

ANALYSIS OF WATER BASED FRACTURE FLUID FLOWBACK TO
DETERMINE FLUID/SHALE CHEMICAL INTERACTION

A Thesis

by

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ABSTRACT

Concerns about the substantial amounts of water and chemicals pumped into the subsurface during hydraulic fracturing are valid because long term effects of these stimulation actions are unknown at the present time. Although less than 1% of the hydraulic fracturing fluid composition is made up of the various chemicals, reactions are likely to occur when said chemicals are in contact with other elements from the rock.

To reduce the amount of water being used in these fracture treatments, flowback from stimulated reservoirs are considered as base fluid to prepare additional fracture fluid. However, in order re-use the fluid, it must be treated appropriately since the produced waters are chemically altered. Hence, the changes that ensue in both the rock and fluid have to be studied and quantified where possible.

Shale samples from the Barnett, Eagle Ford and Marcellus were exposed to a cross-linked gel composition for 1, 5, 10 and 30 days at simulated reservoir conditions (elevated temperature and pressure). Collected samples were sent to a commercial laboratory for analysis. Concentration of the cations, anions and dissolved metals in the fluid were measured before and after contact with the rock to establish any reactions that might have taken place.

To uncover the effects of hydraulic fracturing treatment on the different rock types, the mineralogy was determined using X-Ray fluorescence (XRF). Also, tests of total organic content (TOC) were performed to ascertain what kinds of changes may have affected the elements within the rock. Differences in measured quantities of

cations, anions etc. confirm that chemical reactions occur. Furthermore, the variations observed between the base fluid and those exposed to the different shale types corroborate that the different composition of elements in the rocks can be correlated to the different concentrations of measured properties of the simulated flowback.

DEDICATION

I dedicate this thesis to my Dad, Cyprian O. Agim who always believed in me and supported all my dreams.

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Finally, special thanks to my Husband and family for their unrelenting prayers and continuous encouragement.

NOMENCLATURE

BBL	Barrels
CEC	Cation Exchange Capacity
EF	Eagle Ford
FF	Fracture Fluid
HF	Hydraulic Fracturing
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
lb	Pounds
Mgal	Thousand gallons
TOC	Total Organic Carbon
XRD	X- Ray Diffraction
XRF	X- Ray Fluorescence

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1. INTRODUCTION

Unconventional resources are those that, owing to low reservoir permeability or fluid properties cannot be produced at economic flow rates or in economic volumes unless the well is stimulated by a large fracture treatment, drilled horizontally, or treated with a special recovery method. (Holditch 2009). These previously avoided resources are fast becoming the solution to the increased demand for power generation and fuels. Advances in horizontal drilling, multilateral laterals and hydraulic fracturing (HF) technologies have revolutionized the oil and gas business.

The major difference between conventional and unconventional resources is that conventional resources, though small in volume, are easy to produce from the reservoir, while unconventional resources (tight-gas sands, coal-bed methane, oil and gas shales, heavy oils and hydrates) are in large volumes, but are difficult to develop. Today, unconventional resources play a huge role in the contribution to the energy needs; natural gas wells are able to produce economically, even in ultra-tight sands and shale formations, heavy oils are mined or produced with enhanced oil recovery methods and more efficient completion techniques to improve the economical production from shale oil wells are constantly being perfected daily.

For example, in 2009, the United States saw an increase in the annual oil production since 1991. 92% of the increase was attributed to production from shale and other tight formations in Texas and North Dakota (Ratner, 2013).

As expected, with every advancement in technology, there are advantages and disadvantages. The success experienced by the Oil and Gas sector in increasing oil and

gas production from unconventional reservoirs via hydraulic fracturing, has also created a lot of negativity towards the practices of the industry. This process in particular, has been very misunderstood by outsiders and condemned as an extremely unsafe practice for the environment, health of the people and nation as a whole.

Therefore, the goal of this project is to analyze the chemistry that occurs in the rock and hydraulic fracturing fluid components and determine what kind of interactions take place. This knowledge can be used not only to clarify the safety of the process, but also to bring to light any areas that need improvement. This will ensure safer practices are adopted and employed by the industry.

1.1. Statement of Problem

Multi-stage transverse hydraulic fracturing, in conjunction with directional drilling, are the two most important processes that have advanced the production of hydrocarbons from unconventional reservoirs. Concerns have been raised about this stimulation practice for two major reasons; the amount of water needed to create the artificial fractures (about 3-5 million gallons of water for a stage) and the “harmful” chemicals being pumped into the ground (Adams et. Al, 2013; Shramko, et al., 2009). These are valid points as the need for fresh water to stimulate wells creates competition with other industries like agriculture, manufacturing etc. Also, contamination of drinking water aquifers from wells with poor cement jobs can pose a serious hazard to our communities and environment.

With this in mind, this work seeks to clarify the chemistry that occurs in the subsurface when the chemicals from the fracturing fluid contact the shale rock. The degradation of chemicals, alteration of minerals, exchange of ions and the resulting products of this interaction are of particular interest. Determining the chemical reactions that occur can aid in the treatment and re-use of fracture fluid, thereby reducing the need for fresh water. The effect of the chemical additives will be better understood and hopefully, more efficient fracture fluids can be created with the knowledge obtained. And most important, perhaps, the general public can be educated on the effects of the chemicals in the subsurface and their fears put to rest.

With results from the experiments performed, recommendations can be made to the Oil and Gas industry that will help improve the effectiveness of the hydraulic fracturing process by minimizing unwanted chemical interactions, improving fracture conductivity and increasing the volume of flowback if desired.

1.2. Literature Review

Numerous studies have been conducted to determine shale-fluid interactions. The driving force behind such research is usually focused on shale and wellbore instability when water-based fluids interact with shales. This instability has been attributed to the “convective” and “diffusive” movement of water and ions and changes in near-wellbore pressure. (Ewy, 2002) This weakens the mechanic properties of shale as the clays swell. Various solutions, such as use of oil-based fluids (when possible), inclusion of chemical additives such as surfactants, etc. have contributed to the success of stabilizing clays and

therefore, improving borehole stability. These changes have led to major improvements during drilling (Morton et al., 2009).

However, other reasons for studying shale-fluid interactions such as the effect on gas production of wells (Osholake et al., 2011; Ezulike, 2013), formation damage/degradation (King, 2010; Flippen, 1997), proppant diagenesis (LaFollette et al., 2011; LaFollette et al., 2010; Duenckel et al., 2012) are conducted to ensure that drilling and completion techniques do not adversely affect production from shales. More recently, environmental concerns and government regulations have led to more in-depth research on how to effectively dispose of and/or re-use flowback water (Rimassa et al., 2009; Blauch et al., 2010).

Chemical analysis of waters that return after hydraulic fracturing reveal very high levels of unexplainable salinity. The biggest impact of the salinity is finding economic methods for the disposal and/or reusability of flowback waters (Kaufman et al, 2008). This phenomenon is not fully understood and is currently being investigated in several research projects. Most significant are the results from Blauch et al.'s work published in 2009. This study utilized over 100 flowback samples from two wells in different parts of the Marcellus Shale play namely, the southwest and northeast regions. It was noted that the flowback from the Marcellus has high TDS in the form of soluble chloride salts (Blauch, 2009).

Using mineralogical and inorganic geochemical analyses of the shale samples, Blauch attempted to ascertain if the salt origin and presence or absence of particular minerals could explain the existence of the high salinity. The authors concluded that the

resulting salinity could be as a results of ~~primary~~ dissolution of autochthonous salt”, ~~primary~~ dissolution of allochthonous salt”, ~~encroachment~~ of basinal brine”, mobilization of hypersaline connate fluid” or combinations of the former instances.

Some conclusions from Blaich’s flowback studies of Well A can be seen in Figures **1.1—1.4**. There is an increase in dissolved constituents the later the flowback is collected. An increase in sodium, calcium and iron were also observed in latter stages of flowback and these two former ions are said to be the most prevalent cations. The increase in calcium can be attributed to the decrease in alkalinity and pH. The formation of barium sulfate scale and the low solubility of barium sulfate could explain the abrupt increase in barium levels during later collections of flowback.

Figure 1.1 – Blanch’s concentration of cations in well A. Namely sodium, calcium, magnesium, barium, potassium, iron, strontium). The trends discussed above are evident in the graph.

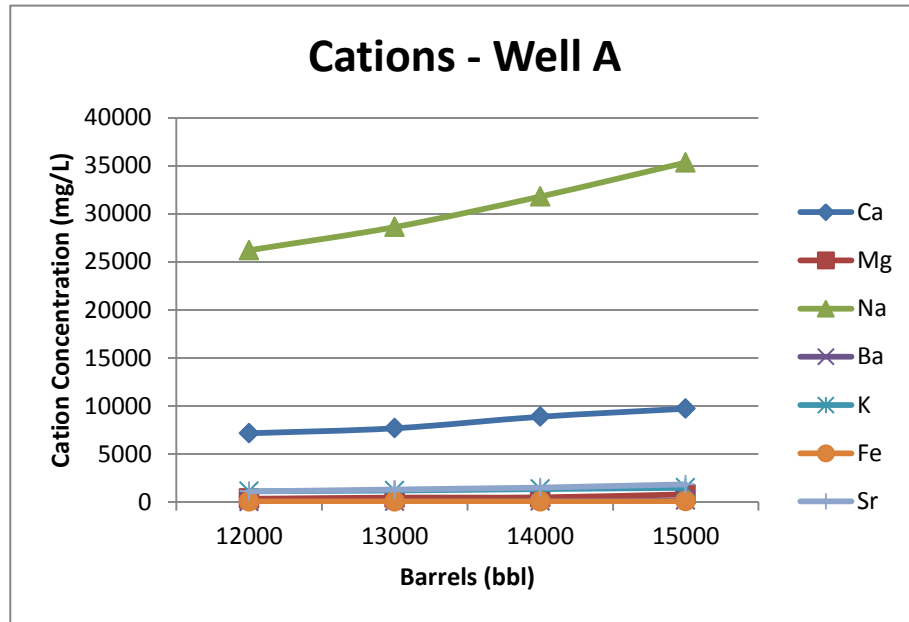


Figure 1.2 – Blanch’s concentration of anions in well A. Namely chloride, sulfate and alkalinity as CaCO₃.

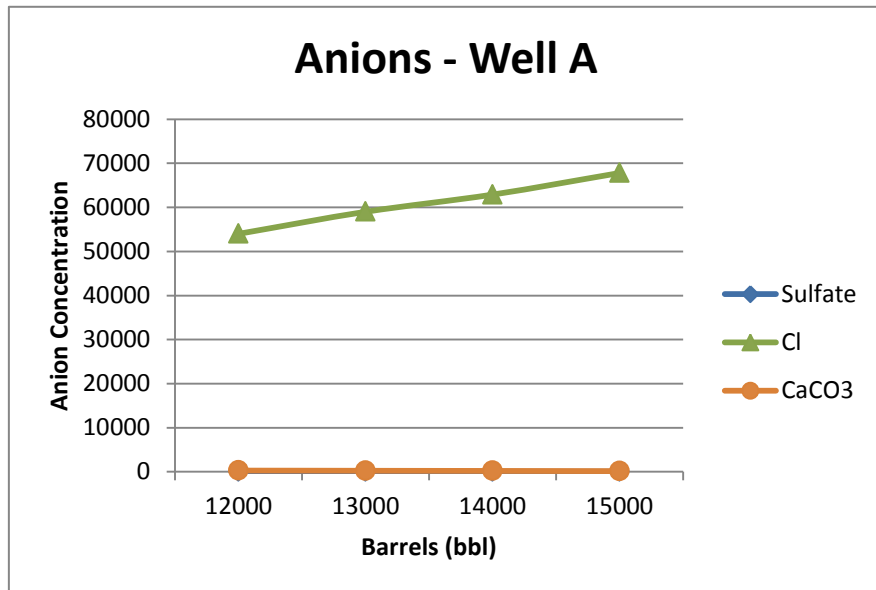


Figure 1.3 – Blauch’s concentration of the total suspended solids (TSS) in well A. The concentration increases the later the flowback sample collection.

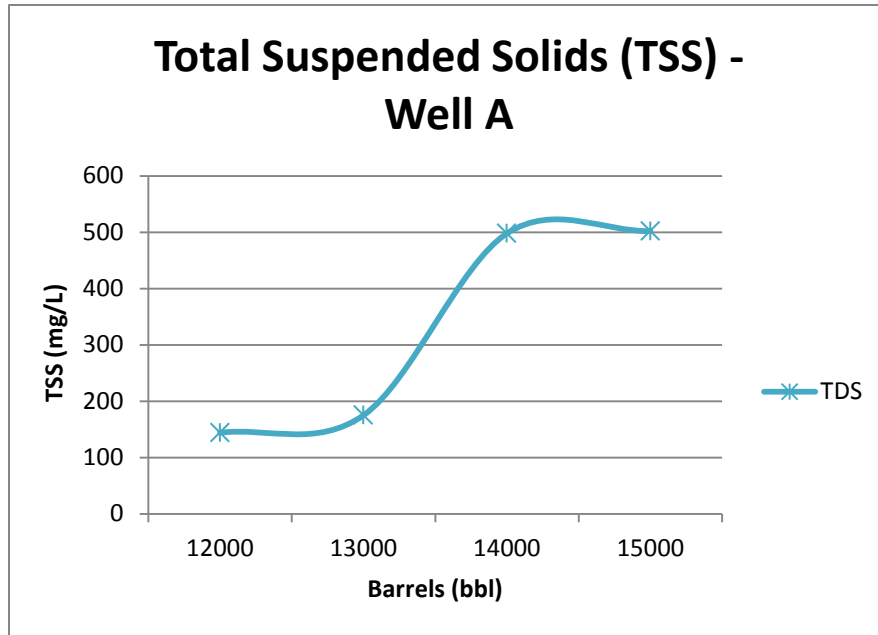
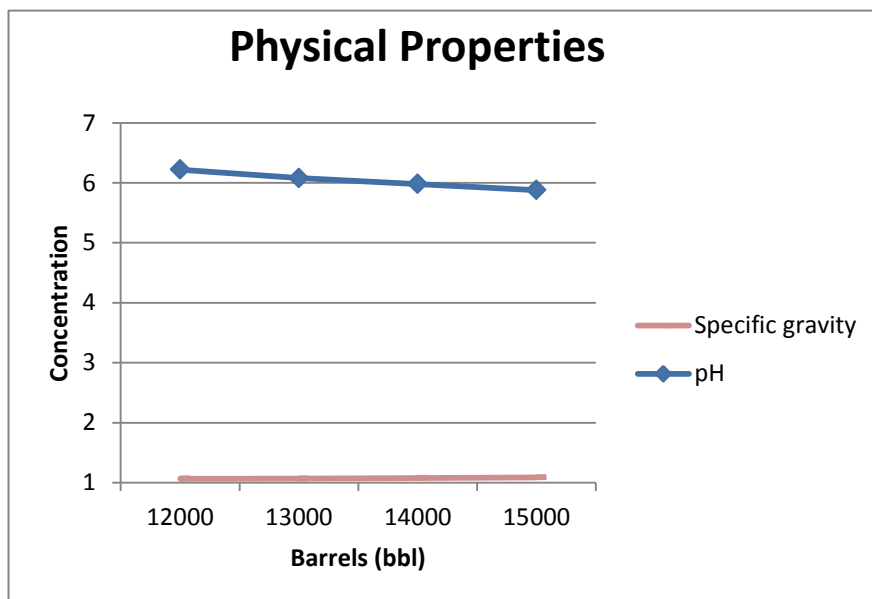


Figure 1.4 – Blauch’s decrease in the pH value and specific gravity in well A.



For Well B, flowback was collected at random times over 55 days. A lot more data was collected, hence a lot of variation is observed in graphs (**Figures 1.5-1.7**). Although the strontium levels in Appalachian Basin Marcellus wells are usually high, Well B had much higher levels than Well A. Also, the barium levels measured in this well were significantly higher than those in Well A.

