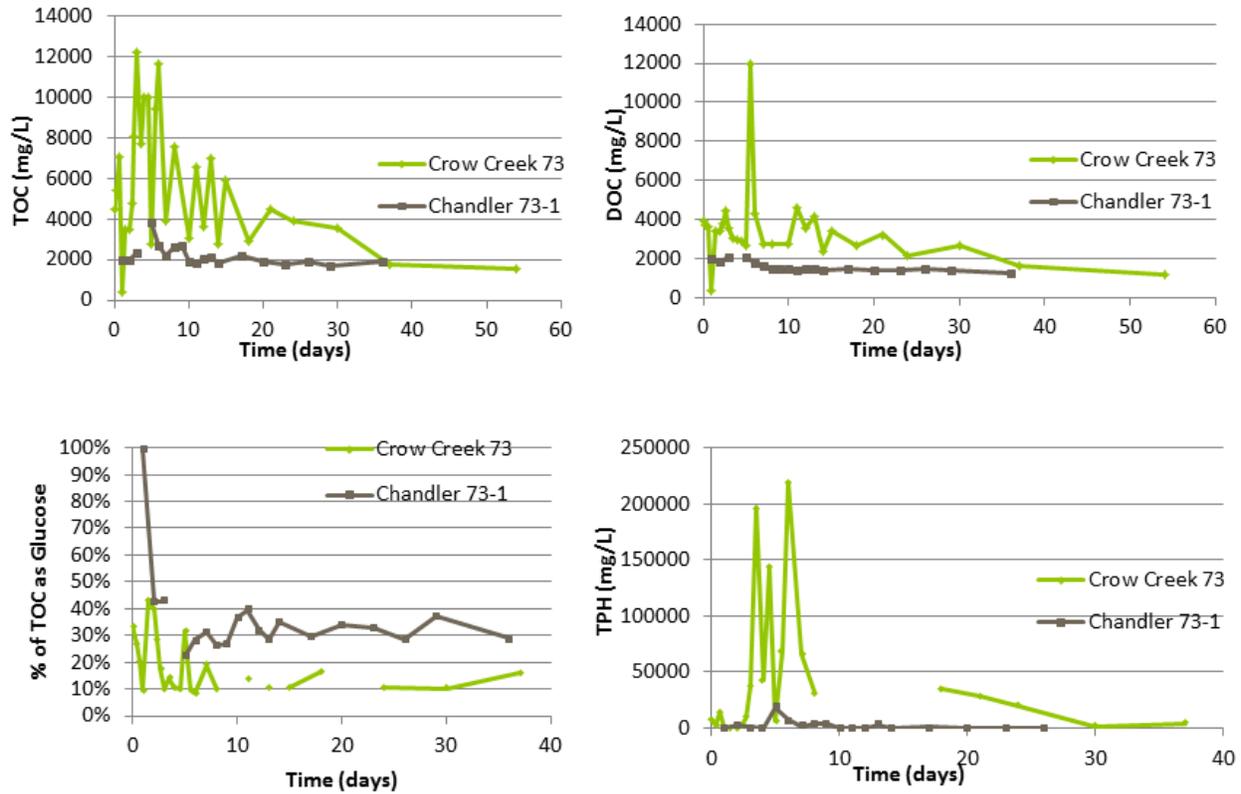


Figure 3.24: Selected Organic Results: Recycled Comparison

Organic concentration and TPH were lower for the recycled Chandler well. The % TOC as Glucose was also higher for the Chandler, much like the fresh well comparison.

3.5.3 Additional Wells Ranch Comparison

In addition to the Chandler and Crow Creek Studies, a previous study was conducted on wells ranch, comparing two wells, AE16-69 and AE16-68. AE16-69 was fractured with Fluid-B and AE16-68 was fractured with Fluid-A. Both wells were fractured with fresh water as a base fluid. The two wells had similar true vertical depths and were located directly next to each other on the same pad. The following figure shows comparisons of the Chandler, Crow Creek, and Wells Ranch fresh wells.

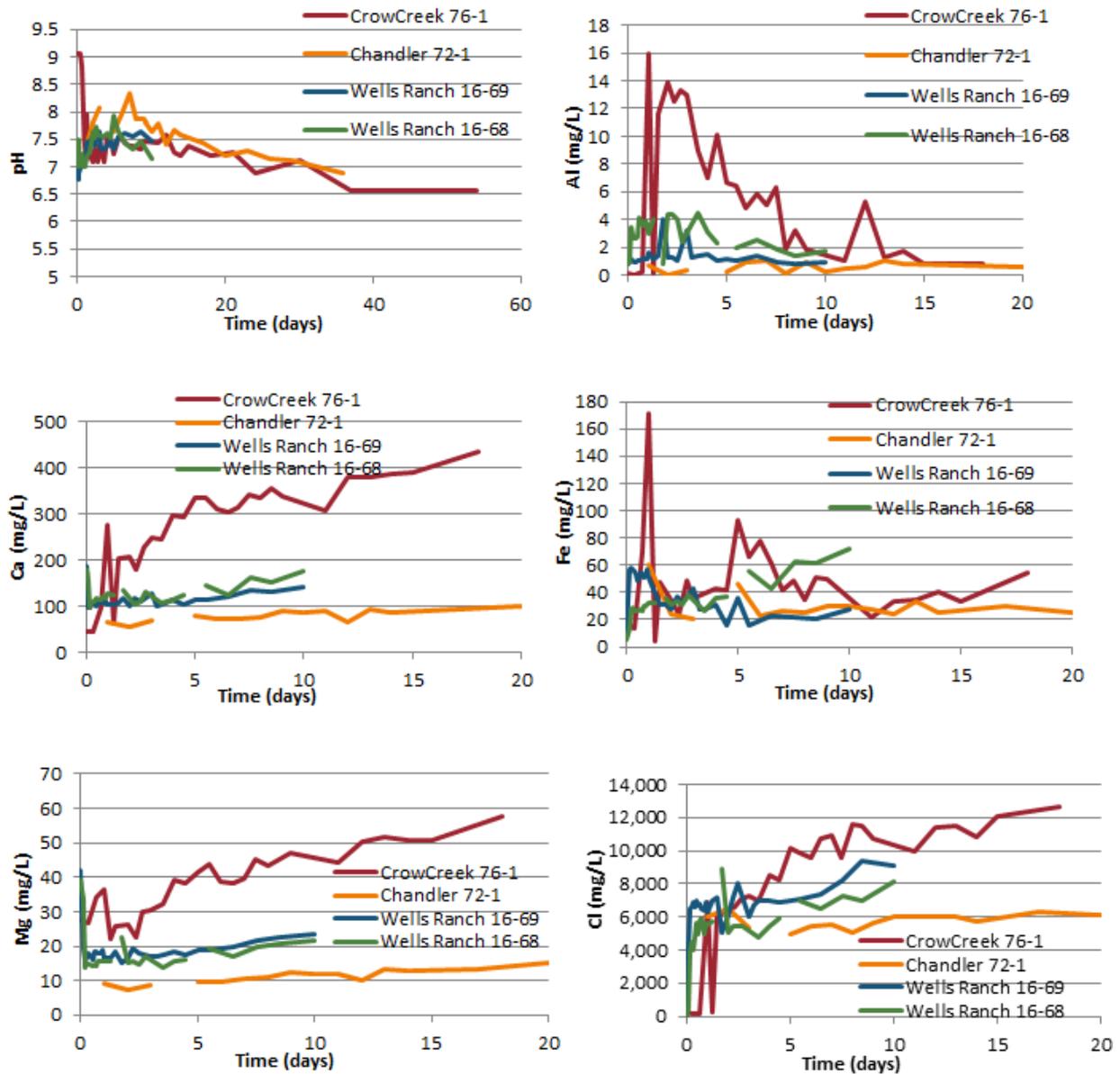


Figure 3.25: Selected Results: Three Site Comparison

The results of the 16-68 and 16-69 study were limited, but the metals and pH results show similar temporal trends as the Chandler and Crow Creek wells. All of the metals results show the Wells Ranch wells in between the Chandler and Crow Creek wells, except for Iron, which looks to have very similar concentrations between all four wells. It is important to note that the data for 16-68 and 16-69 only extends to ten days.

3.5.4 Chandler State Characterization Discussion

The results of the Chandler State Study seem to have consistent temporal trends with the results of the Crow Creek Study. As fracturing fluid influenced flowback moves towards formation influenced produced water, TDS increases and organic concentrations decrease. The interesting difference between the Chandler State and Crow Creek Study is that there was no discernable organic difference between the Chandler Wells. It appeared that the TOC, DOC, and Glucose concentrations were very similar between the wells. Observationally, there was also no discernable difference between the fresh and recycled wells. However, there was a difference in the metals results, showing the 5:1 with the highest divalent cation concentrations and the fresh well with the lowest divalent cation concentrations.

There are a number of possibilities for why the two studies did not have similar results. The first possibility is that the sample collection procedures were different between the two studies. At Crow Creek, samples were collected from the wellhead until day 28, when it was no longer feasible to collect from the wellhead. One reason for this was because there were no dedicated separators for each well at Crow Creek. At Chandler State, samples were collected post separation. This was done because separators were present for each well, but also because of the decisions made from the lessons learned at Crow Creek. Sampling reproducibility was challenging at Crow Creek. The nature of the oil and water cut from the well made for different samples every day. Some days, the water and free oil would separate within 5 minutes. Other days, it would take 30 minutes to get the same result. Because of this, it seemed appropriate to sample from the separator which, operationally, should be the same between each well. However, it is entirely possible that the separators did such a good job removing oil from water

that the inherent TPH and organic concentrations shown in the Crow Creek Study were removed before samples were collected at Chandler State.

Another possibility for differences between the two studies is Fluid-A vs. Fluid-B fracturing packages. Perhaps the recycled vs fresh differences can only be seen in the Fluid-A package. In an attempt to answer this, 16-68 and 16-69 results were included in this summary report. As shown, the differences in metals results between 68 and 69 was small, so it may seem that for fresh wells, the difference in fracturing fluid has no influence on water quality characteristics. Organic data for the Wells Ranch wells was not collected, so it is not possible to include TOC, DOC, or TPH in this report. It is also important to note that the Wells Ranch study was only for fresh wells. It may be that the difference in fracturing fluid has an influence when a blend of recycled water is used to fracture a well.

A third factor that may influence water quality is geographic location. Chandler State wells are closer to the core than the Crow Creek State wells. This results in a higher temperature in the fractured formation and a higher gas to oil ratio (GOR). It is possible that the recycled water interacts differently with the formation at a high GOR than a low GOR, explaining the differences in results between Crow Creek and Chandler. It is possible that the magnitude of the influence of recycled water on production surrogates in the water (TPH, emulsified oils, etc.) and inorganics (TDS, metals, etc) is more dependent on formational characteristics than previously thought.

4. INFLUENCE OF INORGANIC IONS ON HYDRAULIC FRACTURING FLUID VISCOSITY STUDY

4.1 Summary

This chapter contains the journal paper submitted to the Society of Petroleum Engineers. This study summarizes findings from research developed in collaboration between CSU, Noble, and Halliburton. The report has been modified to better match the formatting of the thesis. Proprietary information pertaining to fracturing fluid additives names and certain concentrations has been modified. Other than these changes, the study appears as whole.