Figure 1.5 – Blanch’s concentration of cations in well B. Namely sodium, calcium, magnesium, barium, potassium, iron, strontium. Most concentrations show an initial increase and then a decrease after Day 20.

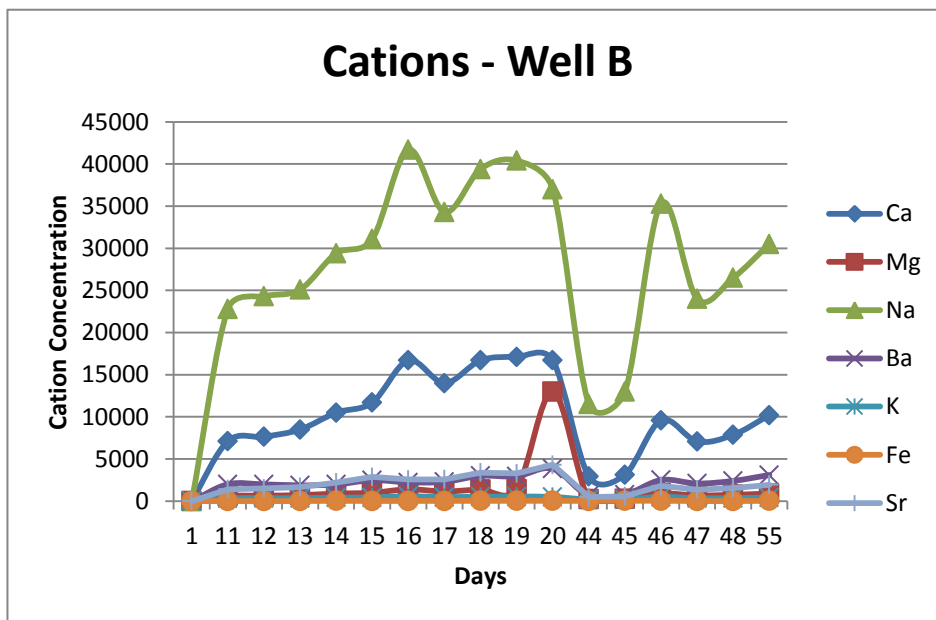


Figure 1.6 – Blauch’s concentration of anions in well B. Namely chloride, sulfate and alkalinity as CaCO₃. Concentrations increase initially, then a decline is observed around Day 44, after which the concentrations begin to increase again.

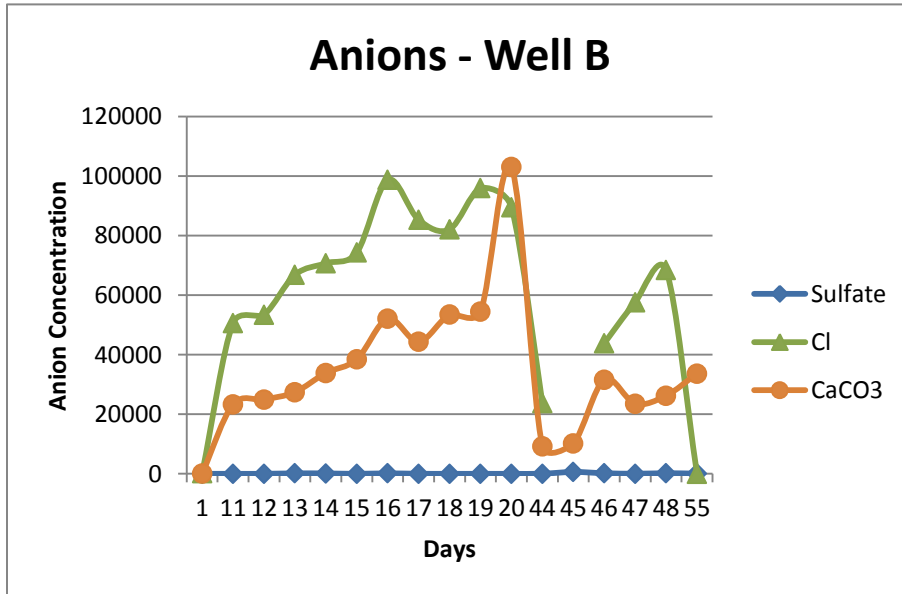
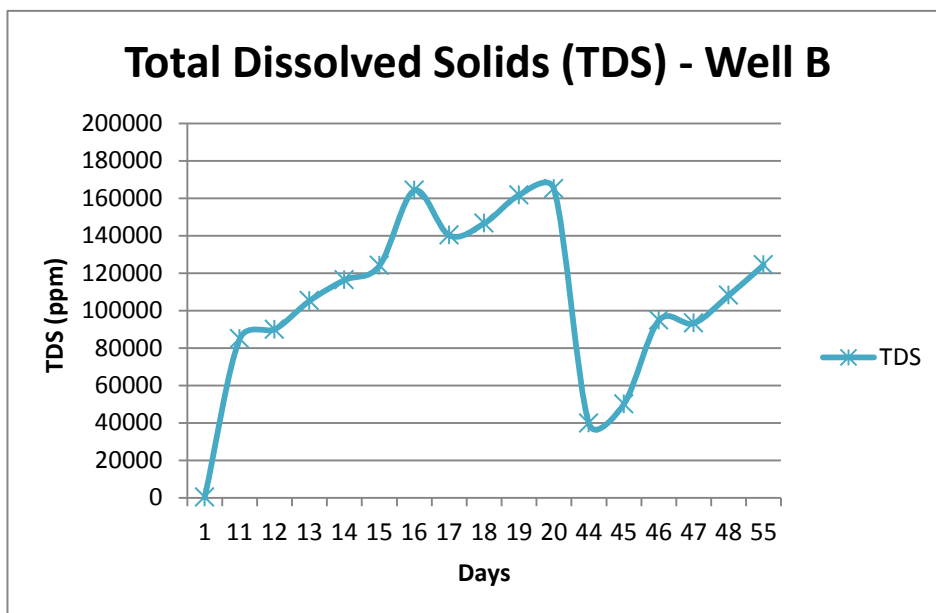


Figure 1.7 – Blauch’s total dissolved solids (TDS) in well B. Generally, TDS increases and reaches a maximum at Day 20.



In Lafollette’s 2010 study on Proppant Diagenesis, experiments using static temperature and pressure bombs were carried out in a laboratory on shale, proppant and fracture fluid to determine the physical and chemical changes that occurred to the proppant. Hayneville shale samples, ceramic proppants and broken high pH borate cross linked gelled water were used in the experiments. Tomball, Texas tap water was used as the base for the fracture fluid. The results from experiments published (Figures 1.8 - 1.11) show general trends in the cation, anion and physical properties concentrations from shale/fracture fluid interactions.

Figure 1.8 – Lafollette’s concentration of cations. Namely sodium, calcium, magnesium, barium, potassium, iron, boron, silicon. An initial increase in noted in sodium, calcium and silicon concentrations. However, the potassium, magnesium and boron concentrations decrease over time. There is no change observed in the barium and iron concentrations. *Day 0 on the graph indicates the baseline.

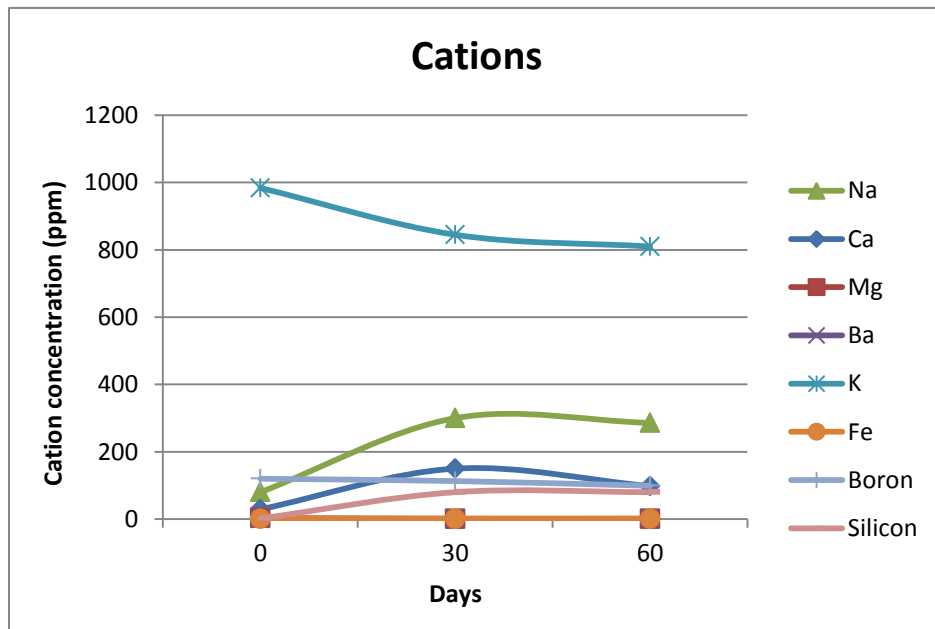


Figure 1.9 – Lafollette’s anion concentrations. Namely chloride, sulfate, carbonate, bicarbonate, alkalinity as CaCO₃. With the exception of carbonate, there is an increase in all concentrations. The decrease in carbonate is as a result of the fracturing fluid buffer.
 *Day 0 on the graph indicates the baseline.

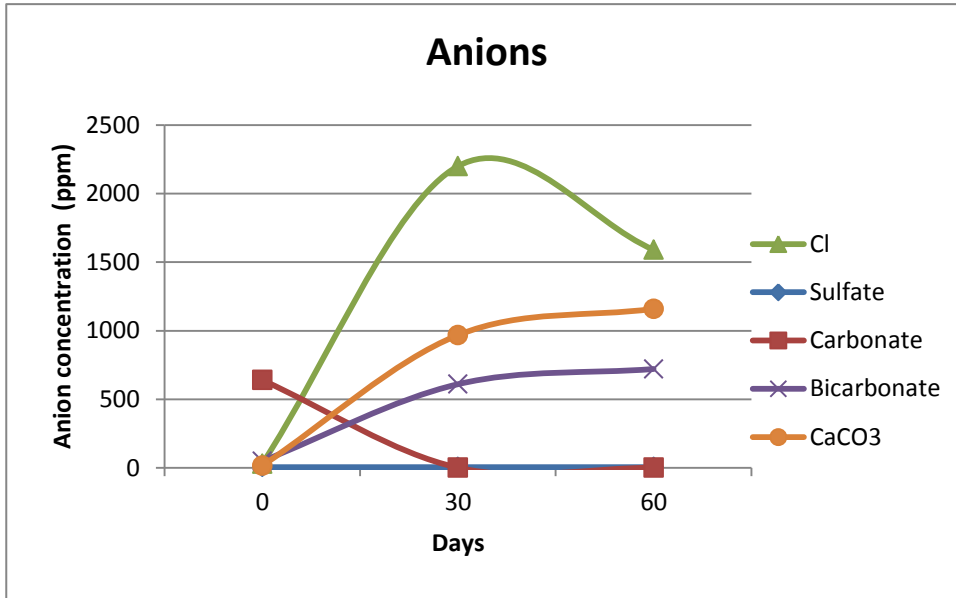


Figure 1.10 – Rapid increase in TDS in the first 30 days (Lafollette). Then a slight decrease over the next 30 days is observed. *Day 0 on the graph indicates the baseline.

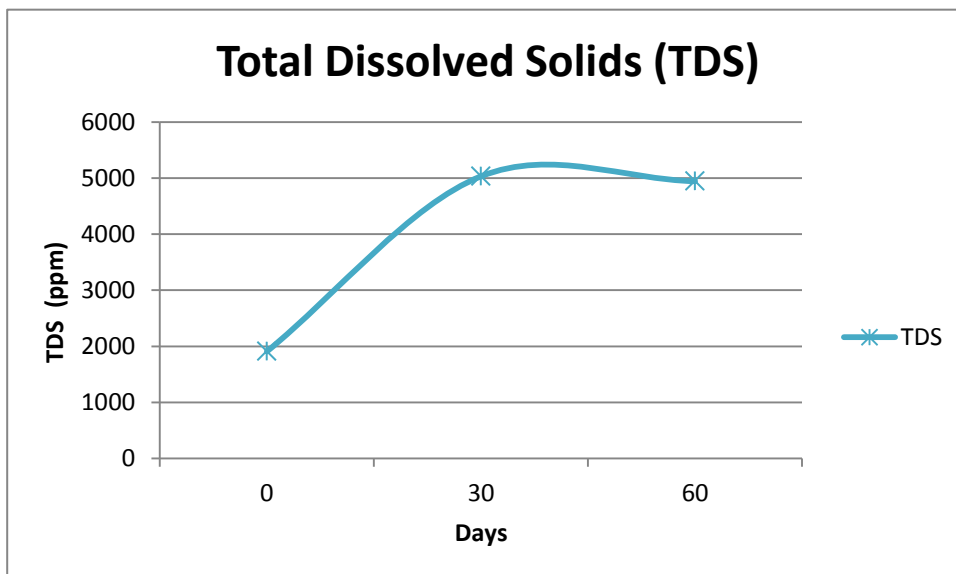
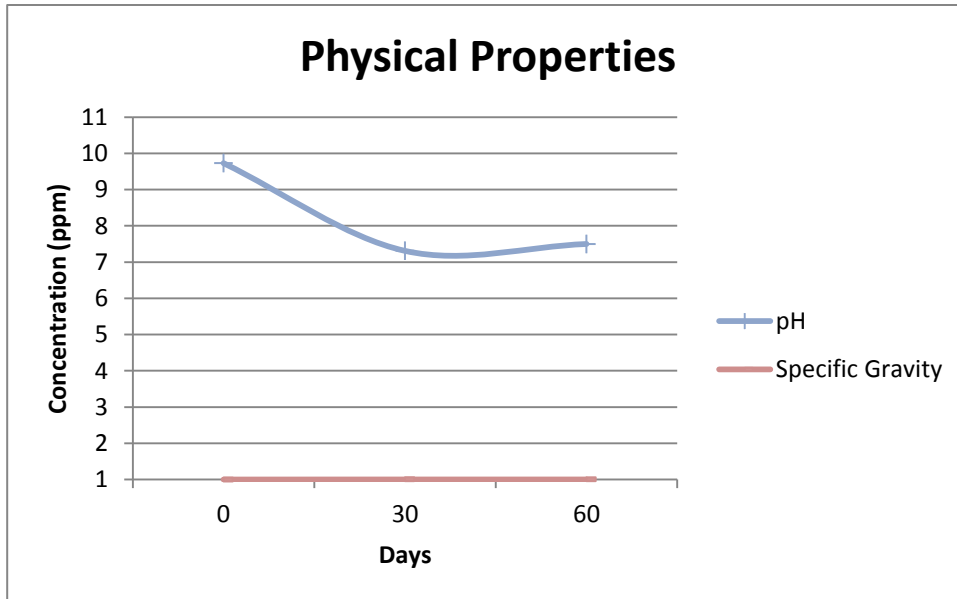
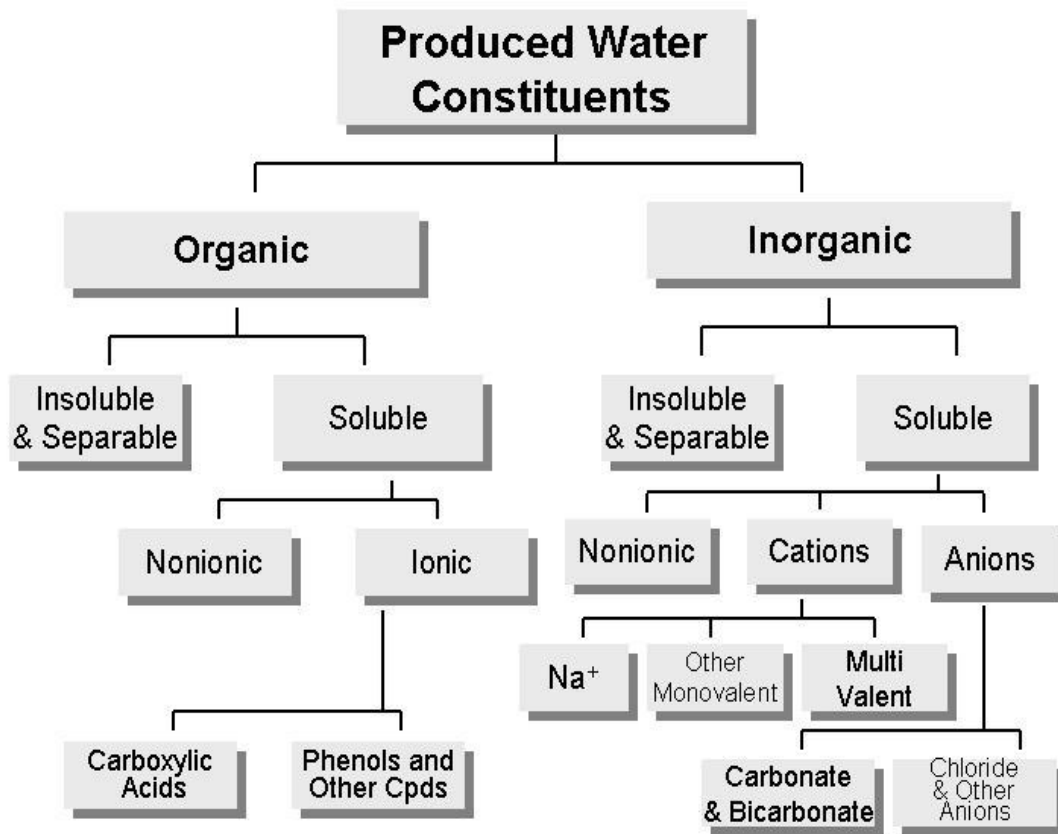


Figure 1.11 – Decrease in the pH and specific gravity (Lafollette). *Day 0 on the graph indicates the baseline.



Similarly, Hayes characterized the flowback from the Barnett and Marcellus Shale plays. Concentrations of cations, anions and other general chemistry measures were collected at different time periods. Hayes concluded that flowback water was a constitution of elements of produced water and the additives from hydraulic fracturing. The work further broke down the chemistry and composition of produced water using a very detailed flowchart (**Figure 1.12**)

Figure 1.12 – Hayes, 2011 complex breakdown of produced water constituents.



The flowback sampling and analysis in this study was taken from 19 different locations in the Marcellus Shale and 5 locations in the Barnett Shale. The samples were taken at days 0, 5, 14 and 90. Day 0 samples were the raw water before any chemical additives were added and raw water with chemical additives before the addition of proppant. Water chemistry analysis of this study is reported with ranges and median values of the each measurement.

Figure 1.13 – Decrease in pH values over time (Hayes, 2011)

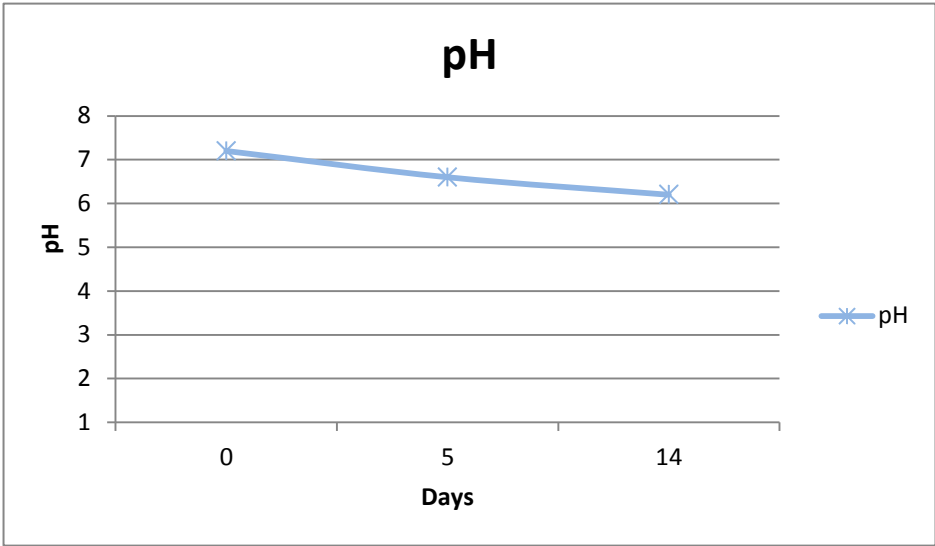
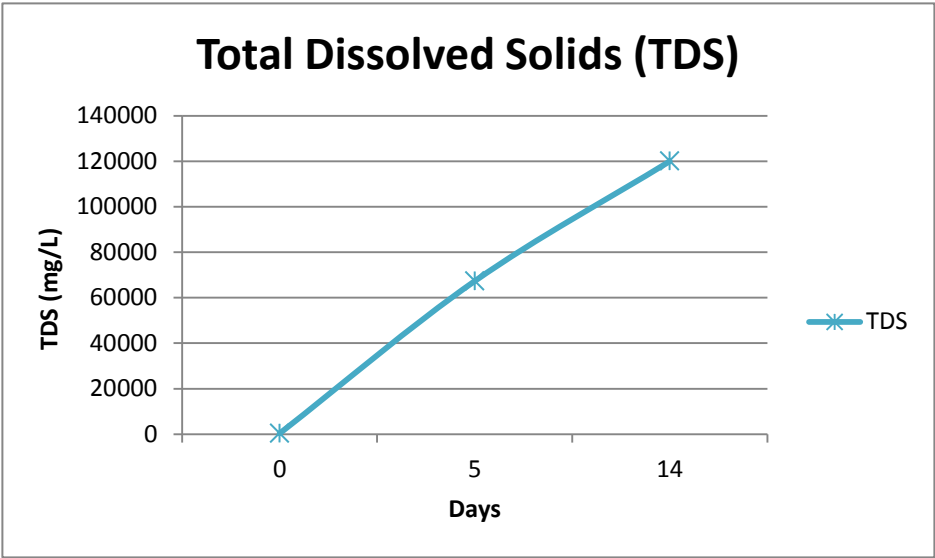


Figure 1.14 – Increase in TDS over time (Hayes, 2011)



Hayes also explains that the high values recorded for the hardness of the water (17,700 and 34,000 mg/L for day 5 and 14 respectively) can be credited to the abundance of soluble calcium which is formed due to the low carbonate concentrations (i.e. low to modest alkalinity of the water with values of 50 and 327 mg/L for day 5 and 14 respectively).

Originally, high salinity was attributed solely to the dissolution of minerals in the rock by the fracture fluid but after studying and analyzing the results from four separate studies in the Marcellus Shale (Dresel, 1985; Dresel and Rose; 2010; Pennsylvania Department of Environmental Protection (PA DEP); Hayes, 2009 and Blauch et al., 2009), Haluszczak et al concluded that salinity trends and relationships in brine composition indicate that

- (i) increased salt concentration in flowback is not mainly caused by dissolution of salt or other minerals in rock units,
- (ii) the flowback waters represent a mixture of injection waters with highly concentrated in situ brines similar to those in the other formations, and
- (iii) these waters contain concentrations of Ra and Ba that are commonly hundreds of times the US drinking water standards.” (Haluszczak, 2012).

1.3. Objectives of Research

The objective of this research is to determine how the mineral components of shale interact with the chemicals in the fracture fluid. To achieve this, the project is broken down into these parts:

1. Shale characterization to determine the relationship between the minerals, cation exchange capacity (CEC) and total organic content of the rock and how it is affected by the chemicals found in the fracture fluid.
2. Shale-fluid interaction tests to understand how/if any chemical or mineral components are degraded, altered or generated in both the shale sample and fluid sample. Fluid samples will be analyzed using inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) and Total Organic Carbon (TOC) measurements while the shale samples will be analyzed using X-ray diffraction (XRD), X-ray Fluorescence (XRF) and TOC before and after exposure to the fracture fluid.
3. Different shale plays will be compared to establish any correlation between the effect of the different chemicals on the clay content, amount of metals, abundance of certain elements etc. in the rock.

1.4. Outline of Thesis

Section 2: This chapter will give a background on shales. The minerals that make up the rocks and the different clay compositions for each shale play studied in this work will be discussed. Chemicals that make up the fracture fluid will be presented and each component analyzed and the effects of hydraulic fluids on shale will be looked at briefly.

Section 3: Experimental procedures and the methodologies for the Shale-Fluid interaction test will be explained in great details in this chapter. Methods used by the various independent laboratories for procedures such as XRD, XRF, etc. will also be presented.

Section 4: In addition to the results from the Shale-Fluid interaction tests, the results for the mineralogy for each shale type will be presented.

Section 5: In this chapter, results from the previous chapter will be discussed, parallels between shale mineralogy and the resulting concentrations of cations and anions will be drawn in an attempt to understand the chemistry that occurs during the interaction of rock samples and fracture fluid. Finally, recommendations for future work will be presented.

2. BACKGROUND

2.1. Shales

Shale is a type of clastic sedimentary rock. They are the most abundant type of sedimentary rocks in the world (about 60% of sedimentary rocks). Generally, the term shale is used to classify rocks that are clay rich. However, the more accurate way to describe shales is as a mudstone because it is composed of very fine grains (silt) and clay sized mineral particles (less than 2 microns) which are compacted as it is buried. Shales are formed when sediments carried by rapid moving waters are deposited in river floodplains or at the body of a large body of water (lakes, ocean etc.).

Shales are relatively soft and are described as fissile and laminated. When exposed to water, shale becomes mud. The fissile nature and lamination of shale distinguishes it from other mudstones. The laminated nature of shales means it is made up of thin layers. Fissile means that the rock splits into thin pieces along the laminations.

Depending on the organic matter contained in shales, the color varies from gray to black (**Figure 2.1**). The darker the shale, the more organic matter it contains. Black shales are common source rocks for oil and gas while gray shales can act as a seal for a reservoir rock in a petroleum trap (Hyne, 2012).

Shales are made up of 50-60 wt. % clay minerals. The major clays found in shale are

- Chlorite; $(\text{Mg,Fe})_3(\text{Si,Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{Mg,Fe})_3(\text{OH})_6$
- Illite; $(\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$
- Kaolinite; $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
- Smectite; $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$

Figure 2.1 – Different colors of shales (www.geology.com)



Initially, shales were considered only as source rocks in conventional petroleum systems due to the extremely low permeability (nanodarcies) of such rocks. However, in the early 1990s, shale gas pioneers began to experiment on ways to release the gas locked in the tiny pore spaces of shale. By the end of that decade, some companies had successfully developed completions methods for drilling and producing natural gas from shale reservoirs economically (King, 2012). The major breakthrough was employing HF techniques safely and successfully in such unconventional reservoirs (Coulter, et al., 2004).

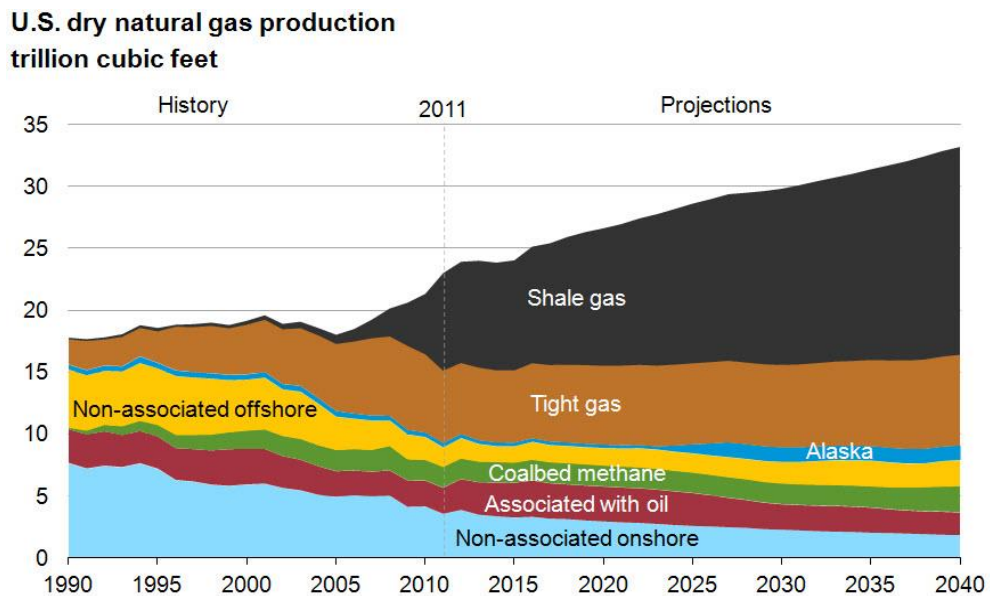
Shale gas and shale oil, according to the resource triangle (see **Figure. 2.2**), are considered unconventional resources because of the vast resource concentrations in low quality reservoirs which require special technology and stimulation in order produce the natural resource in economic quantities. From **Figure. 2.3**, the importance of unconventional for meeting future energy needs can be seen; as majority of the natural resources fall within that category. Hence, developing such reserves is very important for providing affordable energy worldwide.

Figure 2.2 – Resource triangle with conventional and unconventional resources. (Canadian Society of Unconventional Gas, 2003).



Source of Image: Canadian Society for Unconventional Gas. Submission to the Council of Energy Ministers, September 2003

Figure 2.3 – Projection of natural gas production in the United States by its source (EIA 2011).



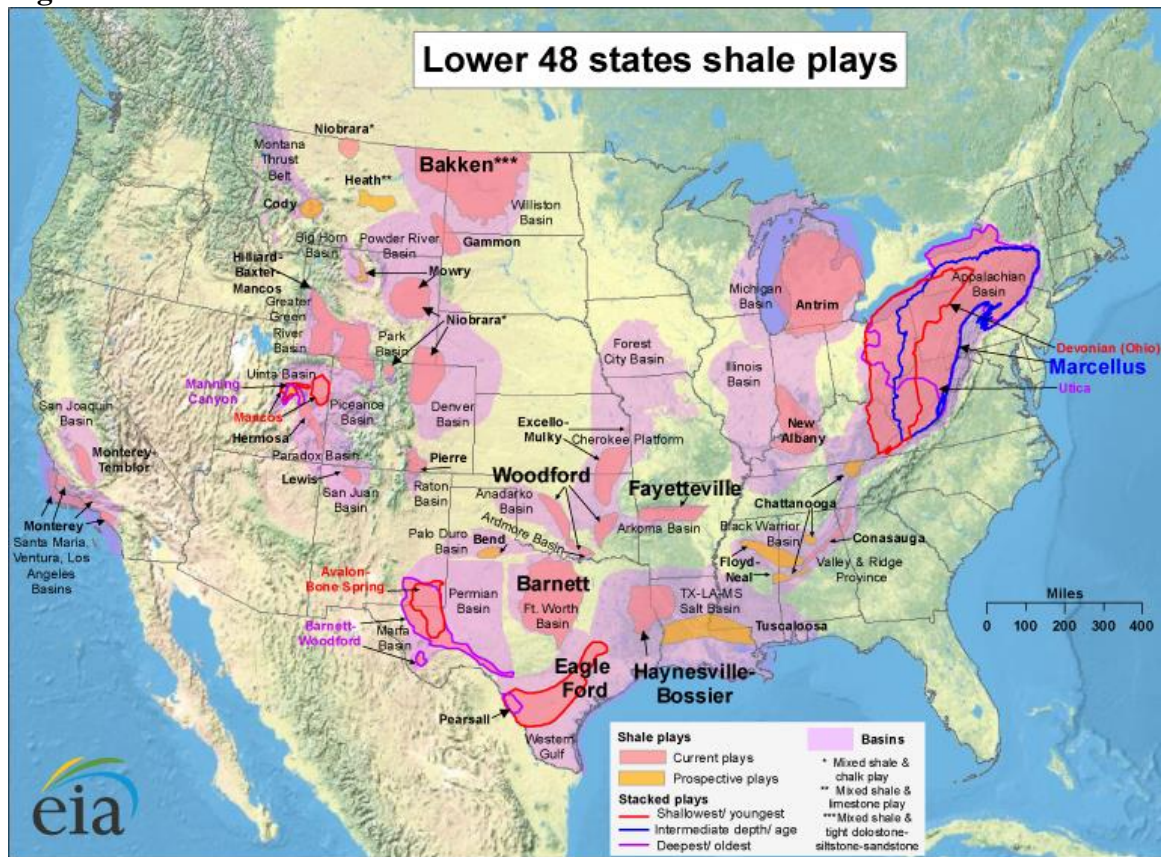
Source: U.S. Energy Information Administration, *Annual Energy Outlook 2013 Early Release*

2.2. Shale Plays

As mentioned earlier shale is the most common type of sedimentary rock. In this United States, there are numerous shale basins that have been developed and natural resources are being produced economically on a daily basis. See (**Figure 2.4**).