In an effort to determine impacts of the increased use of treated produced water in new fracs, the rheology of two fracturing fluids, Fluid-A and Fluid-B was observed for varying water qualities. Specific Ions of interest were spiked at varying concentrations into tap water which was used as a base for the fluids. Apparent viscosities were measured using a Chandler 550 viscometer once fluids were created. Empirically, it was determined that at 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 stability until a critical concentration was reached, resulting in lowered viscosities and a less stable fluid. Fluid-A was more resilient to aluminum, potassium, and sodium, and other ions that negatively impacted stability than Fluid-B. Fluid-B also benefited from divalent cations more than Fluid-A. The effect of using concentrated gel hydrated with fresh water and then diluted with concentrated ion solutions was also evaluated and did not show any improvement in fluid stability. Finally, combinations of divalent and trivalent ions tested did not show conclusive results in the potential synergy of divalent and trivalent ions.

Theoretically, mechanisms of action were determined for the factors that influence fracturing fluid stability. It appears that specific cations compete for crosslink sites on the gel polymer either through shielding or complexing with active sites that the added crosslinker would normally complex with. This results in less crosslinked sites and a less stable fluid. In addition to crosslinked sites that an added crosslinker would complex with, hydrogen bonds can also make a weak crosslink. In the case of calcium and magnesium, the added cations displace hydrogen bonds and form a slightly stronger crosslink. However, this crosslink is not as strong as the ones made by the added crosslinker, and when a critical concentration of calcium or magnesium is reached; the cation competes with the added crosslinker as well, reducing fluid stability.

4.2 Introduction

A better understanding of how treated produced water quality influences the stability of hydraulic fracturing fluids is essential for exploration and production companies such as Noble Energy Inc. (Noble) to reduce their demand on local fresh water resources, while maintaining oil and gas production.

Characterizing the spectrum of water qualities that are likely to occur when using produced water from several potential sources (IDP operations), and is treated at varying fixed and mobile water treatment facilities, will allow Noble and Halliburton to optimize fracturing (frac) fluid formulations, water treatment operations, and management strategies for produced water that achieves acceptable frac fluid stability. This will also result in minimized treatment costs and reduced 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 such as Halliburton have been developing hydraulic fracturing fluids that are less sensitive to water quality, reducing treatment requirements and minimizing associated costs to the operator (LeBas, et al. 2011). 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, including Early Time Flow Back and Produced Water, 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/l (Acharya, et al. 2011) but tradeoffs may exist with these fluids when considering 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 possible (Pearce 2008). A limited number of reports have placed wide ranging water quality limits on other inorganic parameters (Boschee 2012), but no studies have examined the influence of specific water quality parameters beyond the scope of solids and a few inorganic parameters.

Recycled flowback and recycled 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 essential in the continued use of recycled water in practice. Table 4.1 outlines typical water quality concentrations seen in varying water sources for fracturing base water.

Table 4.1: Typical Water Quality Concentrations for Assessed Parameters.

mg/L	Municipal Water		Surface Water		Ground Water		Treated Produced Water		Early Time Flowback Water	
	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

The initial water quality parameters assessed were chosen based on anticipated impacts to the stability of frac fluid and the water quality treatment requirements as well as their prevalence in treated produced water. Iron and aluminum are commonly found in produced water originating either from the formation or as residuals from the coagulant used during the treatment process.

Divalent cations (calcium, magnesium, strontium, and barium) come from the formation and contribute to scaling and potentially interact with the frac fluid. Divalent cations can be removed by either an ion-exchange (which increases the TDS) or with chemical softening that includes raising the pH, metal precipitation and solid-liquid separation. The percent removal of specific divalent cations depends on the pH (and chemical additions). Understanding the influence of each divalent cation and TDS to fracturing fluid stability is critical to optimizing the design of water treatment processes.

The last two columns of the above table are of interest because of their increased use as recycled water for new fracs. Note the increased chloride and iron concentrations, resulting in a higher TDS concentration for treated produced water and flowback water.

4.3 Goals

The objective of this study is to characterize the influence of, and interactions between individual water quality parameters, and the potential mixtures of water quality parameters that would simulate produced water combinations, on the stability of specific fracturing fluid formulations that are preferred for use by Noble. The results of this study will provide data on the applicability of two frac fluids (Fluid-A and Fluid-B) used throughout Noble assets in the DJ Basin, allowing for more certainty in fluid performance when using varying amounts of treated produced water combinations in future frac operations.

An assessment of the water quality limits for Halliburton's Fluid-A and Fluid-B hydraulic fracturing fluids requires understanding several variables (e.g. water composition, frac fluid formulation, rheology testing and fluid stability under shear and bottom hole temperature conditions, retained conductivity, and their impact on well productivity), against a backdrop of potential water qualities representative of what will be seen in the field due to mixtures of recycled waters as a function of field logistics.

This study examines the influence of specific individual water quality components on the formulation and performance of frac fluids using fresh water as a base fluid. Specific individual water quality components will be incrementally elevated to the highest concentrations anticipated in the field.

4.4 Materials and Methods

4.4.1 Spiked Base Water Preparation

A base tap water was used to make samples of individual spiked ions at specific concentrations. Colorado State University (CSU) tap water was utilized in every test to minimize variability between samples. 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 4.2 contains an inventory list of all reagents added to CSU tap water for the study.

Table 4.2: Reagent inventory.

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

4.4.2 Fracturing Fluid Sample Preparation

Water samples were taken to the Halliburton fluids testing lab, where fracturing fluids were constructed. 1000mL of prepared water was poured into a blender where initial pH and temperature were noted. An initial pH range of 6.5-7.5 was required to hydrate gels. To achieve this, HCl or NaOH were used to adjust pH if needed. Each fluid was created using only the gels

and crosslinkers shown in Table 4.3. No other additives such as surfactants or breakers were used during the study. Table 4.3 outlines the ingredients used and their respective setpoints.

Table 4.3: Gel/Crosslinker Concentrations.

Fluid	Gel	Cross linker 1	Cross linker 2	Notes
Fluid-A	Gel-A 5.4g/1000mL (45ppt)	CL-1A 1.5ppt	CL-2A 0.75ppt	Low residue polysaccharide gel / Low pH system
Fluid-B	Gel-B 3.35g/1000mL (28ppt)	CL-1B 0.6ppt	CL-2B 0.2ppt	Guar gel/ High pH system

Gel was added to the 1000mL sample within a 30 second period and mixed for 9 minutes in a blender to allow for complete hydration. During blending, viscosities were measured to determine gel hydration efficiency. After blending, the samples were buffered to the desired pH noted in Table 4.3. Crosslinkers were added and final pH was recorded.

4.4.3 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. All samples created with this methodology are described as “[specific reagent] concentrate” in the results section.

A 90ppt gel was hydrated in 500mL of non-spiked tap water. After 12 minutes of hydration, 500mL of concentrate water was added to make a 1:1 dilution (Fresh: Spiked). Crosslinkers were added followed by the same rheological testing as all other samples.

4.4.4 Rheological Testing

High temperature rheological measurements were taken using a Chandler Model 5500 HPHT Viscometer with R1B1 configuration. The instrument is a concentric cylinder viscometer that measures apparent viscosity through the deflection of bob within the annulus of the rotor. 78mL of sample was used for each test. All tests began under 90°F, were increased to 200°F at 500psi within 10minutes, had a constant shear rate of 40 reciprocal seconds, and ran for 45.5minutes. Viscosity measurements were taken in one second intervals.

4.5 Results and Discussion

4.5.1 Baseline Testing

Initial baseline samples for each fracturing fluid were tested and used as a control for the study (Figures 4.1 and 4.2). 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.

In both Figures 1 and 2, split runs 1 and 2 were the same sample. One hour of wait time occurred between split runs 1 and 2 to determine if wait times impacted fracturing fluid rheology. For Fluid-A, the differences between split 1 and split 2 were negligible. However, the differences in Fluid-B were observable, resulting in a higher peak and final viscosity the longer the fluid sat before measurements took place. To prevent this source of error, all spiked samples were tested immediately after being made for the duration of this study.

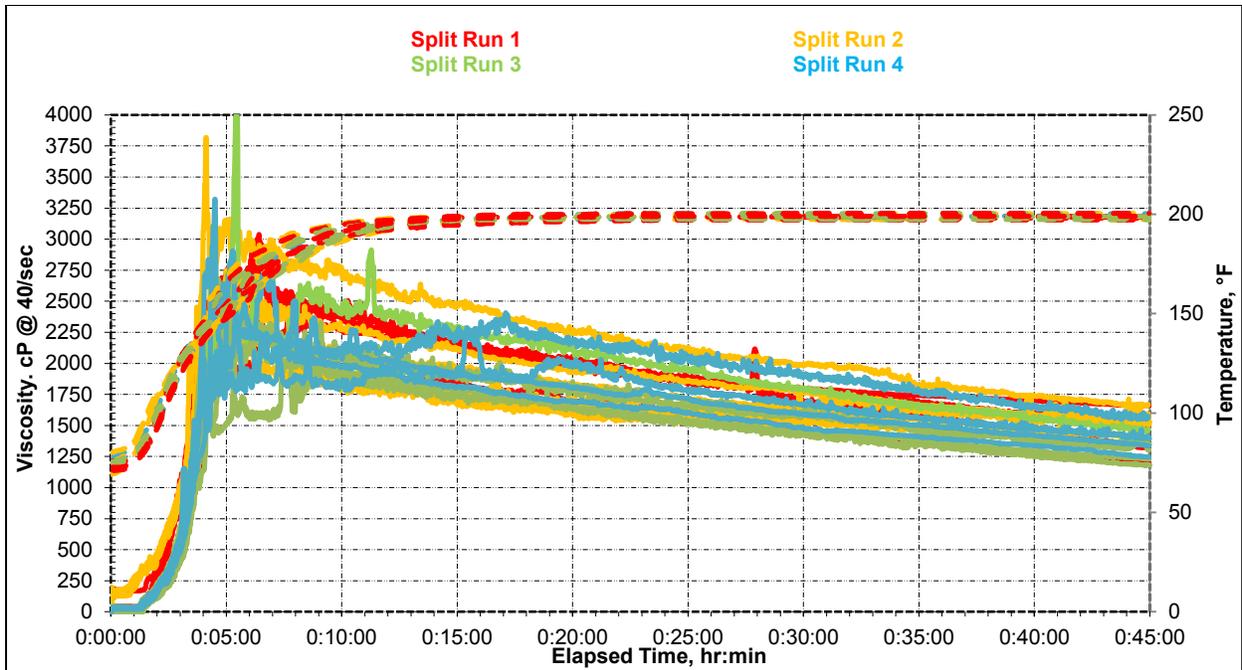


Fig. 4.1: Fluid-A Baseline Tests.

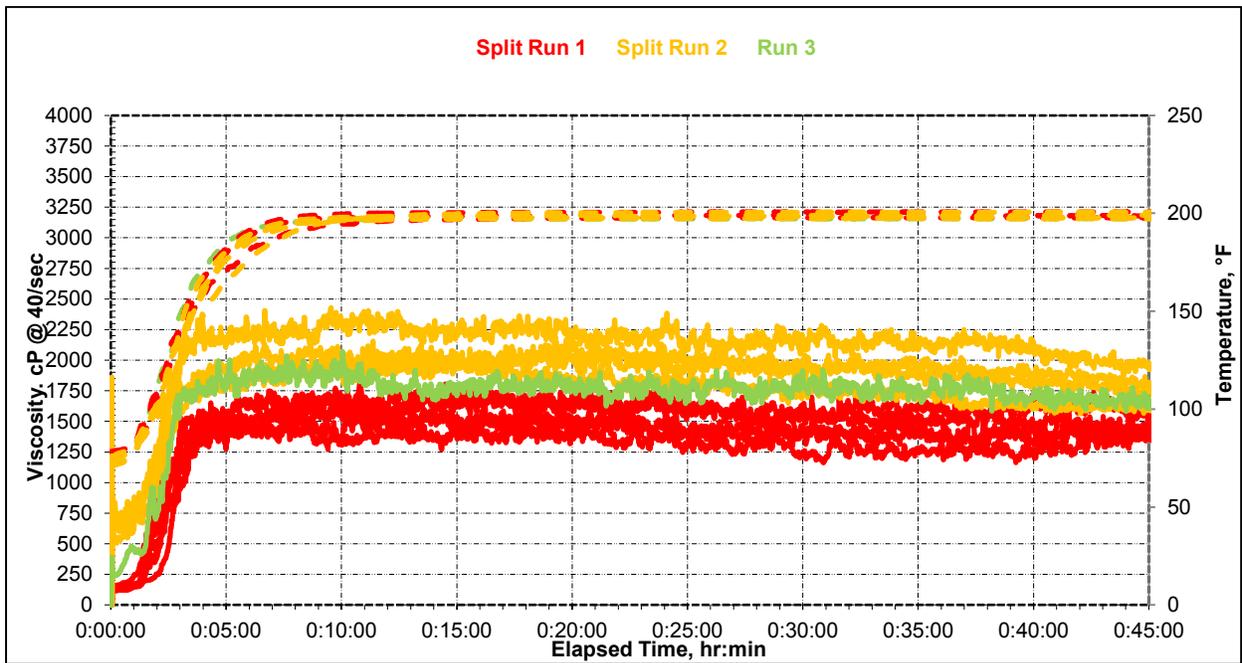


Figure 4.2: Fluid-B Baseline Tests.

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 trends- such as the linear decline in viscosity shown in the Fluid-A baseline tests. Criteria for an acceptable rheology run were determined. Table 4.4 shows the criteria used. By comparing the results of the spiked water with the baseline runs, it is possible to determine which ions impact fracturing fluid viscosity and which tests passed or failed. It is important to note that the baseline runs were constructed using optimized gel and crosslinker concentrations for recycled water. Baseline viscosity results are not entirely optimal since CSU tap water was used.

Table 4.4: Ranges for Acceptable Results

	Fluid-A	Fluid-B
Expected Initial Peak Viscosity (cp)	2200	1750
Minimum Acceptable (cp)	1500	1250
Expected Final Viscosity (cp)	1500	1500
Minimum Acceptable (cp)	1350	1000

4.5.2 Spiked Ions Results

Due to differences in gel formulations, crosslinkers, and their respective concentrations between the two fluid systems, ions had varying effects on each system. Table 4.5 summarizes the impact of each ion for the two fluid systems. 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 substantial difference in the trend when compared to the baseline tests.

Table 4.5: Summary of Ions' Effect Based on Spiked Concentrations.

Fluid-A					Fluid-B			
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		Substantial	15	20	Lowers Viscosity
Ammonium	None		50		Small		50	Increases Viscosity
Barium	None		15		None		15	
Bicarbonate	Small		3000	Increases Viscosity	Substantial	1500	1500	Lowers Viscosity
Boron	Small		25	Increases Viscosity	None		25	
Bromide	None		200		None		200	
Calcium	Substantial	600	600	Increases Viscosity	Substantial		400	Increases Viscosity
Iron	Substantial	75	125	Destabilizes Viscosity	Substantial	75	75	Lowers Viscosity
Magnesium	Substantial		125	Increases Viscosity	Substantial		125	Increases Viscosity
Nitrate	None		100		Small		100	Increases Viscosity
Phosphorus	Substantial	5	10	Destabilizes Viscosity	Substantial	5	10	Lowers Viscosity
Potassium	Substantial	9000	2400	Destabilizes Viscosity	Substantial	5000	9000	Destabilizes Viscosity

								city
Sodium	Substantial	9000	9000	Destabilizes Viscosity	Substantial	5000	5000	Destabilizes Viscosity
Strontium	None		60		Small		60	Increases Viscosity
Sulfate	None		1600		Substantial		1600	Increases Viscosity

Appendix B: Spiked Ion Results shows the results of the rheology tests summarized in Table 4.5 for Fluid-A and Fluid-B. Figures B.1 and B.2 show the effects of the trivalent cations, aluminum and iron, Figures B.3 and B.4 depict the effects of divalent cations, calcium and magnesium, Figures B.5 and B.6 show the impact of phosphorous, Figures B.7 and B.8 show the impact of sodium and potassium, and Figures B.9 and B.10 show the impact of a combinations of ions.

4.5.3 Mechanisms of Action

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 ions such as sodium and potassium do not reach a critical concentration until 7,000 or 9,000mg/L. Divalent ions calcium and magnesium actually improve the apparent viscosity of the fluid until a critical concentration produces the counter effect. Trivalents require even less of a concentration

to show an effect, and the pentavalent ion, phosphorous, has an impact at concentrations 1mg/l and 5mg/L.

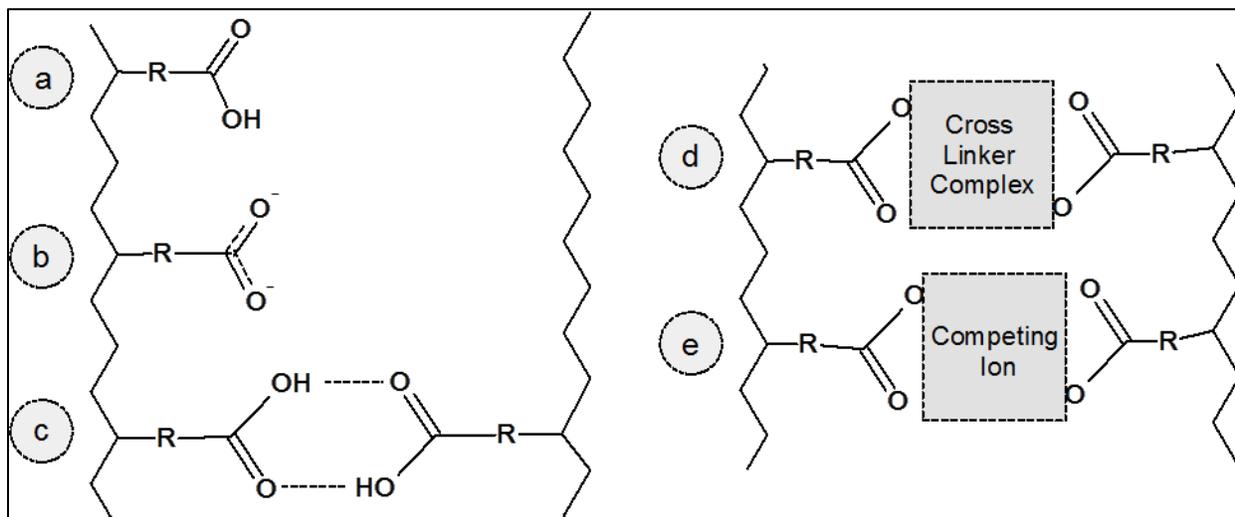


Figure 4.3: Crosslink Mechanisms

Figure 4.3a through 4.3e show possible crosslink mechanisms that occur in Fluids A and B. The initial viscosity of both Fluid-A and Fluid-B is created through hydrating gel in water. Gels are typically derived from guar gum or cellulose. 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. (Lei, Clark 2004, Putzig, Clair, 2007) Due to the carboxymethylation process, functional carboxylic acid groups exist on the polymer chain (Fig. 3a). At pH's of 4.8 and above, this functional group begins to dissociate and form reactive carboxylate anions (Fig. 3b). Once formed, carboxylate anions can self-associate to form carboxylic acid dimers (Fig. 3c). These dimers employ the use of weak hydrogen bonds, but do increase the fluids viscosity. A crosslinker can be added to replace the weak hydrogen bonds with much stronger bonds (Fig. 3d) 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 sites (Montgomery 2013). In the presence of spiked ions, a competition for available carboxylate sites may occur (Fig. 3e). 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.

For divalent cations calcium and magnesium, competition for carboxylate sites improves apparent viscosity initially. As the gel hydrates in the fluid, the divalent cation first competes with hydrogen bonding (Fig. 3c). Although the divalent crosslink is not as strong as the complexed metal crosslink (Fig. 3d), it still improves stability more than the hydrogen dimers. It is not until the concentration approaches a critical point that the divalent cations interfere with the metal crosslinker as well, resulting in a lowered viscosity.

Trivalent cations do not exhibit this same 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. 3e) 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 inactive. Whichever scenario exists, it is clear that the aluminum and iron do not behave in the same way as the calcium and magnesium. 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.

In addition to the mechanisms previously shown, shielding may take place. The monovalent ions potassium and sodium exhibit this effect. Previous studies have shown that in

the presence of high salt concentrations, the ability of the polymer to disentangle is greatly reduced, reducing fluid viscosity (Khaled, Abdelbaki 2012). 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. Tables C.1 and C.2 in *Appendix C: Gel hydration and summary results tables* show the results of viscosity readings from the gel hydration of each test. 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. The more negative the weighted error, the lower the hydration viscosity of the gel at each measurement interval. As seen in the tables for both fluids, sodium and potassium lower the ability of the gel to hydrate, further supporting the theory that shielding is taking place.

In an attempt to minimize the impact of monovalent ions, the concentrate method described in the methods section was used. Based on the results shown in tables C.3 and C.4, the negative impact from monovalent ions is either not fully understood, or still took place after the concentrated ion solution was added into the already hydrated gel.

4.5.4 Summary of Results

Tables C.3 and C.4 include a summary of the results for the two fracturing fluids built. Each ion at each specific concentration represents a single run.

From the results of the summary tables, Fluid-A is affected by fewer ions, or at least has a higher tolerance for certain ions, but both fluids are affected by ions that are prevalent in recycled waters. Based on the results as well as typical concentrations found in Table 4.1, it appears that TDS (sodium) concentrations may be the limiting factor in recycled water use for

new frags. Dilution or reverse osmosis would be among the few solutions for creating a base fluid that would yield acceptable results.

4.5.5 Combination Results

Table 4.6 summarizes the results of the divalent and trivalent combination runs. The table includes calculated ionic strengths for divalent and trivalent cations. Ionic strength is a function of the concentration and charge number of all ions in each solution. The results of the combination runs and their ionic strengths were compared to previous single ion runs.