In this study, shale from three different plays in the United States were used; the Barnett Shale and the Eagle Ford Shale both located in Texas and the Marcellus Shale which is located mainly in Pennsylvania with some parts of the basin also in New York, Maryland, Virginia and some parts of Ohio.

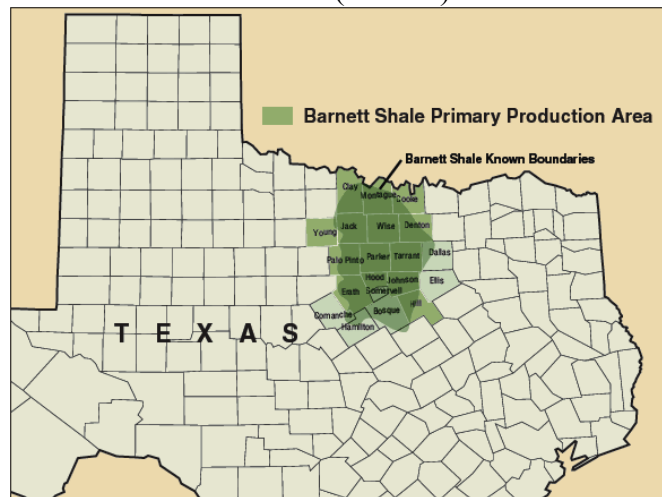
Figure 2.4 – The shale basins in the lower 48 states of the United States.



2.2.1. *Barnett Shale*

The Barnett shale is located in North Texas (**Figure 2.5**). This shale formation covers about 6,400 square miles, and lies about 8000ft below the ground's surface. It holds an estimated 43.4 trillion cubic feet of natural gas (enough natural gas to power all homes presently in Texas for the next 200 years) (Energyfromshale.org, 2013).

Figure 2.5 – Location of the Barnett Shale. (AAPG)



The Barnett Shale is a Mississippian aged shale with quartz and clay as the primary minerals. Depending on the location, it lies at depths between 6800-9000ft and this shale thickness increases from 100 to 1000ft in the northeast direction (Coulter, 2004). It is bounded on the bottom in some areas by the Viola/Simpson limestone and in others by the Ellenburger dolomite which is a water bearing formation (Frantz, 2005). On top is the Marble Falls Limestone, which creates a good barrier for hydraulic fracture attenuation. The proved reserves in this play according to the U.S. Energy Information

Administration (EIA) are 32.6 trillion cubic feet (Tcf) of gas and 118 million barrels of oil (MMBoe).

The Barnett is considered a naturally fractured, tight gas formation with permeabilities in the micro to nano-Darcy range; with an average permeability of .25μD. The porosity is low and is usually in the 1-6% range. (Coulter , 1976.) Like most shales, the Barnett is heterogeneous. Its pressures gradients are between 0.45-0.52 psi/ft., and it is considered slightly over pressured. The total organic content (TOC) in this shale play is between 4-8%, with an average value of 4.5%. The mineral composition of the Barnett is typically 45% quartz, 20-40% illite clay, 8% dolomite and calcite, 7% feldspar, 5% pyrite and 3% siderite (Frantz et al., 2005). This play produces several types of hydrocarbons including dry and wet gas, oil and condensate. The average temperature of the Barnett is 200°F and the pressure is about 4,000 psi.

Wells in the Barnett are completed using multiple fracture stimulations. The lower and upper Barnett zones have to be perforated and fractured independently. Each well on average is stimulated with about 3 to 5 million gallons over the 2000-3800 ft. horizontal lateral (Nicot et al, 2014). To complete the average well in the Barnett costs about \$2.8 million.

The Barnett Shale was one of the most active producers of natural gas in the mid to late 2000s. However, the due to the enormous success of efficiently producing natural gas from this unconventional play; an imbalance between supply and demand was created. This achievement eventually worked against the industry when the price of

natural gas plummeted from about \$15.78/Mcf in 2005 to an all-time low of \$2.32Mcf of gas (Meyer, 2010).

For this study, outcrop was quarried from the surface in San Saba, Texas (**Figure 2.6**).

Figure 2.6 – The Barnett outcrop sample used for the experiments in this study.

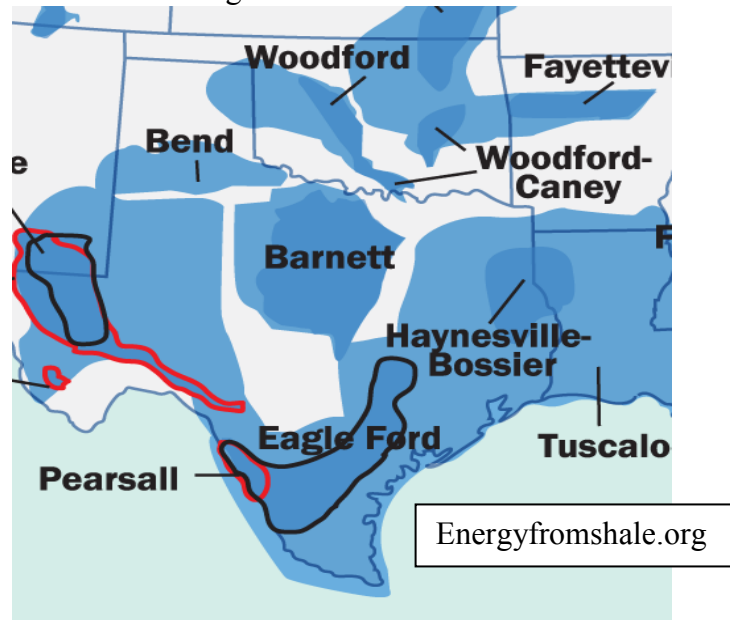


2.2.2. *Eagle Ford Shale*

The Eagle Ford formation is one of the hottest plays in the United States at the moment. As a result of the vast reserves of both shale oil and shale gas, the Eagle Ford is projected to produce the more hydrocarbons (especially oil) than other shales. As of July, 2014, the Energy Information Administration (EIA) reported that 1.6 million barrels of oil and 79 MMcf of gas are produced daily. This shale play is in the Maverick basin, located in the Southern part of Texas and it covers an area of about 5000 square

miles (**Figure 2.7**). The Eagle Ford holds an estimated recoverable reserves of 700 million barrels (the recovery factor is a mere 6% and OOIP is pegged at 28 Billion BOE) (EagleFordShale.com). The OGIP is estimated between 140-200 Bcf per section.

Figure 2.7 – The location of the Eagle Ford Shale.



This basin was formed during the Cretaceous period and has a very high carbonate (>70% in some areas) and low clay content (Martin et al, 2011). The high carbonate content has made HF a lot easier since the formation is very brittle (Arguijo et al., 2012). The location of the shale in the subsurface can be as shallow as 5,000ft below or as deep as 18,000ft and its thickness varies between 50 and 300ft and becomes shallower in the northwest direction. The Austin Chalk formation sits atop of it and Buda lime is below the Eagle Ford. (Shelley et al., 2012)

Porosity in the Eagle Ford ranges from 3-15%, with the typical value of about 11% and its permeability is between 0.0001 and 0.03 mD in most areas. This play is considered moderately over-pressured with pressure gradients varying between 0.4 and 0.7 psi/ft. The average total organic carbon (TOC) is 5% and the approximate mineralogy over the Eagle Ford is 50% calcite, 20% clay and 20% quartz (Martin et al, 2011). The typical reservoir temperature is ranges from 280 to 350°F and pressures are between 8,000—11,000 psi (with the average pressure gradient of 0.65 psi/ft). (Jaripatke, et al., 2013).

Wells in the Eagle Ford are predominantly horizontal wells with the number of fracture stages ranging between 12 and 21 (Centurion et al., 2011) and 4-5million barrels of water are used per well. (Centurion et al., 2012). The fracture fluids used in this play are slick water, high temperature gels and crosslinked fluids. (Cook et al., 2014). The average cost to drill and complete a well is \$4.8 million.

Outcrop shale used for this study was obtained from the surface at Del Rio, Texas.

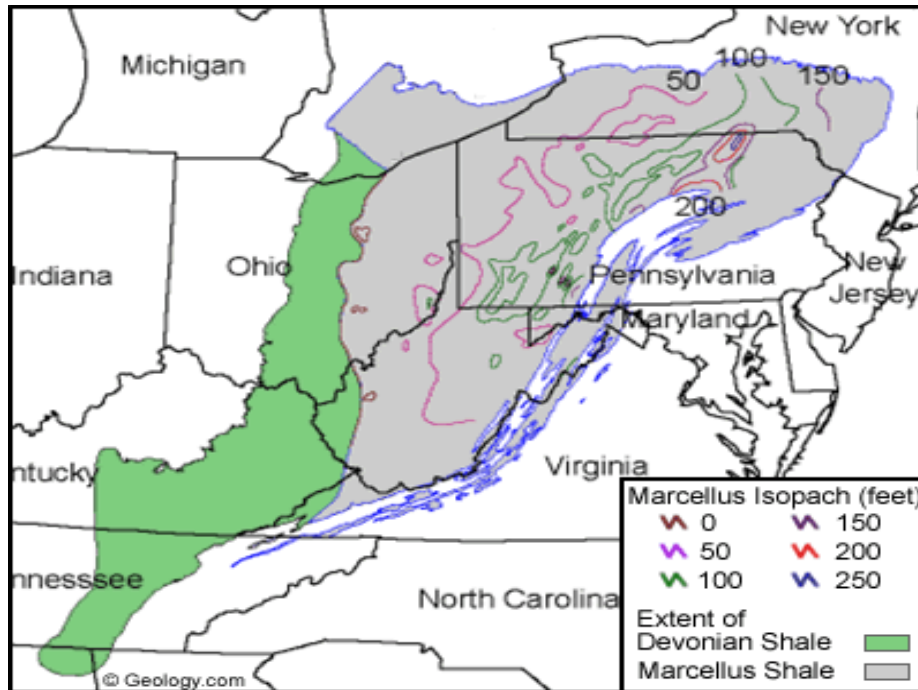
Figure 2.8 – Eagle Ford shale outcrop used for this project.



2.2.3. *Marcellus Shale*

The Marcellus Shale is middle aged Devonian shale that contains limestone beds and concentrations of pyrite (FeS_2) and siderite (FeCO_3). The primary minerals in this play are mixed clays (40-70%), quartz (20-56%) and calcite (0.3-15%) (Belvalkar et al., 2010). Although the major area of production of this shale is in Pennsylvania, it was first discovered as an outcrop in Marcellus, New York in 1839. It covers an area 54,000 square miles and spans New York, Maryland, West Virginia and Ohio. The shale lies at depths between 6000-8000ft and the average shale thickness of is about 350ft. It is bounded on the bottom in northwestern New York by the Onondaga Limestone and in Western Pennsylvania by the Selinsgrove Limestone. On top are the Mahantango Formation and Tully Limestone.

Figure 2.9 – The location and extent of the Marcellus shale.



The Marcellus Shale is the largest shale gas play in North America. This play has faults, fractures and variable shale, carbonate lithology. The original gas in place (OGIP) is estimated to be about 500 Tcf with 50 Tcf of that believed to be recoverable (Hayes, 2009). The formation reservoirs have an average permeability of 1 micro Darcy. The porosity usually ranges from 4-8%. Its pressures gradients are between 0.45-0.52 psi/ft., and it is considered slightly over pressured. The total organic content (TOC) in this shale play is between 4-8%. This play produces dry and wet gas. The average temperature of the Marcellus is 130°F and the pressure is about 4,000 psi.

The cost to complete the average Marcellus well is roughly \$3.5-4 million. (Belvalkar et al., 2010). Wells in this play are completed using crosslinked gel fracture

fluids. Approximately, 3-5 million gallons of water is used to complete a well (Arthur, et al., 2010).

For this study, outcrop was mined from about 30-40ft below the surface (as per information provided by Kocurek Industries, Figure 2.10) and the thermal maturity in Eastern Pennsylvania ranges between 3.0 and 3.5.

Figure 2.10 – Marcellus Outcrop used for the experiment.



2.3. Mineralogy

2.3.1. Mineralogy Analysis

Minerals in the rocks used in this project are classified into three major groups; Clays, Carbonates and Others which consist of mainly Quartz and other silicate minerals, K-Feldspar, Plagioclase, Pyrite, Barite, Fluoroapatite and Gypsum.

2.3.1.1. Clays

Clays are very abundant in the earth and are widely used in different industries such as manufacturing and agriculture. 97 % of all petroleum reservoirs contain some form of clays. Clay minerals are hydrous aluminum phyllosilicates with varying amounts of other mineral such as magnesium, sodium, iron etc. Phyllosilicates are parallel –sheet silicates” (Si_2O_5). Furthermore, clays form in the presence of water and as such, the sheets of silicate have water or a hydroxyl group attached to it; this is why they are considered to be hydrated (Kerr, 1955).

Clay minerals are usually less than two microns in size and are a common component of sedimentary rocks. They generally have a large surface area ($\sim 100\text{m}^2/\text{g}$) and usually carry a net negative charge. The clay mineral group in this study is made up of chlorite, kaolinite, smectite, illite/mica and mixed interstitial clays.

Kaolinite, illite and chlorite has the tendency to disperse in freshwater and clog pore throats, while smectite is known as the swelling clay and has the ability to imbibe freshwater and swell up to a thousand (1000) times its volume. Due to these characteristics of clays, reservoirs containing these minerals have to be treated specially.

For example, freshwater is not used in drilling such formations and hydrochloric acid (HCl) should not be used in formations containing >10% illite.

2.3.1.2. Carbonates

Calcium carbonate, CaCO_3 , is the major component in carbonates. These rocks can be formed in many different environments provided water is present. Generally, they are found in abundance in chemically precipitated sedimentary rocks and these minerals are formed by precipitation from water. Calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and siderite (FeCO_3) are the three main minerals that form carbonates. Dolomite is produced by diagenesis and is magnesium rich while siderite is an iron ore (Bots et al., 2012).

Calcite and dolomite are generally denser rocks with density values of 2.71 g/m^3 and 2.85 g/m^3 respectively. Multiple factors affect the dissolution or precipitation of calcite by groundwater such as pH, temperature and other dissolved ion concentrations. Also, calcite has retrograde solubility which means that it is less soluble in water as the water temperature increases. In addition, only calcite with low magnesium concentrations is stable at surface temperatures and pressures. Examples of carbonate rocks include limestone, dolostone, chalk etc.

According to Rodriguez-Blanco, 2008, Calcite forms from a poorly ordered precursor (amorphous calcium carbonate, ACC). The crystallization process occurs in two stages; firstly, the ACC nanoparticles rapidly dehydrate and crystallize to form individual particles of vaterite; secondly, the vaterite transforms to calcite via a dissolution and reprecipitation mechanism with the reaction rate controlled by the surface area of calcite. The second stage of the reaction is approximately 10 times slower

than the first. However, the crystallization of calcite has been observed to be dependent on the starting pH and presence of Mg in solution. A neutral starting pH during mixing promotes the direct transformation of ACC into calcite. Conversely, when ACC forms in a solution that starts with a basic initial pH, the transformation to calcite occurs via metastable vaterite, which forms via a spherulitic growth mechanism. In a second stage this vaterite transforms to calcite via a surface-controlled dissolution and recrystallization mechanism. Mg has a noteworthy effect on both the stability of ACC and its transformation to crystalline CaCO₃, resulting in the formation of calcite directly from ACC, as this ion unstabilizes the structure of vaterite.”