Table 4.6: Combination Results

Run	Ions (mg/L)	Fluid-A	Fluid-B	Calculated Ionic Strength (Divalent)	Calculated Ionic Strength (Trivalent)
Reference 1	Ca 600	Fail	Pass	2.99E-02	0.00E+00
Reference 2	Fe 75	Fail	Fail	0.00E+00	6.04E-03
Reference 3	Al 15	Pass	Fail	0.00E+00	2.50E-03
Combination 1	Al 7.5, Fe 25	Pass	Pass	0.00E+00	3.27E-03
Combination 2	Al 15, Fe 75	n/a	Pass	0.00E+00	8.55E-03
Combination 3	Ca 200, Mg 75, Ba 5, Sr 30	Fail	Pass	1.69E-02	1.69E-02
Combination 4	Ca 400, Mg 125, Ba 15, Sr 60	Fail	Pass	3.18E-02	0.00E+00
Combination 5	Al 7.5, Fe 25, Ca 200, Mg 75, Ba 5, Sr 30	Fail	n/a	1.69E-02	3.27E-03
Combination 6	Al 7.5, Fe 25, Ca 400, Mg 125, Ba 15, Sr 60	n/a	Pass	3.18E-02	3.27E-03
Combination 7	Al 15, Fe 75, Ca 400, Mg 125, Ba 15, Sr 60	n/a	Fail	3.18E-02	8.55E-03

Based on the calculated ionic strengths, Combination 1 or 2 should not have passed for the Fluid-B, Combination 3 should not have failed for Fluid-A. Combinations 5 through 7 were used to determine if a synergistic effect of divalent with trivalent could allow for higher iron or

aluminum concentrations without failure. However, it is not possible to determine this since combinations 1 and 2 passed even without the divalent cations.

A source of error is that it is impossible to study a cation or anion of interest without adding a counterbalancing ion. For every sodium or iron ion added, a counterbalancing anion, usually chloride, was added to solution. In the cases where chloride or sodium was the counterbalancing ion (except for the TDS runs), the concentration of chloride was far below a concentration that showed an impact in the TDS runs. In the TDS runs, it is difficult to determine if the sodium, potassium, or chloride ions were the impactful ion, but based upon the mechanisms discussed, it appears that cations are the reactive ions.

4.6 Conclusions and Future Work

The interaction between ions was not studied in depth in this report, and individually spiked ions in tap water along with a few combinations are not a complete representation of typical recycled water. The purpose of this study was to provide an initial working database on ions that impact fracturing fluid stability. Frac fluid testing was done only with gel and crosslinkers. Surfactants, breakers, and other chemicals were not included to limit variables in the study.

It is important to understand the limitations of this study when making any conclusions of ions and their impacts. The results of this study should be used as a guide for ions and their concentrations that may possibly impact fracturing fluid stability. It appears that calcium, iron, magnesium, phosphorous, potassium and sodium have an impact on Fluid-A viscosities. The above mentioned ions as well as aluminum, strontium, and sulfate appear to impact Fluid-B viscosities. Differences in valence states between ions vary the impacts that ions have on fluid stability. Higher valence state ions require lower concentrations to reach critical concentrations.

Not only do concentrations vary, but the behavior of ions and their subsequent impact on fluid stability varies between valence states.

For future work, the addition of surfactants and breakers should be considered as well as organic loadings. The spiked CSU tapwater had minimal organic matter concentration. In reality, recycled water, especially that of early time flowback, has elevated organic loadings. Total organic carbon concentrations can be over 10,000mg/L in some cases. Since a majority of these organics are in the dissolved state, they contribute to overall total dissolved solids. Also, more complex mixtures should be made that accurately model the entire inorganic TDS of recycled water. Attempting to model the entire recycled water quality instead of individual ions should give a better empirical understanding of combinations of ions.

4. CONCLUSIONS

Conclusions in this chapter are made from both studies' results. The conclusions made are with respect to specific well sites and fracturing fluids, and may not accurately reflect other wells or fracturing fluids.

1. As time progresses over the flowback period, water quality becomes more consistent. Noise exists in the early time flowback for all wells, whether or not they are recycled or fresh wells.
2. Inorganic water quality characteristics such as dissolved ion concentrations in flowback and produced water do not vary between recycled and fresh wells.
3. For wells in region 1 (Crow Creek site), total organic carbon (TOC) concentrations were observed to differ between recycled and fresh wells. Recycled wells showed a TOC concentration 8,000mg/L higher for some samples when compared to samples on the same day from fresh wells.
4. Differences in TOC occur due to observed higher emulsified oil content in recycled wells' water. Higher oil emulsions could be indicative of recycled water fracturing fluids more closely matching the ionic character of the formation, resulting in the potential for improved production.
5. Recycled wells did not have a higher concentration of residual frac fluid than that of fresh wells. By measuring total carbohydrate as glucose, it was seen that there was no difference in residual frac fluid concentrations between fresh and recycled wells.

6. For wells in region 2 (Chandler State site), there were no observable differences in inorganic or organic characteristics between recycled and fresh wells. Flowback and produced water samples from all wells had very little emulsified oils. This can be seen in the similarities of the lowered turbidity results between all three wells on the Chandler State site.
7. By observing the similarities in water quality of the Wells Ranch wells, it can be determined that variability between fracturing fluid designs do not contribute to differences in return water quality. However, geographic location does contribute to water quality differences, as all three sites had dissimilar results. As well locations move closer to the core of the formation, inorganic ion concentrations decrease in return water.
8. Based on treatment results, it was shown that for early time flowback, ferric at 1,000mg/L was a better treatment option than ACH. There was an observed direct correlation between TOC and optimum coagulant dose. As TOC concentrations decreased with time, the coagulant dose required also decreased.
9. Specific ionic limitations for two widely used fracturing fluids were found, such as an iron limit of 75mg/L for Fluid-A and a TDS limit of 5,000mg/L for Fluid-B.
10. A mechanism of action for ion interactions with fracturing fluid gels and crosslinkers has been proposed. Competitive complexing at active sites and ionic shielding can reduce fluid stability. Replacing hydrogen bonds with divalent cationic complexes can improve stability.

5. FUTURE WORK

1. Due to sampling constraints and well scheduling, variables such as fracturing fluid methods, recycled water dilutions, and geographic locations were not able to be isolated for proper analysis. Future study of water quality comparisons should look to minimize variables between wells to allow for a one to one comparison of each variables impact on flowback and produced water quality. By limiting variability, future work could look to understand spatial variability between water qualities on a deeper level.
2. When determining ionic influence on fracturing fluid rheology, the addition of surfactants and breakers should be considered, as ions may impact or alter their behaviors.
3. In reality, flowback and produced water have organic characteristics such as residual gels and hydrocarbons. Studying the potential impact of these organic components is essential in understanding the overall impact recycled water has on fracturing fluid stability. Possible studies could increase a base fluids total petroleum hydrocarbon concentration to model produced water. Researchers could also spike a base fluid with broken residual gel to better model flowback water.
4. Simulating entire water qualities of flowback and produced water and not just specific ions or combinations of ions could give a better empirical understanding of combinations of ions and their associated impacts on fracturing fluid rheology.

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APPENDIX A: WATER QUALITY CHARACTERISTICS

Table A.1: Summary of Water Quality Characteristics- Crow Creek

		AC36-73HN			AC36-76-1HN			AD31-79HN			AC36-73-1HN		
		PRIMARY RECYCLED			PRIMARY FRESH			SECONDARY RECYCLED			SECONDARY FRESH		
Characteristic	Unit	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max
pH		7.5	6.5	8.1	7.4	6.6	9.1	7.2	6.9	7.6	7.4	7.0	7.7
TOC	(mg/L)	5486	362	12170	3108	759	5982	4523	1928	12040	3768	2026	9184
DOC	(mg/L)	3059	366	4596	2722	741	4155	2623	1315	4610	2687	1647	3703
COD	(mg/L)	37308	1340	126400	22209	2350	79600	33750	10150	62100	21487	8330	43339
Turbidity	(NTU)	10364	33	43990	2658	46	15130	10063	53	43339	6672	60	33430
Total Carbohydrates	(mg/L glucose)	2335	86	3745	1794	41	3882	1984	821	3937	2010	815	3374
UV254	Absorbance	2.066	0.224	2.560	1.985	0.491	2.443	2.271	2.111	2.428	2.082	1.660	2.352
Alkalinity	mg/L CaCO3	1366	234	2264	1223	240	1722	1367	1160	1698	1360	1120	1608
TS	(mg/L)	27067	10260	33360	23965	1540	32560	29668	23900	34740	27280	19880	32280
TDS	(mg/L)	25339	10240	31160	23529	1420	33760	27768	23460	30000	27250	19940	31540
TSS	(mg/L)	650	22	1542	466	21	1329	444	22	900	363	21	605
TVS	(mg/L)	6345	360	10100	4306	540	8300	5820	2540	9220	4480	2460	8180
VDS	(mg/L)	4650	340	9300	3913	480	10940	4388	2000	8180	3947	2160	6180
VSS	(mg/L)	614	4	1524	437	5	1332	429	6	862	348	6	591

Al	(mg/L)	5.0	0.9	12.5	5.7	0.1	16.0	6.2	1.8	10.7	6.3	1.0	11.6
Ba	(mg/L)	2.1	0.4	4.8	2.2	0.1	5.6	2.0	1.5	2.2	1.7	0.6	3.6
Ca	(mg/L)	263	64	359	274	43	435	289	203	380	284	191	421
Fe	(mg/L)	39	24	171	48	4	171	57	52	65	37	28	48
Mg	(mg/L)	35	21	49	39	22	58	38	27	52	35	19	56
Mn	(mg/L)	0.6	0.2	2.8	0.6	0.2	1.6	0.7	0.6	0.9	0.4	0.3	0.5
Na	(mg/L)	5939	3029	10199	5241	107	8053	6447	4643	7599	7845	7108	8563
Sr	(mg/L)	31.3	6.5	49.1	32.3	0.1	60.4	28.5	21.9	40.6	29.6	15.2	45.2
Zn	(mg/L)	0.1	0.0	0.8	0.1	0.0	0.4	0.2	0.0	0.4	0.1	0.0	0.3
Cl	(mg/L)	8530	4289	11791	8146	163	12689	9273	6641	11929	8586	6035	12464
HCO3	(mg/L)	1406	488	3660	1022	63	1925	1952	854	3660	5417	756	12444
SO4	(mg/L)	369	322	436	368	316	446	357	318	387	394	317	497
GRO	(mg/L)	186841	19	969426	51358	4	439792	21839	541	57008	4711	14	13247
DRO	(mg/L)	2293	93	6238	967	7	6302	897	76	3072	365	31	1042
ORO	(mg/L)	365	12	1260	107	6	434	118	53	168	45	7	101
TPH	(mg/L)	182489	0	971803	52248	26	440997	22825	617	57149	4984	14	13294
Benzene	(ug/L)	163191	332	628373	84071	11	542895	87655	13155	211256	26434	1983	59848
Toluene	(ug/L)	456571	664	2221141	223244	53	1258858	282729	12724	690125	67961	1652	155184
Ethylbenzene	(ug/L)	166191	46	879530	74539	38	437914	82784	1216	184484	21111	167	47997
Total Xylenes	(ug/L)	518715	303	2883968	238604	206	1327321	250248	6397	517514	67243	1287	145630
BTEX	(mg/L)	1305	1	6517	576	0	3284	703	33	1603	183	5	409