2.3.1.3. Others

Quartz is silicon dioxide, SiO₂, which is the simplest form of silicates. This white, hard mineral can be found in sedimentary, igneous and metamorphic rocks. It is the second more abundant mineral in the Earth’s crust. In nature, quartz forms relatively easily when silica rich solutions and oxygen are present. It does not require a particular temperature or pressure to form making it a very stable mineral. Also, quartz is resistant to physical and chemical weathering.

K-Feldspar, potassium feldspar (KAlSi₃O₈) is the most abundant mineral in the Earth’s continental crust therefore, it is considered as a “rock-forming” mineral i.e. most rocks are composed mainly of feldspar (Deer et.al, 1992). The color of K-feldspar ranges from white to brick red. Similar in chemical structure to quartz, the major difference between the two elements is that various metals such as Na, K or Ca partly replace the silicon. Depending on the temperature, there are three crystal structures that potassium

feldspar can form namely: microcline, sanidine and orthoclase (Alden, 2011). The former is stable below 400°C, orthoclase is stable above 500°C and sanidine is stable above 900°C.

Plagioclase, $(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$, is part of the feldspar mineral group. It is a tectosilicate mineral and it is a major component of the Earth's crust. It is composed of sodium (4.25%), calcium (7.40%), Aluminum (9.96%), Silicon (31.12%) and Oxygen (47.27%). There are two major minerals that are found in plagioclase; anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and albite ($\text{NaAlSi}_3\text{O}_8$). The ratio of each of those minerals determines the type of plagioclase feldspar the mineral is. This mineral has an average density of 2.68 g/cc.

Pyrite, iron disulfide (FeS_2), is called fool's gold as a result of its shiny, yellow color. It is composed of Iron (46.55%) and Sulfur (53.45%). Pyrite is the most common sulfide mineral and can be found in coal, sedimentary and metamorphic rocks. When exposed to water and air, iron pyrite breaks down into iron oxides and sulfate and it is generally unstable in the environment. Pyrite has an average density of 5.01 g/cc.

Barite, has the chemical formula BaSO_4 . It is composed of Barium (58.84%), Sulfur (13.74%) and Oxygen (27.42%) and has a density of 4.48 g/cc. This mineral could be either colorless or white. According to Hanor (2000), barite can be deposited through biogenic, hydrothermal and evaporation and it is present in numerous of depositional environments. Barite is essential to the petroleum industry because it is used as a weighting agent in drilling mud. It is very insoluble, hence it isn't considered toxic despite containing barium.

Fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ aka calcium fluorophosphate is a hard, crystalline solid. This mineral is found in a range of colors including blue, violet, green etc. It is composed of calcium (39.74%), phosphorus (18.43%), oxygen (38.07%) and fluorine (3.77%) and has an average density of 3.15 g/cc. Fluoroapatite is the most common phosphate mineral and it's synthesized in two steps. Initially, calcium phosphate is generated by combining calcium and phosphate salts. Next it is reacted with a fluoride source such as sodium monofluorophosphate (Holleman, 2001). Fluoroapatite is used in the production of hydrofluoric acid which is used in the oil and gas industry to acidize sandstones.

Gypsum is a sulfate mineral with chemical formula $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$. It is a soft mineral with density 2.3 g/cc and contains 23.28% calcium, 2.34% hydrogen, 18.62% sulfur and 55.76% oxygen. It is found in sedimentary rocks and is usually deposited in strata. Groundwater hydrates hydrothermal anhydrite to form gypsum. Although being moderately water-soluble, according to Bock (1961), gypsum has the retrograde solubility property. Heating it in air causes it to lose water and become calcium sulfate hemihydrate after which it becomes anhydrite upon further heating. Gypsum is widely used in making fertilizers.

Below is a table containing the various mineral compositions of the samples used in the experiment. There is great variation in the mineralogy makeup of the rocks which is common in shales.

Table 2.1 — Bulk and clay mineralogy of shale samples used in this work

	Barnett	Eagle Ford	Marcellus
Mineral	%	%	%
Smectite	0.0	0	2
Chlorite	4.0	0	Tr
Kaolinite	5.0	7.2	0
Illite/Mica	32.0	1	16
Mx IS	9.0	0.9	7
Calcite	Tr	60.1	12
Dolomite	0	0	1
Siderite	0	0	0
Quartz	31	20.2	41
K-Feldspar	2	0	2
Plagioclase	2	0	6
Pyrite	1	5.2	12
Barite	0	0	0
Fluoroapatite	11	0	1
Gypsum	3	5.4	Tr
Totals	Clays	50	25
	Carbonates	0	13
	Gypsum	50	62

2.4. Hydraulic Fracturing

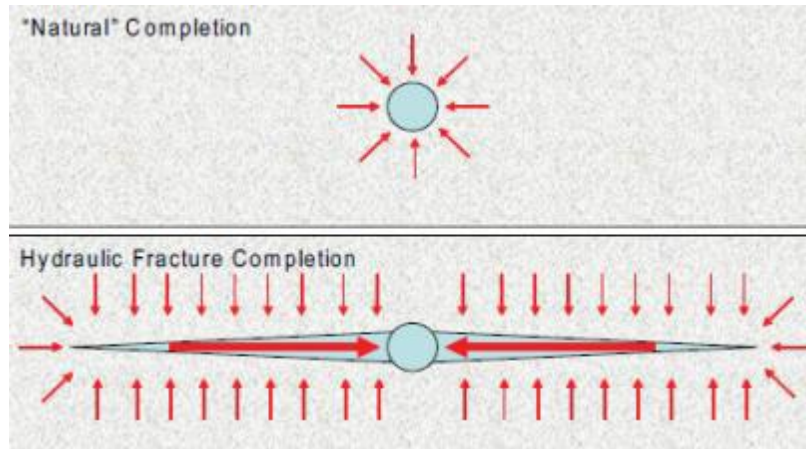
In simple terms, hydraulic fracturing is a technique that involves large volumes of water and sand (98 to 99.5%), and very small volumes of chemical additives injected into the subsurface at high pressures to open existing fractures in the rock, or create new ones in order to increase the production of oil or natural gas. In other words, by enhancing the permeability of the formation, fluids can flow more readily to the wellbore during production. (Veatch et al, 1985) Prior to pumping the fracture fluid,

perforations are made along the wellbore. These “cracks” are where the fluid or slurry (fracture fluid and proppant) is supposed to travel into. The sand present (or proppant) is used to keep the cracks open which allow the hydrocarbons to flow much easier.

Prior to hydraulic fracturing, the industry used to detonate explosives (liquid nitroglycerin) in wells. The explosive would create a large cavity which was then cleaned out and completed as an open hole. Although this was effective, it was very dangerous. (Hyne, 2012). HF was developed in 1948 and in 1949, the first commercial job was successfully completed. Today, it is almost impossible to complete and produce a well without using HF and statistics show that of all the wells drilled in the U.S. in 2010, over 60% of them were hydraulically fractured. (Hyne, 2012).

Hydraulic fracturing is meant to increase both the production rate (by 1.5 to 30 times) and the ultimate production from a well. When fractures are created, they extend further into the formation and are in contact with more of the reservoir. This essentially increases the effective wellbore radius. Considerations of minimum and maximum horizontal stresses have to be taken into account during fracture design as this affects the length and width fractures will propagate. In addition, natural fractures and their orientation are also important during fracture design. (Figure. 2.11)

Figure 2.11 – Difference between the surface area of a naturally completed well and one that was hydraulically fractured.



This process (HF) is usually done in three steps. First, the fracture fluid is pumped into the reservoir at high enough pressure to initiate the fractures. Then, the slurry is pumped downhole to extend the fractures and while the propping agents keep them open. Finally, the well is flushed to remove the excess fracture fluid in the wellbore.

Over the years, this completion technique has been refined and improved as a result of scientific and engineering advancements. The technology behind the chemicals used for both gel and slick water fracture fluids and proppants are investigated on a daily basis to determine the safest and most economic ways to use means to perform HF (using the optimum composition of chemicals and the right balance of proppant and fluid).

Generally, the composition of a gel fracture fluid is 99.5 % water and sand and the remaining 0.5% are the chemicals additives. **See Figure 2.12.**

Figure 2.12 – Composition of a typical gel fracture fluid.



The major problem facing the petroleum industry today starts with the massive amounts of water brought to the drill sites (a typical stimulation job requires multiple stage fractures and each stage requires about 3-5 million gallons of water). Next, the equipment (trucks, mixers, pumps) have to be transported to the location to create the fracture fluid and locals complain of the noise and destruction of property and infrastructure during this process. In order to reduce some of the issues mentioned about, suggestions about reusing flowback and produced waters are being considered.

2.4.1. Hydraulic Fracturing Fluid Composition

As the popularity of HF has risen, a lot of concern for environment has also been raised. As a result, there is an increase in legislation to ban HF in many parts of the world. A lot of misconceptions have been formed and the general public needs to be

educated further on the procedure and the steps taken by the industry to ensure the safety of the general public.

Majority of the chemicals used in HF are also used in everyday life. The table below lists the chemicals used in fracture fluids and their corresponding everyday application.

Table 2.2 — The chemicals used in hydraulic fracturing fluids and everyday life

Additive Type	Main Compound	Purpose	Common Use of Main Compound
Dilute Acid		Helps dissolve minerals and initiate cracks in the rock	Swimming pool cleaner
Biocide	Glutaraldehyde	Eliminates bacteria in the water to prevent corrosive byproducts	Disinfectants used to sterilize medical and dental equipment
Breaker	Ammonium persulfate	Breaks down polymer chains to reduce viscosity and allow fracture fluid flowback	Hair coloring, disinfectant
Clay stabilizer	Choline Chloride	Prevents clay from swelling	Used in chicken feed
Friction Reducer		Minimizes friction between fluid and pipe	Depending on the type, water treatment, soil condition, laxative, candy
Gelling agent	Guar Gum	Thickens the water so it can carry proppant	Ice cream, sauces, toothpaste etc.
pH Adjuster	Sodium Hydroxide (activator)	Adjust the pH of fluid to maintain the effectiveness of other components	Soaps, detergents, water softener etc.
Gel stabilizer	Sodium Thiosulfate		Lessen side effect of some cancer medication

2.5. Flowback and Produced Water

Generally, water produced from oil and gas wells are called interchangeably called flowback or produced waters. These two terms actually stand for different waters that come back from the well after hydraulic fracturing. Flowback is defined as the fluid that flows back out of the well in the first two weeks after it has been stimulated and fractured. (Haluszczak et al, 2012) It usually contains chemicals using in the fracture fluids and dissolved solids from the reservoir (Basu, 2011).

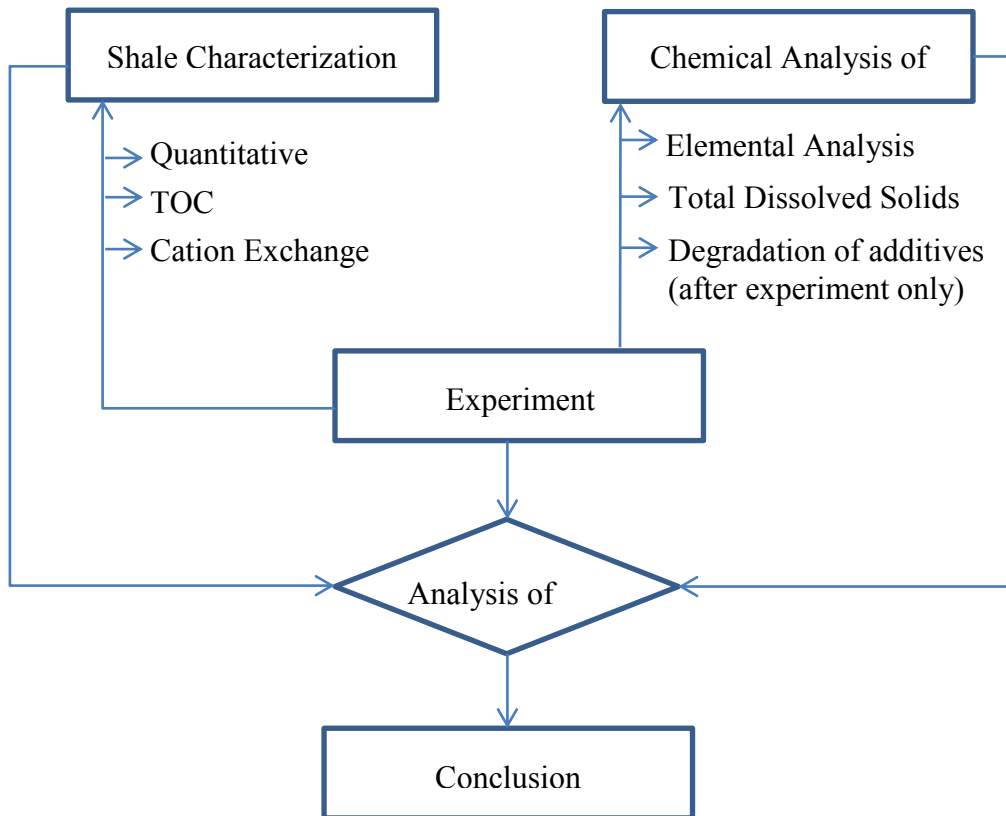
Produced water, on the other hand, is described as the remaining fluid that flows out from the well after two weeks and throughout the lifetime of the well. This water has chemicals naturally occurring in the reservoir such as Total Dissolved Solids (TDS), Total Organic Carbon (TOC) and Natural Occurring Radioactive Materials (NORM) such as radium isotopes. Minerals from the shale including barium, calcium, iron and magnesium are leached out and carried to the surface in produced water. It also contains dissolved hydrocarbons such as methane, ethane and propane.

These two types of water can be differentiated by their chemical composition and the rate of return. Typically, flowback water is produced at a higher flow rate over a shorter period of time which produced water returns to the surface at a slower rate and over a longer period of time. Over time, flowback transitions to produced water and distinguishing between both of them is a difficult task as both their chemical compositions are very similar. Flowback and produced water components are dependent on the initial fracture fluid additives, the development of the play (contamination from other wells) and pay maturity. (Blauch et al., 2010)

3. EXPERIMENTAL STUDIES

Soil characterization and mineralogy assessment are carried out to determine the properties of the different shales used in the laboratory experiments. These tests were done by independent laboratories. The Shale-Fluid interaction tests were carried out to establish what chemical reactions may have occurred in when the rock and fluid were in contact. The experimental flowchart is presented in **Figure 3.1** below.

Figure 3.1 – Experimental flowchart



Disaggregate outcrop shale samples from the Barnett, Eagle Ford and Marcellus shale plays used in these experiments were purchased from Kocurek Industries, Caldwell Texas.

X-Ray Diffraction (XRD) tests were performed by Ellington Laboratories, Houston Texas. This test was used to determine the percentage composition of the clays, carbonates and other minerals in each of the three shale types. X-Ray Fluorescence (XRF) tests (also by Ellington Labs) were used to quantify the elemental or oxide content of the shale samples. It also provides major and trace elements in solid samples. Soil characterization was carried out by the Soil Characterization Laboratory of Texas A&M University. These tests were used to also determine mineralogy but in addition, the cation exchange capacity (CEC) and organic carbon were obtained.