Table A.2: Water Quality Summary- Chandler State

		D15-72-1HN			D15-73-1HN			D15-74-1HN		
		Fresh Water			Recycled (7:1)			Recycled (5:1)		
Characteristic	Unit	Average	Min	Max	Average	Min	Max	Average	Min	Max
pH		7.618333	7.11	8.33	7.51	6.96	7.88	7.348824	6.17	8.99
TOC	(mg/L)	2242.167	1555	4845	2185.5	1691	3856	1985.948	80.06	2549
DOC	(mg/L)	1552.889	1272	2125	1588.889	1371	2084	1523.229	87.13	2037
Turb	(NTU)	1347.167	176	5216	1567.056	137	4854	1126.889	7	2636
Carbs	(mg/L glucose)	1823.091	1248.299	2518.367	1890.727	1329.932	4852.381	1734.454	87.7551	2214.286
% Glucose	(as Carbon)	34.83%	17.40%	46.83%	36.31%	22.19%	99.64%	28.07%	0.00%	41.92%
UV254	Absorbance	2.101407	1.883	2.293667	2.179963	1.761	2.475	1.991294	0.2503	2.525
Alkalinity	mg/L CaCO₃	1114.667	904	1464	1063.556	856	1488	943.7778	432	1296
TS	(mg/L)	15138.82	9020	17260	16695.56	12900	18820	19562.22	14920	40060
TDS	(mg/L)	15354.12	12960	23080	16188.89	12880	17960	17924.44	14420	22840
TSS	(mg/L)	362.4706	48	1229	229.5556	44	532	230.7222	129	500
TVS	(mg/L)	4208.235	2900	6920	4015.556	2860	5600	4941.111	940	24480
VDS	(mg/L)	3903.529	2800	5420	3628.889	2760	4840	3547.778	780	4700
VSS	(mg/L)	352.2353	25	1208	219.2222	23	513	216.7222	41	474
Al	(mg/L)	0.612533	0.112	1.06	0.542571	0.238	1.18	0.6726	0.146	1.09
B	(mg/L)	14.43125	10	19.3	14.90063	9.51	20.4	16.34125	4.96	20.4
Ba	(mg/L)	4.661875	3.03	6.24	6.1875	3.93	8.1	6.28125	1.51	8.91

Br	(mg/L)	29.4375	25	34	32.9375	27	50	34.375	27	40
Ca	(mg/L)	80.225	53.8	101	90.725	60.9	115	117.75	78.9	148
Fe	(mg/L)	29.55625	20	60.4	32.79375	23.4	50.3	22.96519	0.543	33.6
K	(mg/L)	52.8875	39.5	92.3	70.95625	51.5	95.8	289.8	60.3	3399
Mg	(mg/L)	11.29125	7.45	15.2	12.9925	7.95	17	16.875	10	22.3
Na	(mg/L)	3677.375	2878	4323	4269	3341	7156	4313.438	2339	5356
Si	(mg/L)	45.28125	33.5	52.5	45.09375	34	52.3	46.90188	3.83	59.6
Sr	(mg/L)	12.19625	7.7	16	13.905	8.44	18.6	17.7775	9.34	24.8
Zn	(mg/L)	0.694	0.269	1.29	1.310875	0.388	6.72	1.037563	0.292	2.95
Cl	(mg/L)	5831.563	4980	6590	6710.938	5630	9985	7072.813	5540	9070
NH₄	(mg/L)	16.875	10	22	17.8125	12	24	25.5625	14	130
HCO₃	(mg/L)	1093.73	927.2	1476.2	1044.091	878.4	1195.6	915	512.4	1049.2
SO₄	(mg/L)	27.53333	5	53	28.0125	5	72	43.7125	4.4	268
GRO	(mg/L)	3511.293	5.39	26376	2043.347	67.2	9643	1269.72	66.8	5721
DRO	(mg/L)	869.1067	20.4	7723	733.6333	13.7	7409	283.2533	24.3	1301
ORO	(mg/L)	247.3723	6.825	1552	203.2483	5.18	1476	63.16429	6.8	210
TPH	(mg/L)	4496.149	5.39	27012.83	2742.392	0	18528	1511.181	0	7209

APPENDIX B: SPIKED ION RESULTS

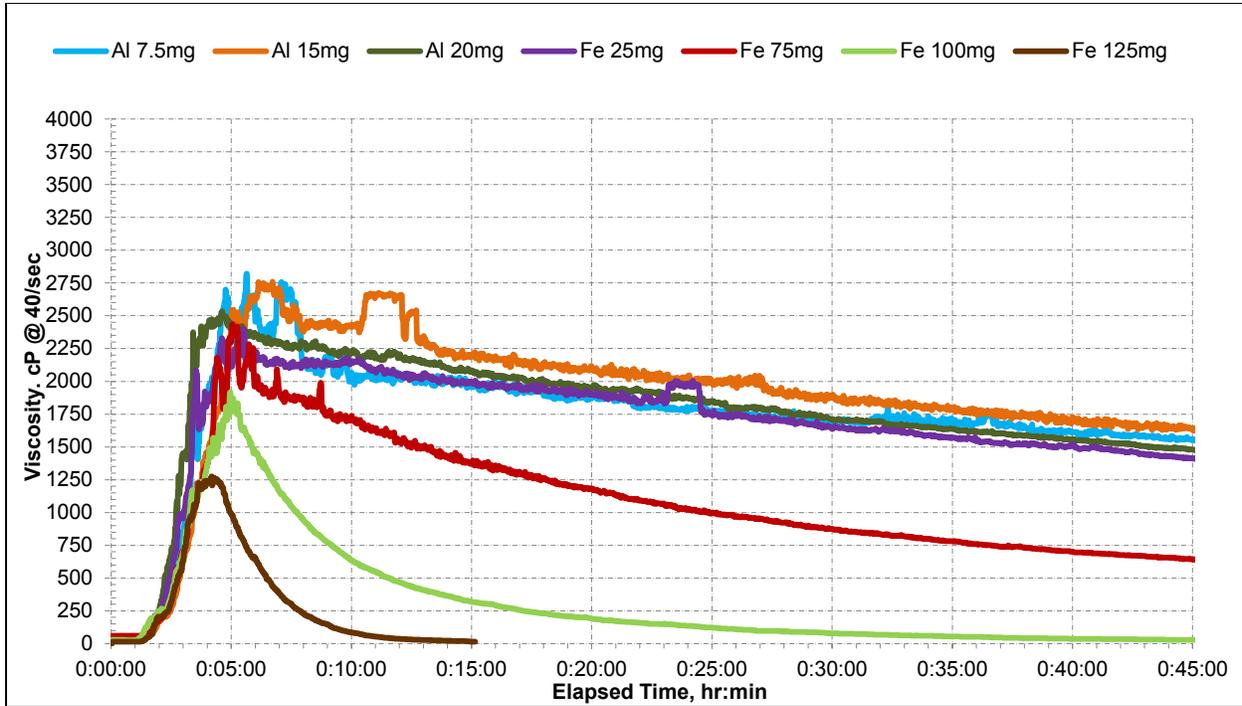


Figure B.1: Fluid-A Aluminum and Iron Results

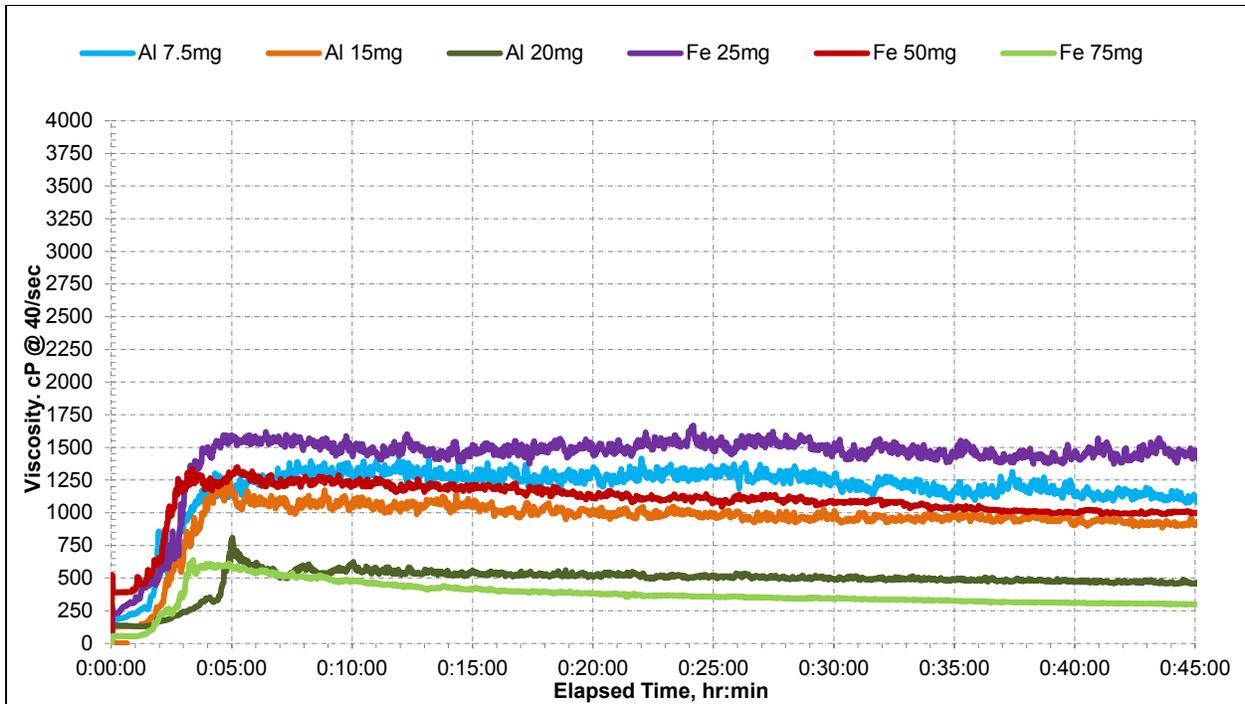


Figure B.2: Fluid-B Aluminum and Iron Results.

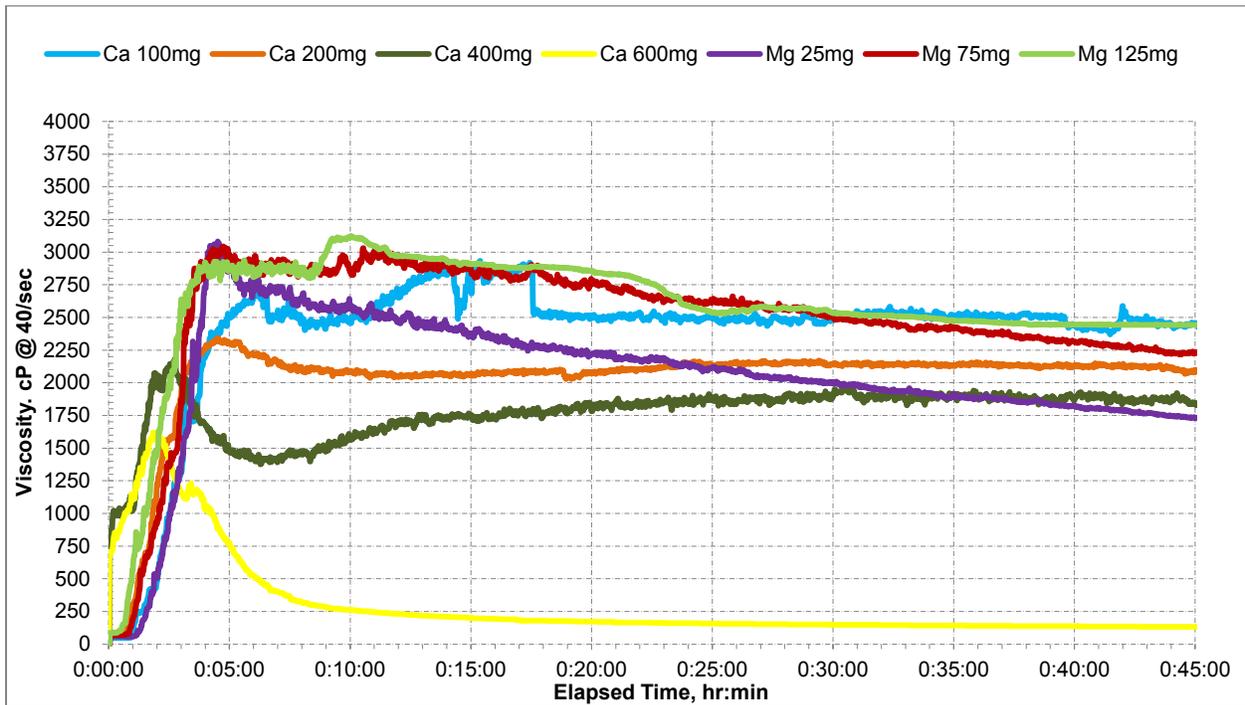
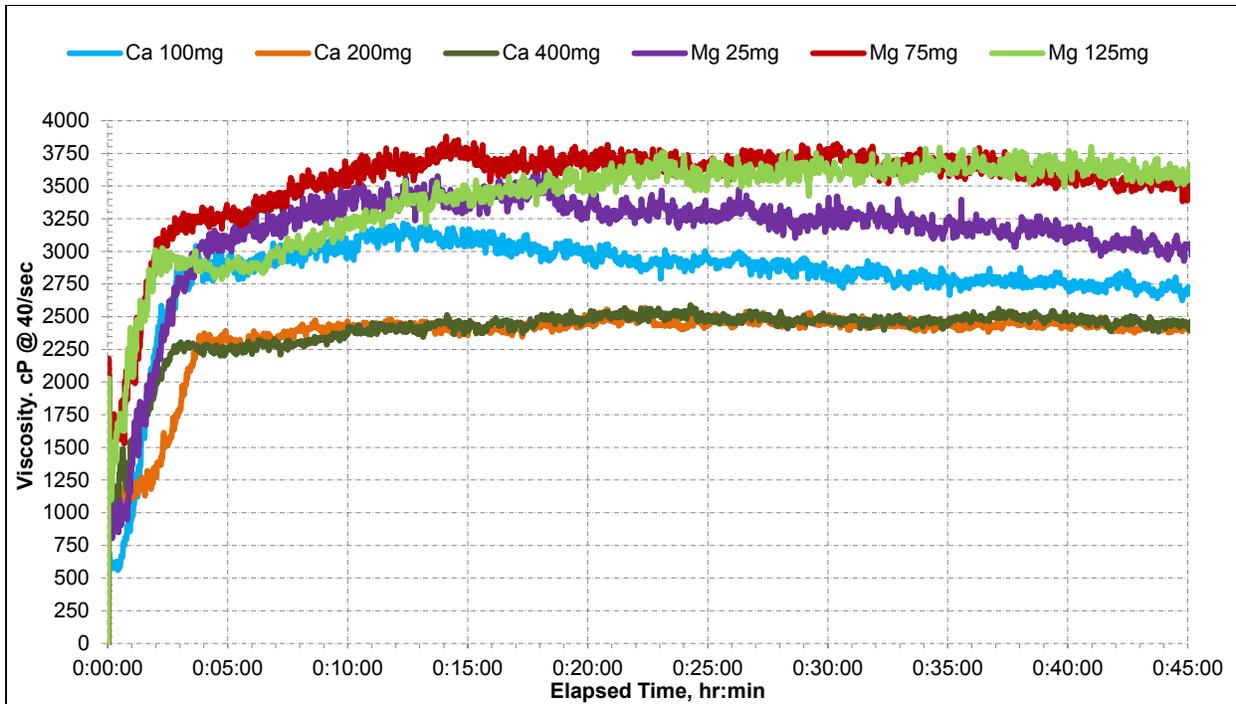


Figure B.3: Fluid-A Calcium and Magnesium Results.