3.1. Determination of Mineralogy

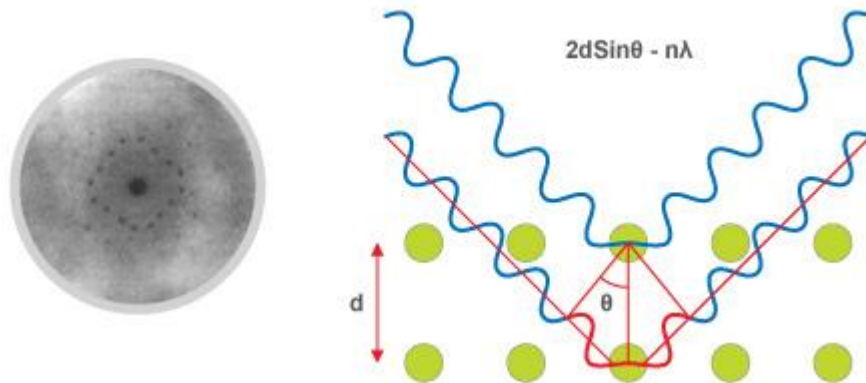
3.1.1. X-Ray Diffraction

For XRD tests, a few grams of the sample (in powder form) is placed in a holder with a flat surface and exposed to an X-Ray beam with one wavelength (one color). This beam reflects off the tiny crystals in the sample and the reflection is usually several beams at different angles. These reflected beams are measured by a detector that swings around the sample, registering the strength and positions of the beams. Different diffraction patterns result since each chemical compound reflects x-rays at slightly different wavelengths.

3.1.2. X-Ray Fluorescence

In the case of XRF, x-ray beams are used to excite a sample and this sample in turn creates secondary x-rays that can be measured using a spectrometer. Wavelengths of the x-ray beams used in this test should have as wide a range as possible (the closer to white light, the better). When the x-rays are exposed to the sample, the atoms of each different element give off one color (wavelength) of an x-ray beam. A detector measured the strength of the x-ray emitted and its intensity is relative to the amount of that element in the sample.

Figure 3.2 – X-ray beam reflection when exposed to a sample.



3.2. Soil Characterization

Characterizing soil provides the properties of the soil and it helps determine the geologic, climatic and biologic history at the location from which the soil is taken. Results from multiple tests are used to characterize the soil. Some of these tests are

- KCl Aluminum Extraction
- Ammonium Oxalate Extractable Iron.
- Cation Exchange Capacity (CEC)
- Chitticks Test
- Extractable Bases
- Gypsum
- Saturated Paste Extract
- Soil Reaction (pH)
- Total Carbon

The main tests that will be discussed in this section are the CEC, Chittick Test and Total Carbon.

3.2.1. Determination of Cation Exchange Capacity (CEC)

The Soil Characterization laboratory used the pH 7.0 ammonium acetate procedure of Chapman (1965). The samples were ground to particle sizes of less than 2mm. The procedures provided by the laboratory are as follows:

Equipment:

1. 24 place, mechanical extractor
2. 24 each, 60 cc plastic (polypropylene) syringes, sample tubes, and reservoirs.

Reagents:

1. Sodium Acetate (NaOAc) 1 N, pH 8.2. Mix 136.08 g of NaOAc in deionized H₂O for each liter of solution desired. Allow time for solution to cool to room temperature. Adjust pH to 8.2 with sodium hydroxide (NaOH) or acetic Acid (CH₃COOH) as needed.

2. Ethanol, 95%.
3. Ammonium Acetate (NH_4OAc), 1 N, pH 7.0. Mix 68 ml of reagent grade ammonium hydroxide (NH_4OH) and 57 ml of reagent grade acetic acid (CH_3COOH) per liter of solution desired. Bring to volume with deionized water, and cool to room temperature. Adjust pH to 7.0 with NH_4OH or CH_3COOH as needed.

Procedure:

1. Pack approximately .5 g filter pulp into each sample tube.
2. Weigh 2.50 g, < 2 mm air dry soil and transfer into sample tube. Install tubes in the upper disc of the extractor.
3. Install Na syringes.
4. Using a squeeze bottle containing pH 8.2 NaOAc, wash down the inside of the sample tubes.
5. Add NaOAc to the 20 ml mark of each sample tube.
6. Extract rapidly until the depth above each sample pad is about 3 to 5 ml.
7. Install Na reservoirs.
8. Add about 40 ml of NaOAc to each reservoir.
9. Extract for 2 hours; remove reservoirs.
10. Discard NaOAc extract.
11. Return extractor to starting position.
12. Reattach Na syringes to sample tubes.
13. Rinse wall of sample tube with ethanol and fill to 20 ml mark.
14. Extract rapidly until the depth of ethanol above each sample pad is 3 to 5 ml.
15. Install NH_4 reservoirs and fill to 40 ml mark with ethanol.
16. Extract for 45 min.
17. Remove reservoir and syringe and discard ethanol extracts.
18. Return extractor to starting position and add about 5 ml of ethanol to the sample.
Reattach the NH_4 reservoirs.
19. Add about 40 ml of ethanol to NH_4 reservoirs and extract for 45 minutes.

20. Remove reservoirs, discard ethanol, and return extractor to starting position.
21. Install numbered syringes.
22. Add pH 7.0 NH₄OAc to 20 ml mark.
23. Extract rapidly until depth of NH₄OAc above sample pad is about 3 to 5 ml.
24. Install NH₄ reservoirs and fill to 40 ml mark with NH₄OAc.
25. Extract for 2 hours.
26. Remove syringes. Transfer extract to a tared bottle and record weight of extract.
27. Determine concentration of Na in the extract by flame emission on the atomic absorption spectrometer. Use standards with the proper matrix (NH₄OAc) at 0, 5, 20, 40ppm.

Calculations:

CEC as (meq/100g) = (extract wt.) (mg/1 Na) (dilution)/ (sample wt.) (230)

3.2.2. Determination of Calcite, Dolomite and Calcium Carbonate Equivalent

To calculate total carbon, the calcite, dolomite and calcium equivalent have to be first determined using the Chittick test. The procedures used by the Soil Characterization Lab are as follows:

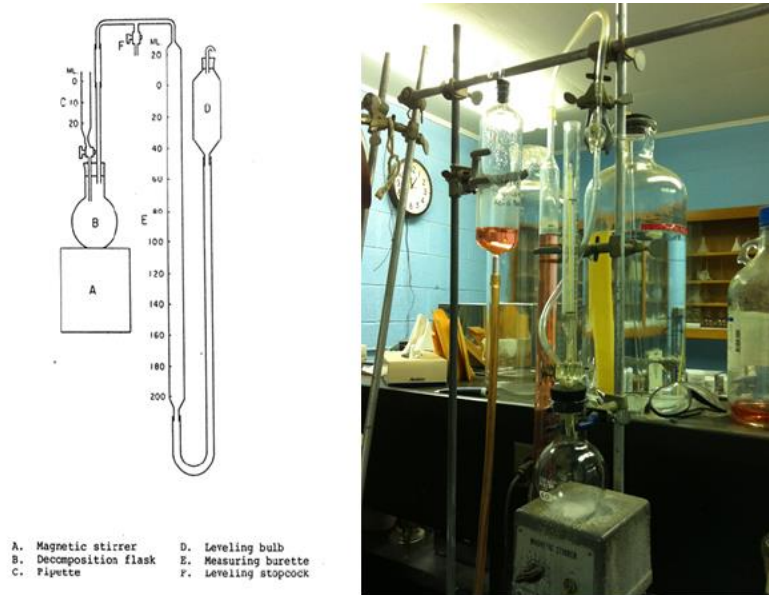
Apparatus:

Chittick apparatus as shown in **Figure. 3.3** (Dremanis, 1962)

Reagents:

Hydrochloric acid (HCl), 6 N, with 3% ferrous chloride (FeCl₂). Dilute concentrated HCl 1:1 with water and allow to cool. Determine approximate amount of acid to be used during the day's determinations and weigh appropriate amount of FeCl₂ (3 g per 100 ml) into a beaker. Add acid and stir until FeCl₂ dissolves. This solution deteriorates. Do not mix in advance of the determination.

Figure 3.3 – Chittick test apparatus



Procedure:

1. Mill grind 15 to 20 g of < 2mm samples for .20 minutes in the large mill.
2. Weigh appropriate amount of mill ground soil (see table below) to the nearest milligram into a decomposition flask.
3. Use table below to determine the sample weight

Table 3.1 — Sample weight as determined by fizz test.

Effervescence Class	Sample Weight (g)
0	Do not run
1	3
2	2
3	1
3+ or Carbonate Rock	0.5

4. Place a stir bar in the flask and add 2 drops of amyl alcohol.
5. Fill the buret tip with HCl-FeCl₂ solution and install the sample flask in the system. Fill the buret to the 5 ml mark with HCl- FeCl₂.
6. Open the 3-way stopcock to the atmosphere and adjust the liquid level in the measuring buret to +20 ml (above 0) with the leveling bulb.
7. Close the system to the atmosphere with the 3-way stopcock (180° rotation) and lower the leveling bulb about 5 ml.S
8. imultaneously begin to add HCl-FeCl₂ solution to the sample and begin lowering the leveling bulb. The leveling bulb should be kept 1 to 2 cm below the liquid level in the measuring buret.
9. After the sample is moistened, turn on the magnetic stirrer at a slow stirring rate.
10. Close stopcock after 20 ml of acid has been dispensed (25 ml mark).
11. After 30 sec. from the time you open the stopcock, equalize liquid levels in the leveling bulb and the measuring buret and read and record the volume of CO₂ that has been evolved. Also record the temperature and barometric pressure.
12. Turn off magnetic stirrers except for 15 to 30 sec stirring period every 5 to 10 min. Maintain liquid level in leveling bulb 1 to 2 cm below that in the measuring buret.
13. After 30 min., repeat measurements as in step 10.

Note: If CO₂ is still, evolving at the end of 30 min., do not make this measurement until gas evolution has stopped.

Calculations:

The calculations involved here require that CO₂ density and air density be estimated from temperature and barometric pressure. The equations given here are based on multiple regression analysis of values from standard tables and van der Waal's Equation of State against temperature (T) and barometric pressure (P).

$$\text{Air density} = 0.00977 + 0.00171 P - 0.00000609 TP + [0.0000130 T^2]$$

$$\text{CO}_2 \text{ density} = 0.0208 + 0.00262 P - 0.0000093 TP + [0.0000186 T^2]$$

Air Mass (g) = (355.0*)(Air density at 30 sec.)

CO₂ Mass 1 = (30 sec. volume)(CO₂ density at 30 sec.)(1000)

Air volume = (Air mass)/(Air density at 30 min.)

CO₂ Mass 2 = (30 min. reading + 355.0 - Air volume)(CO₂ density at 30 min.)(1000)

CO₂ from dolomite = (CO₂ Mass 2 - CO₂ Mass 1)(0.96[#])

CO₂ from calcite = CO₂ Mass 2 - CO₂ from dolomite

Calcite (%) = (CO₂ from calcite X 100)/(0.4401) X (sample wt.)

Dolomite (%) = (CO₂ from dolomite X 100 X 1.05^{**})/(0.4773 X sample wt.)

CaCO₃ equivalent (%) = % calcite + (1.085 X % dolomite)

* = approximate volume of air in the system.

= 4% of the dolomite is assumed to react within the first 30 sec.

** = 5% of the dolomite is assumed to remain unreacted after 30 min.

3.2.3. *Determination of Total Organic Carbon*

A quantitative technique is used to by the Soil Characterization Laboratory. The difference between the total carbon and the inorganic carbon (the chittick test above is used for this) is measured and then calculations are applied to find the total organic carbon (Nelson, 1982; Page, 1982) . The procedures provided by the laboratory are as follows.

Apparatus:

1. Tube furnace and scrubbing train.

Procedure:

1. Preheat combustion furnace to 950°C. Begin sweeping system with oxygen at a rate of approximately 100 cm³ per minute.
2. Determine initial weight of two adsorption bulbs.

3. Connect the inlet of one of the bulbs to the flow tube and immediately open the stopcock.
4. Insert sample of known weight into the center of the furnace (mark on rod) and immediately reinsert the stopper to begin flow.
5. Ignite the sample for 10 minutes.
6. At the end of the ignition period, close the stopcock on the adsorption bulb and immediately disconnect the bulb from the flow. Remove the ignited sample from the furnace and allow oxygen to sweep the system while the second bulb is readied.
7. Weigh the bulb and record as final weight.
8. Repeat steps 3 through 7 for subsequent samples.

Calculation:

% carbon = (final bulb weight – initial bulb weight)(27.3) / sample weight

Remarks:

1. CaCO₃ is used as a standard to insure 100% of the carbon is being recovered by the carbon train (See Fig 4). Standards should be run initially until both bulbs show 100 + /-3% recovery. A standard should also be run after every 10 samples. 0.2274 g of dry CaCO₃ is normally used and should yield 0.100 g of CO₂.
2. The final weight of the adsorption bulb should be measured and samples for analysis weighted during the 10 minute period while a sample is combusting. A new sample can be started as soon as the old one is removed from the furnace and the bulbs are changed. The final weight of the bulb becomes the initial weight the next time the bulb is used.
3. 0.25 g of manganese dioxide (MnO₂) is weighed into the combustion boat before

the sample or standard is weighed. Sample weight varies and is based on effervescence rating. Disk mill ground soil should be used.

Effervescence	Sample Weight
Slight (1)	2 g
Moderate (2)	1 g
Violent (3)	0.5 g

If the sample appears to be high in carbon (dark color) a 1.0 g ample should be used.

- When connecting and disconnecting adsorption bulbs, care should be taken to insure that the inlet side of the bulb is disconnected, and that the stopcock is opened immediately after connection, and the system is flowing freely. The two bottles of sulfuric acid should have approximately the same bubble rate if the system is flowing freely. Failure of the system to flow freely may lead to sulfuric acid being drawn into the furnace and producing a noxious gas.

Total Carbon Calculations

Table 3.2— Example of Sample weight as determined by fizz test.

FIZZ	SOIL WT.
0 – 1	2 g
2	1 g
3	.5 g
Standards	.2 g CaCO₃

If soil is very dark, use 0.5 g or less!!!

Standard Calculation

CO₂ = After wt. – Before wt.

(Standard wt.)(.44) = C

$$(\text{CO}_2 / \text{C})(100 \%) = \% \text{ Recovery}$$

Acceptable Range:

97 – 103 %

% Carbon Calculation

$\text{CO}_2 \text{ wt.} = \text{After wt.} - \text{Before wt.}$

$\text{C} = \text{CO}_2 \text{ wt.} (.2727)$

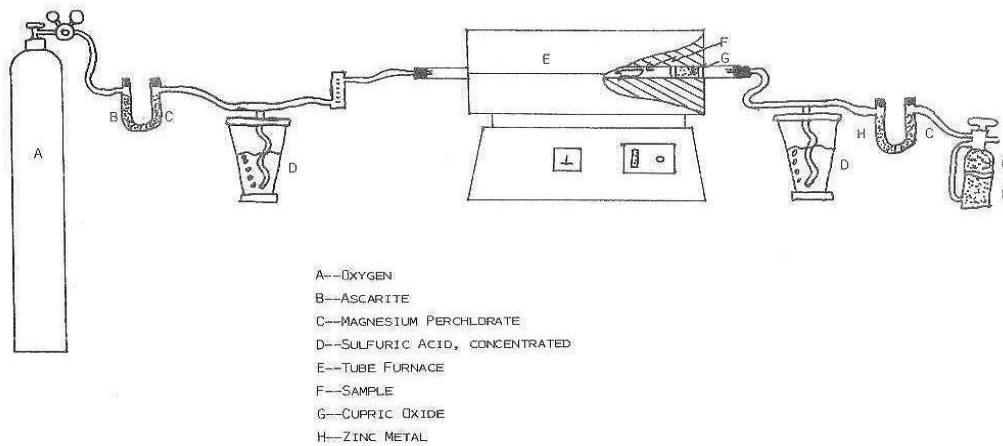
$\% \text{ C} = \text{C} / \text{Soil wt.} (100 \%)$

Error:

$A - B \leq .05$ if $\% \text{ C} \leq 1 \%$

$A - B \leq [(A + B) / 2] * .05$ if $\% \text{ C} > 1 \%$

Figure 3.4 – Carbon Train Apparatus (Holmgren, 1977) .