FigureB.4: Fluid-B Calcium and Magnesium Results

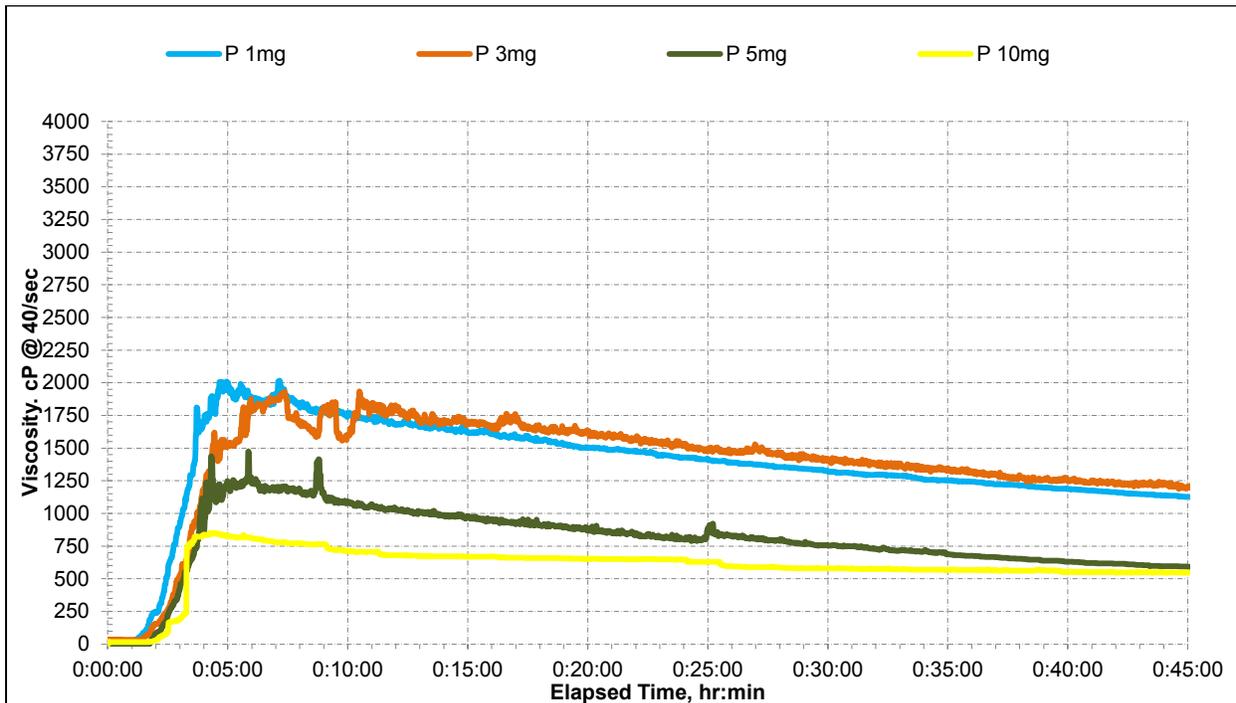


Figure B.5: Fluid-A Phosphorous Results

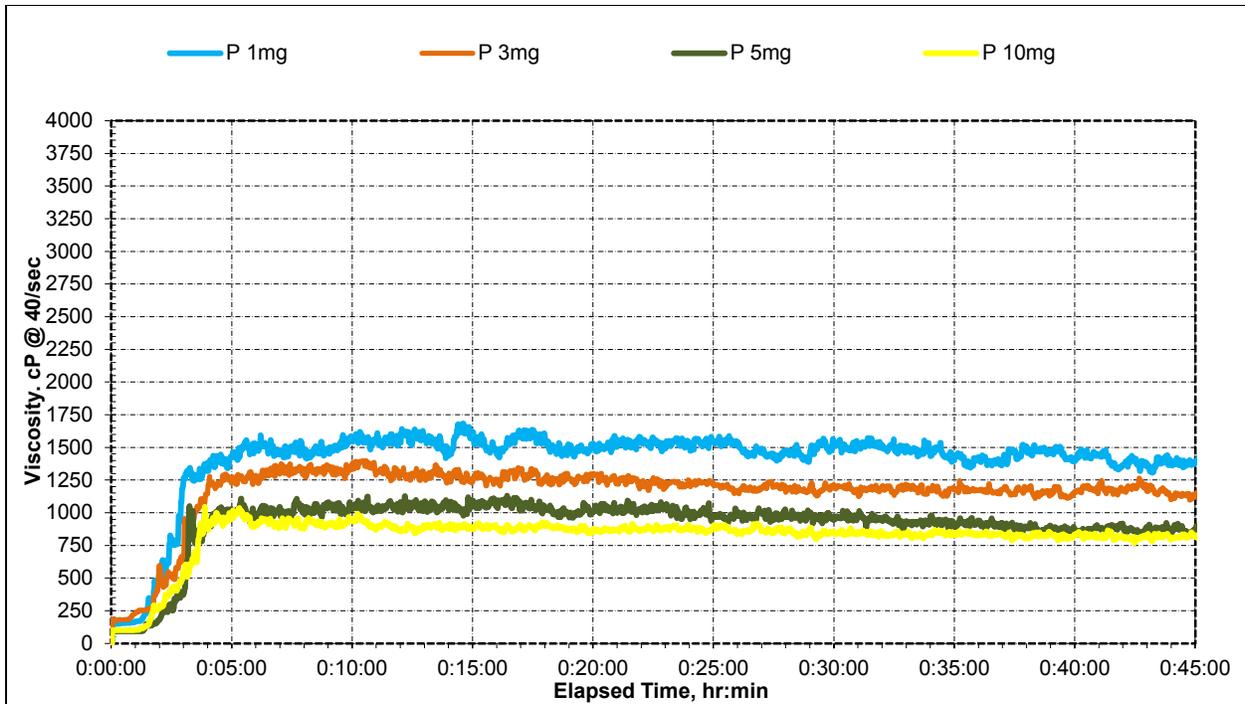


Figure B.6: Fluid-B Phosphorous Results

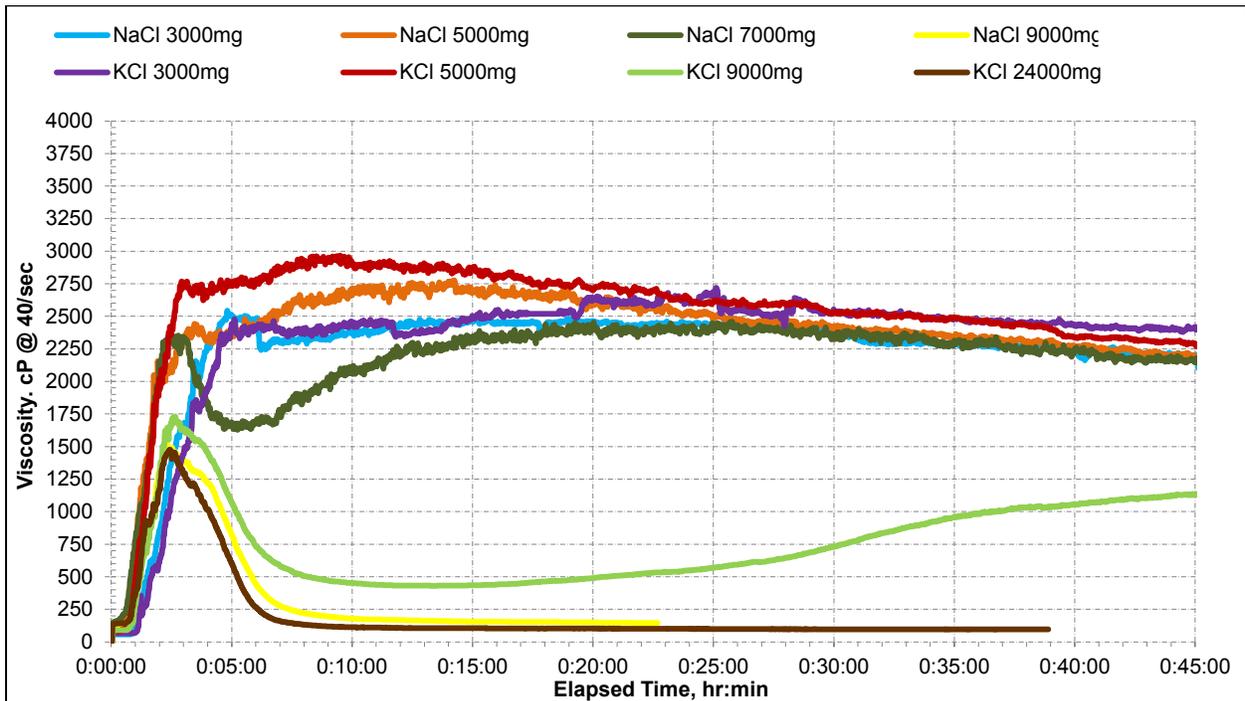


Figure B.7: Fluid-A Potassium and Sodium Results.

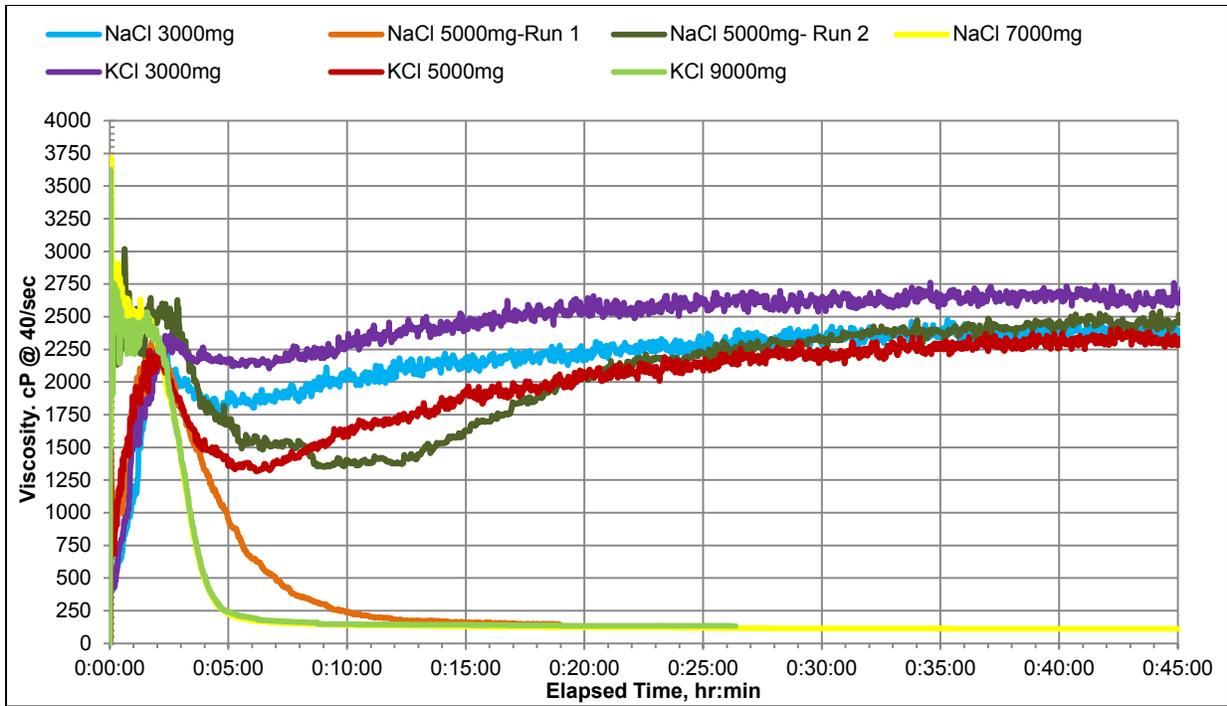


Figure B.8: Fluid-B Potassium and Sodium Results.

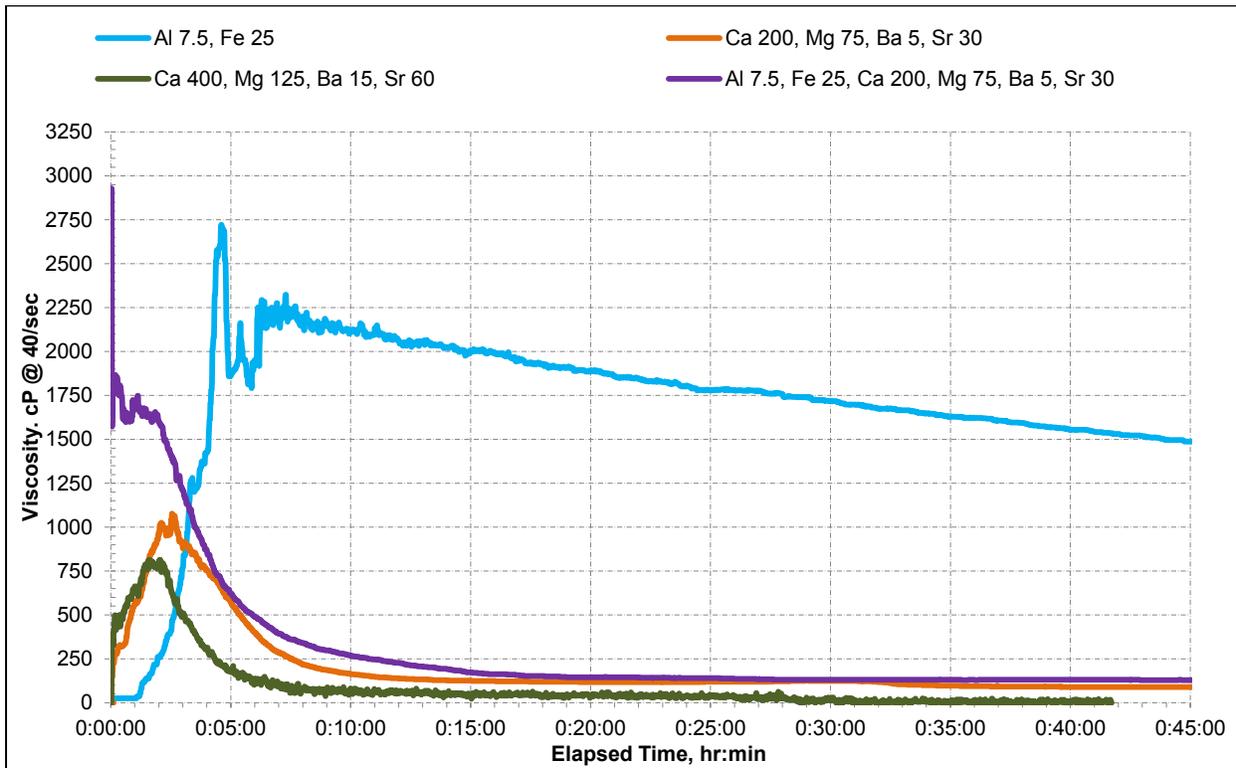


Figure B.9: Fluid-A combination results

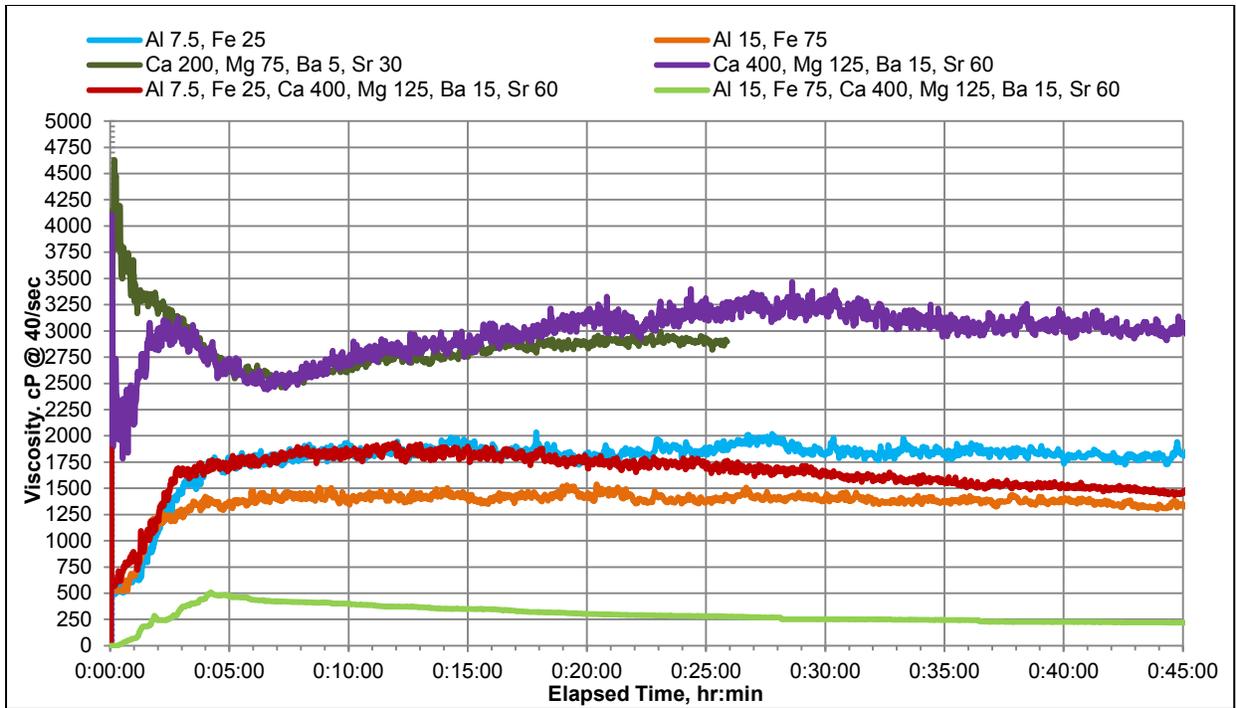


Figure B.10: Fluid-B combination results

APPENDIX C: GEL HYDRATION AND SUMMARY RESULTS TABLES

Table C.1: Fluid-A Gel Hydration Results.