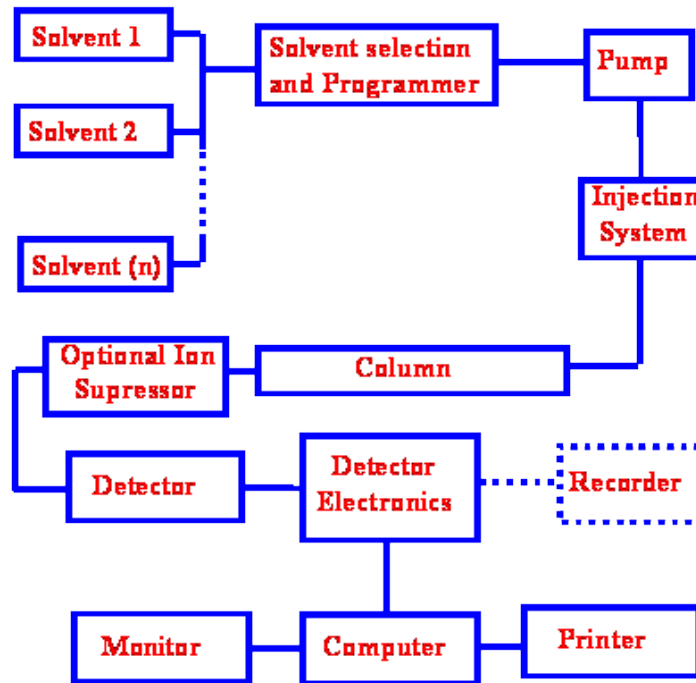


3.3. Concentration of Elements in Fluid

3.3.1. Determination of Inorganic Anions by Ion Chromatography

Energy Laboratories, College Station performed this test using the U.S. Environmental Protection Agency's (EPA) E.300.0 method (Pfaff, 1993). This method is used to measure the concentrations of Chloride (Cl) and Sulfate (SO₄). To begin, a small volume of the sample (2-3 mL) is introduced into an ion chromatograph. The anions of interest are then separated and measured using a system comprised of a guard column, analytical column, suppressor device and conductivity detector (**Figure 3.5**).

Figure 3.5 – Ion chromatography instrumentation. www.chromatography-online.org



3.3.2. *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry*

Energy Laboratories, College Station performed this test using the U.S. EPA Method E.200.7 (Martin, 1990; Martin, 1991, 1994) . This method is used to determine the concentrations of Aluminum (Al), Barium (Ba), Boron (B), Calcium (Ca), Iron (Fe), Magnesium (Mg), Potassium (K), Silicon (Si), Sodium (Na), and Strontium (Sr).

This is a summary of the method from the EPA's manual. —A aliquot of a well-mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

The analysis described in this method involves multielemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch (Pfaff, 1993). Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities

of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis.” (Kopp 1982)

3.3.3. *Measurement of Physical Properties*

Physical properties such as pH, Total Dissolved Solids (TDS), Hardness and alkalinity were performed by Energy Laboratories, College Station. The following methods were used.

3.3.3.1. Method 4500-H⁺ pH value

pH is defined as $-\log[H^+]$ (Sorenson). As one of the most significant tests in water chemistry, pH is used in nearly every phase of water supply and wastewater such as acid-base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control. In addition, temperature affects the measurement of pH and it should be recorded.

—The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode commonly is used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting

the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Because single ion activities such as a_{H^+} cannot be measured, pH is defined operationally on a potentiometric scale. The pH measuring instrument is calibrated potentiometrically with an indicating (glass) electrode and a reference electrode using National Institute of Standards and Technology (NIST) buffers having assigned values so that:

$$pH_B = -\log_{10} a_{H^+}$$

where:

pH_B = assigned pH of NIST buffer.

The operational pH scale is used to measure sample pH and is defined as:

$$pH_x = pH_B \pm \frac{F(E_x - E_s)}{2.303 RT}$$

where:

pH_x = potentiometrically measured sample pH,

F = Faraday: 9.649×10^4 coulomb/mole,

E_x = sample emf, V,

E_s = buffer emf, V,

R = gas constant; 8.314 joule/(mole °K), and

T = absolute temperature, °K.

3.3.3.2. Method 2540 Solids

According to EPA Method 2540, solids are defined as “matter suspended or dissolved in water or wastewater.” The amount of dissolved solids in water can affect the quality and usability of the water. Total Solids refers to “the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature”. Total Solids are made up of two parts, Total Suspended Solids (TSS) and Total Dissolved Solids (TDS). The former represents the part of the solids that does not pass through the filters and the latter; the solids that pass through a filter that is $\leq 2.0\mu\text{m}$ in size.

The temperature at which the solids are dried play a great role on results obtained because it affects the weight of the solids that remain. For example, weight loss due to evaporation of water of crystallization, gases from heat-induced chemical decomposition etc. or weight gain from oxidation. This project measures the Total Dissolved Solids (TDS) dried at 180°C. At this temperature, most of the mechanically occluded water and water of crystallization will evaporate. In addition, organic matter and carbon dioxide may be lost.

The sample to be analyzed is mixed well and filtered. The filtrate is then evaporated in a weighed dish at 180 °C until the weight becomes constant.

3.4. Total Organic Carbon (TOC) Measurement of Fluids

Measurements for TOC were carried out using the GE Sievers InnovOx Lab and On-Line TOC analyzer in the Global Petroleum Research Institute (GPRI) laboratory.

According to the manual, this machine uses the patented “Supercritical Water Oxidation (SCWO) technique” that heats and pressures the samples to a supercritical state in order to the most efficient oxidation possible which in turn results in greater TOC measurement accuracy and precision.

Collected samples should be decanted or filtered of large particles then samples diluted as needed. For this work, the fracture fluid flowback should be diluted to a 1:40 flowback water ratio. Water flowback samples need about a 1:5 sample flowback water dilution. This is done to ensure that the machine can flush itself adequately before running consequent samples and to prevent the internal capillary tubes from becoming clogged. Samples were run a minimum of four times and the values averaged after the outlier is eliminated.

3.5. Shale-Fluid Interaction Test

3.5.1. Sample Preparation

Care should be taken when preparing both the shale samples and fracture fluid samples. Protective Equipment should be used at all times because harmful chemicals were used for these experiments. Ensure all chemicals are stored in appropriate containers and at the right temperature. The work area should be kept clean as much as possible to prevent accidents, but more importantly to ensure samples are not contaminated.

3.5.1.1. Shale Preparation

When working with more than one shale sample, make sure every container is labeled to prevent mixing the samples up. The shale samples have to be ground and sifted to ensure uniformity of the grains.

Equipment

- Mechanical Shale Grinder (Recommended)
- Mortar and Pestle (if no mechanical shale grinder is available)
- 2 micron mesh sieve
- Googles
- Face masks

Procedure

1. Make sure the equipment to be used is clean (mortar and pestle)
2. Disaggregate shale using a hammer initially, then a mortar and pestle to grind particles into finer fragments.
3. Transfer shale from mortar to sieve using a clean spoon.
4. Use the sonic sifter to get the desired size.
5. Put the sifted shale into a clean container (air tight preferably).
6. Return pieces left in the sieve to the mortar and repeat steps 2 - 5.

* The experiment requires about 30g of shale. So make sure there are adequate amounts of ground shale before beginning the experiment.

3.5.1.2. Fracture Fluid Preparation

Again, ensure all the apparatus used for the experiment is clean and well labelled before beginning.

Equipment

- Waring blender
- Rheostat
- Pipette (if pipette is unavailable, use syringes)
- pH paper or pH meter
- Filter paper
- Scoop
- 100, 200 or 500mL graduated cylinder
- 2 100mL beakers
- Top loading balance

Procedure

1. Put 1000mL of warm water in the blender. Check the pH to ensure it is between 7 and 7.5. If the pH is greater than 7.5, add some acid until the desired pH is reached.
2. Turn the waring blender on, adjusting the rheostat until you have created enough shear (vortex).
3. Measure 3g of the gelling agent (J580) and add to the vortex. Allow the gel to completely hydrate. This will take approximately 5 minutes (or more) depending

on the temperature and pH of the water. The viscosity of the water should be consistent with honey when the gel is properly hydrated.

4. Using the pipette, add 1.9mL of the biocide (B244B), 1.9mL of the surfactant (F112), 7.57mL of the Gel Stabilizer (J535L), 3.79 mL of the Clay Stabilizer (L071) to the blender. Allow them to mix for one minute.
5. Measure 0.12 g of the High Temperature Breaker (J490) and 0.06 g of the Low Temperature Breaker (J218) separately and add them to the blender one at a time. Allow this to mix for one minute. Do NOT mix the two breakers in their dry forms.
6. When the gel is hydrated, add 3.79 mL of the activator (U028) to the blender (be careful because this material can burn skin in its raw form if contacted).
7. Shake the cross-linker (J604) vigorously and add 5.68 mL of it to the blender. Continue mixing the fluid for several more minutes (2-3) in the blender and the fluid should continue to thicken up somewhat with time.
8. Pour some of the contents into the 100 mL beaker. Continue to pour the fluid from beaker to beaker to observe that it is fully cross-linked with a “tipping” characteristic when leaning the container to its side and it should then retract back into the cup when the cup is tipped back. See **Figure 3.6**.

Figure 3.6 – Fully cross-linked gel fracture fluid. Lipping characteristic is observed.



* If the fluid is heated somewhat, the cross-link effect will occur quicker than just allowing it to happen on its own at ambient temperature.

** If using a pipette, make sure to change the disposable head is changed before dipping into another chemical.

*** Make sure all syringes are labeled for the appropriate chemical it used to measure.

3.5.2. *Shale-Fluid Interaction Test*

These are the detailed steps for exposing the shale samples to the fracture fluid and collecting samples for analysis. Extra caution should be taken when extracting samples from the oven. The samples have to be digested (procedure below) in order to preserve the iron in the solution. Further explanation about this process can be found in the results chapter. Again, all the equipment used for the experiment should be clean and well labelled before beginning. Plastic ware is preferable for collecting shale-fluid

mixture because it's easy to keep plastic clean and less contaminants can adhere to the surface.

To determine the ratio of rock to fracture fluid volume, the procedure from Byrne's paper is used. Calculations from the paper yielded a ratio based on the porosity of the rock. For example, a ratio for rock-fluid volumes would be calculated as follows:

Surface area of fracture rock: 24-60 million ft²

Volume of fluid injected: 120,000 bbl (670,000 ft³)

The assumption is that 70% ± 10% of fluid leaks off into the formation:

$$0.7 * 670000 = 469000 \pm 67000 \text{ ft}^3$$

To determine the depth of invasion, the volume of the fluid injected divided

$$\frac{536000 \text{ ft}^3}{24000000 \text{ ft}^2} = 0.0223 \text{ ft}$$

Equipment

- Roller Oven (See **Figure 3.7**)
- Aging cells (see **Figure 3.8**)
- Teflon liners for aging cells (See **Figure 3.9**)
- Allen key
- A pair of pliers
- Nitrogen gas and/or vacuum pump.
- Oven mitts
- Water bath
- 50mL test tubes

- 15 mL test tubes
- Disposable pipettes
- Concentrated nitric acid

Figure 3.7 – Roller Oven



Figure 3.8 – The Aging Cells used in the experiments.



Figure 3.9 – Teflon liners that go in the Aging Cells.



Procedure

1. Make sure all the equipment and instruments are clean.
2. Set roller oven to 250°F.
3. While the oven is heating up, set out aging cell and their lids, Teflon liners and their lids. Label each set clearly to indicate which shale samples will be placed in it and the time frame for the experiment. Ex. Marcellus, Day 10.
4. Create the required amount of fracture fluid. (See fracture fluid recipe above).
5. Insert the Teflon liners into the corresponding aging cells.
6. In 2 aging cells, measure 150 mL of fracture fluid only. Purge the air out with vacuum.
7. In the remaining nine aging cells, measure and put 100g of the 2 micron sized shale of each shale sample in each cell. In this case, three cells had the Marcellus shale samples, three had the Eagle Ford samples and the last three had the Barnett samples.
8. Add 150 mL of fracture fluid to the aging cells and stir/mix with a clean plastic spoon. For the 500 mL aging cell, a maximum of 350 mL of fluid can be used to run the experiment to remain in the acceptable pressure/temperature range for the cell.
9. Insert Teflon piston into the aging cell. Press it down until it comes in contact with the fluid/rock. Screw cap on firmly.
10. Seal the aging cell in the appropriate manner (if the lid has screws, tighten them with the Allen key). Make sure valves are attached to the lid of the aging cells.

11. Purge all the air out of the cell using a vacuum pump; then use nitrogen gas to remove the oxygen.
12. Correctly attach the nitrogen gas tank's outlet pump to the valve of the aging cell. Make sure the aging cell's valve is open then pressurize the aging cell with nitrogen gas to 100 psi. Close valve tightly (using pliers) before removing from the nitrogen connection.
13. Submerge aging cells into a water bath to ensure there are no leaks. If any leaks are observed, check the aging cell lid, valves and screw to determine origin of the leak. Replace faulty part.
14. Insert the aging cells in roller oven ensuring the temperature is now at 250°F.
15. Allow mixture to sit in the oven for the desired time, setting it to roll for an hour about 4-6 times a day.
16. When the time period has elapsed, remove the aging cells from the oven using gloves. Insert cells in a water bath to cool them down. When the cell is at room temperature, depressurize it by releasing the valve and the lid screws (if applicable).
17. Make sure all 50 mL test tubes used to collect simulated flowback are labelled correctly.

* Two separate extractions are made; the first extraction, S+A, must be done as quickly as possible to reduce the amount of time the sample is exposed to air. This first sample will be digested (see process below).

18. For S+A extractions, at least 20 mL of fluid is needed. Using a disposable pipette or Teflon syringe, remove 20 mL of the fluid and immediately transfer it to the 50mL tube labelled for that sample. Start digestion immediately.
19. Next extract 50 mL of fluid sample put it in the 50mL tube labelled for it. This portion should NOT be digested. It will be used for chemical analysis (via ICP/titration).
20. Extract about a 20g of shale. Put it in a 15 mL test tube and seal it immediately. If access to an XRD machine is readily available, put about 10 g of shale on a sample disc and set it in the oven to be dried for at least 24 hours. These samples can then be used for XRD analysis.
21. Repeat steps for other time periods. This study was done for 1, 5, 10 and 30 days for each shale sample.

For the experiments performed with just water, repeat all the steps above but instead of the crosslinked gel fluid, substitute 150 mL of water.

3.5.3. Sample Collection and Analysis

Samples were collected using clean polypropylene test tubes and disposable pipettes. Approximately 10 mL of each of the samples was collected separately and digested. This was used to test for iron. 40mL of the sample was needed for TOC testing and at least 10mL was required for ICP-MS and titration.

3.5.3.1 Sample Digestion Procedure

This procedure was furnished by the Chemistry Department of Texas A & M University.

It describes Method 1638 used by the US EPA (1995).

SOP 9201: TOTAL RECOVERABLE DIGESTION OF WATER SAMPLES (ALTERNATE TOTAL RECOVERABLE DIGESTION PROCEDURE FROM EPA METHOD 1638)

1. **REMEMBER** whenever handling water samples for trace element analysis **CONTAMINATION CONTROL IS CRITICAL**. Trace element levels are so low in most water samples that even an “invisible” amount of foreign material can cause erroneously high data. Most contamination comes from particulates in the air or on uncleaned surfaces. To avoid introducing these contaminants into samples always observe the following recommendations:
 - a. Keep the sample bottles capped and enclosed in a plastic bag (if the original sample came in a plastic bag) at all times except when actually adding or removing material from the bottle.
 - b. Always wear powder-free vinyl gloves and a Tyvek (lint-less) lab coat when handling water samples.
 - c. Do as much of the water sample handling as possible in the clean room.

2. First determine if the digestion can be done using the original bottle in which the sample was shipped. **REMEMBER:** Do not digest samples that are to be filtered for dissolved trace metals analysis (in rare cases, it *may* be necessary to digest samples that have already been filtered). Factors to consider in this decision are as follows:
 - a. Can the bottle and cap withstand the 85 °C temperature?
 - b. What volume of digested water is required for analysis?