Ion	Concentration (mg/L)	Weighted Error
Boron	25	1.7
Phosphorous	1	0.9
Boron	15	0.8
Aluminum	20	0.7
Barium	5	0.6
Phosphorous	5	0.6
Boron	25	0.5
Iron	25	0.5
Phosphorous	10	0.5
Aluminum	7.5	0.3
Iron	75	0.2
Aluminum	15	-0.1
Boron	5	-0.3
Iron	75	-0.5
Strontium	60	-0.5
Strontium	10	-0.6
Bromide	200	-0.7
Ammonium	20	-1.0
Barium	15	-1.1
Iron	100	-1.1
Barium	2	-1.5
Magnesium	25	-1.9
Combination 1		-2.1
Iron	125	-2.2
Bicarbonate	500	-3.5
Calcium	100	-4.1
Nitrate	100	-4.3
Phosphorous	3	-4.4
Sulfate	800	-4.8
Sulfate	1600	-5.3

Magnesium	75	-5.7
Calcium	200	-5.9
Magnesium	125	-6.1
Magnesium	125	-6.3
Ammonium	50	-6.8
Sulfate	400	-7.3
NaCl	3000	-7.3
KCl	3000	-7.5
Calcium	400	-7.7
Bicarbonate	1500	-7.7
Bicarbonate	3000	-8.8
KCl	5000	-9.2
Iron Concentrate	75	-10.6
NaCl	7000	-10.7
NaCl	5000	-10.8
NaCl Concentrate	9000	-10.8
NaCl Concentrate	7000	-11.0
KCl	9000	-11.3
Iron Concentrate	125	-11.8
NaCl	3000	-11.9
KCl	24000	-12.7
Calcium	600	-12.8
NaCl	9000	-13.4
NaCl	9000	-13.7
Combination 5		-13.9
Combination 3		-14.2
Nitrate	50	-15.1
NaCl	5000	-16.0
NaCl	7000	-17.0
Combination 4		-17.5

Table C.2: Fluid-B Gel Hydration Results

Ion	Concentration (mg/L)	Weighted Error
Combination 2		7.5
Combination 6		2.5
Aluminum	15	1.0
Aluminum	20	0.9
Phosphorous	5	0.9
Phosphorous	1	0.8
Combination 4		0.7
Barium	5	0.7
Bromide	50	0.7
Bromide	100	0.4
Barium	15	0.3
Aluminum	7.5	0.2
Combination 7		0.2
Phosphorous	3	0.1
Nitrate	25	0.1
Iron	25	0.0
Boron	5	-0.1
Phosphorous	10	-0.1
Barium	2	-0.2
Strontium	30	-0.3
Boron	15	-0.3
Nitrate	50	-0.3
Ammonium	25	-0.3
Boron	25	-0.5
Strontium	60	-0.6
Strontium	10	-0.7
Magnesium	125	-0.8
Ammonium	50	-0.9
Nitrate	100	-0.9
Sulfate	400	-1.1

Bromide	200	-1.2
Combination 1		-1.2
Ammonium	20	-1.3
Bicarbonate	500	-1.4
Magnesium	25	-1.4
Calcium	100	-1.7
Iron	50	-1.9
Bicarbonate	1500	-2.3
Sulfate	800	-2.5
Calcium	400	-2.7
Magnesium	75	-2.9
Iron	75	-3.6
Calcium	200	-4.2
Sulfate	1600	-4.3
NaCl	3000	-5.0
KCl	3000	-5.0
NaCl	3000	-6.0
Combination 3		-6.3
NaCl	4000	-6.7
KCl	5000	-7.6
NaCl	5000	-8.0
NaCl	5000	-9.5
NaCl	9000	-10.3
KCl	9000	-12.0

Table C.3: Fluid-A Results Summary Table

Ion	Concentration (mg/L)	Peak Viscosity (cp)	Time (min)	Final Viscosity (cp)	Pass/Fail?
Aluminum	7.5	2820	0:05:38	1548	Pass
Aluminum	15	2760	0:06:43	1639	Pass
Aluminum	20	2532	0:04:37	1475	Pass
Ammonium	20	2097	0:04:54	1366	Pass
Ammonium	50	2104	0:05:08	1252	Pass
Barium	2	3307	0:09:47	2009	Pass
Barium	5	2367	0:06:44	1409	Pass
Barium	15	2839	0:05:13	1762	Pass
Bicarbonate	500	2198	0:05:59	1129	Pass
Bicarbonate	1500	2436	0:04:46	1204	Pass
Bicarbonate	3000	2215	0:04:44	1226	Pass
Boron	5	2980	0:04:51	2041	Pass
Boron	15	2002	0:04:50	1068.72	Pass
Boron	25	3310	0:06:28	1931	Pass
Boron	25	3240	0:05:04	1274	Pass
Bromide	200	2311	0:10:29	1365	Pass
Calcium	100	2933	0:15:23	2455	Pass
Calcium	200	2342	0:04:29	2088	Pass
Calcium	400	2185	0:02:45	1798	Pass
Calcium	600	1620	0:01:50	130	Fail
Iron	25	2401	0:05:31	1408	Pass
Iron	75	2436	0:05:03	638	Fail
Iron	100	1916	0:04:57	29	Fail
Iron	125	1276	0:04:11	15	Fail
Iron Concentrate	75	1812	0:08:37	465	Fail
Iron Concentrate	125	1225	0:03:24	16	Fail
Magnesium	25	3082	0:04:31	1720	Pass
Magnesium	75	3043	0:04:44	2213	Pass

Magnesium	125	2507	0:04:03	1985	Pass
Magnesium	125	3120	0:10:00	2438	Pass
Nitrate	50	2292	0:04:19	1518	Pass
Nitrate	100	2642	0:06:06	1517	Pass
Phosphorous	1	2015	0:07:09	1122	Fail
Phosphorous	3	1934	0:10:29	1189	Fail
Phosphorous	5	1474	0:05:51	589	Fail
Phosphorous	10	849	0:04:15	547	Fail
Potassium	3000	2719	0:25:06	2409	Pass
Potassium	5000	2967	0:09:30	2289	Pass
Potassium	9000	1729	0:02:39	1146	Fail
Potassium	24000	1475	0:02:25	96	Fail
Sodium	3000	2544	0:04:49	2047	Pass
Sodium	3000	3337	0:04:45	2111	Pass
Sodium	5000	2775	0:14:14	2187	Pass
Sodium	5000	2165	0:13:24	1750	Pass
Sodium	7000	2457	0:25:42	2148	Pass
Sodium	7000	2156	0:09:32	1580	Pass
Sodium	9000	1527	0:02:15	145	Fail
Sodium	9000	2051	0:02:15	1443	Pass
Sodium Concentrate	7000	2505	0:02:51	2304	Pass
Sodium Concentrate	9000	2020	0:03:15	329	Fail
Strontium	10	2391	0:06:15	1365	Pass
Strontium	30	2499	0:06:51	1340	Pass
Strontium	60	3380	0:04:31	2143	Pass
Strontium	60	2824	0:05:45	1587	Pass
Sulfate	400	3130	0:07:00	2043	Pass
Sulfate	800	3267	0:22:40	2434	Pass
Sulfate	1600	2767	0:10:19	1790	Pass

Table C.4: Fluid-B Results Summary Table.

Ion	Concentration (mg/L)	Peak Viscosity (cp)	Time (minutes)	Final Viscosity (cp)	Pass/Fail?
Aluminum	7.5	1415	0:22:00	1124	Pass
Aluminum	15	1238	0:04:56	918	Fail
Aluminum	20	808	0:05:02	457	Fail
Ammonium	20	1793	0:25:10	1521	Pass
Ammonium	25	1484	0:03:52	1311	Pass
Ammonium	50	2198	0:21:34	1801	Pass
Barium	2	1461	0:15:56	1154	Pass
Barium	5	1681	0:09:12	1421	Pass
Barium	15	1572	0:14:35	1289	Pass
Bicarbonate	500	1457	0:22:31	1111	Pass
Bicarbonate	1500	869	0:15:35	726	Fail
Bicarbonate Concentrate	500	1544	0:04:40	1424	Pass
Bicarbonate Concentrate	1500	1170	0:04:09	1046	Pass
Boron	5	1922	0:11:33	1640	Pass
Boron	15	1674	0:16:20	1478	Pass
Boron	25	1923	0:14:08	1551	Pass
Bromide	50	1598	0:14:01	1364	Pass
Bromide	100	1731	0:03:04	1336	Pass
Bromide	200	1858	0:01:47	1409	Pass
Calcium	100	3215	0:12:19	2701	Pass
Calcium	200	2569	0:22:22	2441	Pass
Calcium	400	2588	0:24:16	2409	Pass
Iron	25	1667	0:24:09	1462	Pass
Iron	50	1348	0:05:14	989	Pass
Iron	75	639	0:03:24	299	Fail
Iron Concentrate	75	590	0:04:43	321	Fail
Magnesium	25	3620	0:17:54	2972	Pass
Magnesium	75	3880	0:14:06	3508	Pass
Magnesium	125	3799	0:40:58	3546	Pass

Nitrate	25	1707	0:10:20	1285	Pass
Nitrate	50	3851	0:12:32	3098	Pass
Nitrate	100	2659	0:13:59	2242	Pass
Phosphorous	1	1683	0:14:36	1445	Pass
Phosphorous	3	1398	0:10:35	1153	Pass
Phosphorous	5	1131	0:16:26	892	Fail
Phosphorous	10	1045	0:03:53	832	Fail
Potassium	3000	2761	0:34:34	2660	Pass
Potassium	5000	2407	0:42:28	2341	Pass
Potassium	9000	3626	0:00:02	132	Fail
Sodium	3000	5335	0:00:02	3586	Pass
Sodium	5000	2676	0:00:04	116	Fail
Sodium	3000	2477	0:35:18	2451	Pass
Sodium	5000	2317	0:01:47	145	Fail
Sodium	9000	4410	0:00:03	91	Fail
Sodium Concentrate	5000	3076	0:00:03	120	Fail
Strontium	10	2385	0:11:34	2129	Pass
Strontium	30	1961	0:11:02	1729	Pass
Strontium	60	2186	0:07:47	1786	Pass
Sulfate	400	2322	0:14:52	2065	Pass
Sulfate	800	2911	0:15:56	2593	Pass
Sulfate	1600	2729	0:31:30	2593	Pass