- c. Can additional QA samples (e.g. lab dups, matrix spikes, etc.) be prepared after the digestion of the whole sample in its original container or must all samples be prepared and digested separately?
 - d. How critical is it to know the exact volume of the water digested?
3. If the original sample container can be used for the digestion proceed as follows:
- a. Estimate the volume of sample in the original container and be sure there is enough headspace to add the digestion acids. If more headspace is required, discard the appropriate sample volume after vigorous shaking.
 - b. If the required detection limits for the water samples are 1 ppb or above, then the digestion acids can be added in the open laboratory as long as careful attention is given to not contaminating the samples from airborne fallout, etc. (see para. 1). If the required detection limits are < 1 ppb (i.e. we are trying to measure actual ambient concentrations), then the acid addition should be done in the clean room.
 - c. Add ultrapure nitric and hydrochloric acids separately in the proportions indicated in the table below.
 - d. Tightly re-cap the sample and shake thoroughly.
 - e. Place in preheated 85 ° C. oven. The container should be placed on an insulating piece of material such as wood or cardboard rather than directly on the typical metal grating. *[In addition, every effort should be made to minimize the possibility of sample contamination from oven corrosion. This may require that the samples are covered with a foil "tent".]* After the samples have reached 85 °C, heat for 2 hours (Total time will be 3-6 hours depending on the sample size). Temperature in the sample bottles should be monitored indirectly using an identical sample container filled with distilled water and a thermocouple to standardize heating and digestion times.
 - f. Allow sample to cool. Prepare necessary duplicates and matrix spikes by shaking the digested sample and pouring into appropriate sized

polyethylene sample containers. Again, if required detection limits are \geq virgin bottles right out of the box. If the required detection limits are < 1 bottles. Prepare the following QA samples in addition to an aliquot of each sample:

1. *Duplicates* at the rate of 5% or one per batch whichever is greater.
2. *Matrix spikes* at the rate of 5% or one per batch whichever is greater. *Note:*
Determine whether samples are to be spiked at the instrument... If they are not:
 Spike with the standard tissue spike solution at the rate of one (1) ml per one (1) liter of sample. You will have to determine the volume of the matrix spike samples by weighing and specific gravity determination. If < 100 ml sample bottles are used spike with 50 microliters. *If samples are to be spiked at machine:*
 Pour off an aliquot of the digested sample into a bottle labeled as a spike and note that the spike must be done at the instrument.
3. *Method blank* at rate of 10% or two per batch whichever is greater. Prepare a blank by adding 0.2N ultrex nitric acid to a container.
4. *Blank spike* at the rate of 5% or one per batch whichever is greater. Spike with the standard tissue spike solution at the rate of one (1) ml per one (1) liter of sample. You will have to determine the volume of the blank spike sample by weighing and specific gravity determination. If < 100 ml sample bottles are used spike with 50 microliters.
5. *Reference material* at rate of 10% or two per batch whichever is greater. Usually SLRS-3 or NIST 1643d SRM's will be used.

Acid volumes to be used for digestion of water samples

<i>Bottle size</i>	<i>req'd headspace</i>	<i>HNO₃</i>	<i>HCl</i>
1000	75	10	5
500	50	5	2.5
250	25	2.5	1.25
125	10	1.25	0.75

If a mixed nitric/hydrochloric solution is used (having the composition 275 DIW, 150 nitric, and 75 hydrochloric acid), add 1.0 ml to the 25 ml sample.

4. If the original sample container cannot be used then proceed as follows:
 - a. If the required detection limits for the water samples are 1 ppb or above, then the digestion acids can be added in the open laboratory as long as careful attention is given to not contaminating the samples from airborne fallout, etc. (see para. 1). If the required detection limits are < 1 ppb (i.e. we are trying to measure actual ambient concentrations), then the acid addition should be done in the clean room.
 - b. Add the following ultrapure acids separately to the original sample original sample container in the proportions indicated:
 - i. **1.** Ultrex II nitric acid at the rate of 10 ml / liter of sample.
 - ii. **2.** Ultrex II hydrochloric acid at the rate of 5 ml / liter of sample.
 - c. Allow the sample to sit 48 hours at room temperature.
 - d. Prepare necessary duplicates and matrix spikes by shaking the original sample in the original sample container and pouring into appropriate sized polyethylene sample containers. Again, if required detection limits are ≥ 1 ppb then this procedure can be done carefully in the open lab using new, virgin bottles right out of the box. If the required detection limits are < 1 ppb then the procedure should be done in the clean room using precleaned bottles. Prepare the same QA samples in addition to an aliquot of each sample as described in para. 3f above.
 - e. Heat all samples as described in para. 3d and 3e above.

4. EXPERIMENTAL RESULTS

4.1. Barnett

4.1.1. Barnett Mineralogy Results

Using XRD and XRF, the bulk and clay mineralogy was obtained. The results indicate that the Barnett outcrop used for the experiments is made up of 50% clay, 50% other minerals including quartz, pyrite, gypsum etc. but no carbonates (See Table 4.1)

After exposure to the fracture fluid for 30 days, the XRD and XRF analysis were repeated for the shale sample. The table (Table 4.1) below also shows the new mineralogy obtained after 30 days compared to the original composition and the differences in each component.

Table 4.1 — Changes in bulk and clay mineralogy of the Barnett Shale sample

Mineral	Original (%)	Day 30 (%)	% change	
Smectite	0.0	0.0	0.0	
Chlorite	4.0	3.9	-0.1	↓
Kaolinite	5.0	5.6	0.6	↑
Illite/Mica	32.0	35.1	3.1	↑
Mx IS	9.0	21.3	12.3	↑
Calcite	Tr	0	0.0	
Dolomite	0	0	0.0	
Siderite	0	0	0.0	
Quartz	31	26.7	-4.3	↓
K-Feldspar	2	0.6	-1.4	↓
Plagioclase	2	0	-2.0	↓
Pyrite	1	1.3	0.3	↑
Barite	0	0	0.0	
Fluoroapatite	11	6.1	-4.9	↓

Table 4.1 Continued

	Mineral	Original (%)	Day 30 (%)	% change	
	Gypsum	3	0.7	-2.3	↓
Total	Clays	50	64.7	14.7	↑
	Carbonates	0	0	0.0	
	Other	50	35.4	-14.6	↓

4.1.2. Barnett TOC and CEC Results

The TOC is measured in units of parts per million (ppm). The initial TOC of the rock is 13.55%. After 30 days exposed to water, it is 11.85% and after 30 days exposed to fracture fluid it is 12.9%.

Table 4.2 — TOC results for Barnett Shale exposed to water and fracture fluid respectively

	Day 1	Day 5	Day 10	Day 30
Water	114.5	222.88	215.6	243.20
Fracture Fluid	4200	4935	4970	6195

The CEC of the Barnett is 18.7 meq/100g and the pH is 4.1.

4.1.3. Barnett ICP-MS Results

Table 4.3 — ICP-MS results for Barnett Shale sample exposed to water

PHYSICAL PROPERTIES	Day 1	Day 5	Day 10	Day 30
pH	3.9	3.9	3.8	4
TDS	3100	4100	4700	3300
Hardness as CaCO ₃	937	1020	1130	1450
Hardness, Calcium in CaCO ₃	512	555	607	688
Hardness, Magnesium in CaCO ₃	425	469	521	758

MAJOR IONS				
Alkalinity, Total as CaCO ₃	ND	ND	ND	ND
Bicarbonate as HCO ₃	ND	ND	ND	ND
Carbonate as CO ₃	ND	ND	ND	ND
Chloride	95	112	106	154
Sulfate	1510	1800	1980	1330
Calcium	205	222	243	275
Magnesium	103	114	127	184
Potassium	40	55	65	85
Sodium	212	210	209	297
Boron	3.3	8	5	11.5
Silicon	111	133	30.6	71.8

METALS, DISSOLVED				
Aluminum	4.1	32.7	19.5	17.8
Barium	0.45	0.63	0.23	0.34
Iron	84.7	166	194	83.2
Strontium	0.08	0.21	0.3	0.16

BALANCE				
Anions	34.1	33.3	44.5	32.5
Cations	33.4	34	33.3	44
A/C Balance	-1	1.1	-14.5	14.9

Table 4.4 — ICP-MS results for Barnett Shale sample exposed to fracture fluid

PHYSICAL PROPERTIES	Day 1	Day 5	Day 10	Day 30
pH	8.6	8.3	7.2	7.5
TDS	12400	14500	16400	16600
Hardness as CaCO ₃	345	372	237	222
Hardness, Calcium in CaCO ₃	334	209	232	215
Hardness, Magnesium in CaCO ₃	12	163	5	7

MAJOR IONS				
Alkalinity, Total as CaCO ₃	1120	622	1080	801
Bicarbonate as HCO ₃	468	759	1320	976
Carbonate as CO ₃	440	ND	ND	ND
Chloride	1310	1240	1880	1850
Sulfate	1870	2430	1840	2140
Calcium	134	84	93	86
Magnesium	3	40	ND	2
Potassium	43	42	35	44
Sodium	2560	2420	3210	3200
Boron	599	425	611	635

METALS, DISSOLVED				
Aluminum	1.1	4	8.5	75
Barium	0.55	0.58	0.47	0.9
Iron	0.4	10.2	10.6	163
Strontium	6.42	2.55	6.54	8.1

BALANCE				
Anions				
Cations	98.6	98.5	116	118
A/C Balance	120	114	145	145

4.2. Eagle Ford

4.2.1. Eagle Ford Mineralogy Results

Using XRD and XRF, the bulk and clay mineralogy was obtained. The results indicate that the Barnett outcrop used for the experiments is made up of 9.1% clay, 60% carbonates and 30.8% other minerals including quartz, pyrite, gypsum etc. After exposure to the fracture fluid for 30 days, the XRD and XRF analysis were repeated for the shale sample. The table (Table 4.5) below shows the new mineralogy from XRD obtained after 30 days compared to the original composition and the differences in each component.

Table 4.5 — Changes in bulk and clay mineralogy of the Eagle Ford Shale sample

Mineral	Original (%)	Day 30 (%)	% change		
Smectite	0	0	0	-	
Chlorite	0	0	0	-	
Kaolinite	7.2	7.3	0.1	↑	
Illite/Mica	1	2.5	1.5	↑	
Mx IS	0.9	3.2	2.3	↑	
Calcite	60.1	63	2.9	↑	
Dolomite	0	0	0	-	
Quartz	20.2	23.6	3.4	↑	
K-Feldspar	0	0	0	-	
Plagioclase	0	0	0	-	
Pyrite	5.2	0.1	-5.1	↓	
Barite	0	0	0	-	
Fluoroapatite	0	0	0	-	
Gypsum	5.4	0.3	-5.1	↓	
Total	Clays (%)	9.1	13	3.9	↑
	Carb. (%)	60	63	3	↑
	Other (%)	30.8	24	-6.8	↓

4.2.2. Eagle Ford TOC and CEC Results

The initial TOC is measured in units of parts per million (ppm). The TOC of the rock is 5.09%. After 30 days exposed to water, it is 4.43% and after 30 days exposed to fracture fluid it is 4.49%.

Tables 4.6 — TOC results for Eagle Ford Shale exposed to water and fracture fluid respectively

	Day 1	Day 5	Day 10	Day 30
Water	157.15	233.24	243.6	289.10
Fracture Fluid	4340	5145	5740	5793

The CEC of the Eagle Ford is 3.3 meq/100g and the pH is 7.5.

4.2.3. Eagle Ford ICP-MS Results

Table 4.7 — ICP-MS results for Eagle Ford Shale sample exposed to water

PHYSICAL PROPERTIES	Day 1	Day 5	Day 10	Day 30
pH	8.1	8	8	8
TDS	3500	4700	3100	2800
Hardness as CaCO ₃	1210	1150	1290	827
Hardness, Calcium in CaCO ₃	1180	1120	1260	800
Hardness, Magnesium in CaCO ₃	26	29	36	27

MAJOR IONS				
Alkalinity, Total as CaCO ₃	170	163	460	267
Bicarbonate as HCO ₃	207	199	561	325
Carbonate as CO ₃	ND	ND	ND	ND
Chloride	122	127	125	132
Sulfate	1270	1270	1330	982
Calcium	472	450	504	320
Magnesium	6	7	9	7
Potassium	11	12	13	14
Sodium	233	245	259	236
Boron	0.7	1.2	1.3	1.8
Silicon	65.5	102	42.4	47.6

METALS, DISSOLVED				
Aluminum	2	6.7	1.2	0.6
Barium	0.6	0.56	0.55	0.31
Iron	2.4	4.1	6.8	12
Strontium	2.81	2.31	1.86	2.18

BALANCE				
Anions	33.3	33.3	40.5	29.7
Cations	34.5	34	37.5	27.2
A/C Balance	1.7	1.1	-3.9	-4.5

Table 4.8 — ICP-MS results for Eagle Ford Shale sample exposed to fracture fluid

PHYSICAL PROPERTIES	Eagle Ford			
	Day 1	Day 5	Day 10	Day 30
pH	9.2	8.5	8.2	7.7
TDS	12800	13100	14400	11600
Hardness as CaCO ₃	1360	954	783	710
Hardness, Calcium in CaCO ₃	1360	951	622	696
Hardness, Magnesium in CaCO ₃	ND	3	161	14

MAJOR IONS				
Alkalinity, Total as CaCO ₃	1260	907	436	857
Bicarbonate as HCO ₃	ND	688	531	1040
Carbonate as CO ₃	532	206	ND	ND
Chloride	845	908	1230	838
Sulfate	2650	2200	3610	1640
Calcium	545	381	249	279
Magnesium	ND	ND	39	ND
Potassium	19	20	46	25
Sodium	2220	2140	2470	2010
Boron	350	358	427	354

METALS, DISSOLVED				
Aluminum	0.9	0.8	4.7	6.5
Barium	0.22	0.39	0.53	0.32
Iron	0.5	2.1	19.9	50.2
Strontium	9.77	8.04	2.83	12.3

BALANCE				
Anions	104	90.9	119	77.2
Cations	124	113	124	102
A/C Balance	8.7	10.7	2.1	13.9

4.3. Marcellus

4.3.1. Marcellus Mineralogy Results

Using XRD and XRF, the bulk and clay mineralogy was obtained. The results indicate that the Barnett outcrop used for the experiments is made up of 25% clay, 13% carbonates and 62% other minerals including quartz, pyrite, gypsum etc.

After exposure to the fracture fluid for 30 days, the XRD and XRF analysis were repeated for the shale sample. The table (Table 4.9) below shows the new mineralogy from XRD obtained after 30 days compared to the original composition and the differences in each component.

Table 4.9 — Changes in bulk and clay mineralogy of the Marcellus Shale sample

	Original (%)	Day 30 (%)	% change		
Smectite	2.0	0.0	-2.0	↓	
Chlorite	Tr	0.8	0.8	↑	
Kaolinite	0.0	0.0	0.0		
Illite/Mica	16.0	23.7	7.7	↑	
Mineral	7.0	7.7	0.7	↑	
Calcite	12	16.7	4.7	↑	
Dolomite	1	1.9	0.9	↑	
Siderite	0	0	0.0		
Quartz	41	42.2	1.2	↑	
K-Feldspar	2	0	-2.0	↓	
Plagioclase	6	2.5	-3.5	↓	
Pyrite	12	4.5	-7.5	↓	
Barite	0	0	0.0		
Fluoroapatite	1	0	-1.0	↓	
Gypsum	Tr	0	0.0		
Totals	Clays	25	32.1	7.1	↑
	Carb.	13	19	5.6	↑
	Other	62	49.2	-12.8	↓

4.3.2. Marcellus TOC and CEC Results

The initial TOC is measured in units of parts per million (ppm). The TOC of the rock is 5.50%. After 30 days exposed to water, it is 4.12% and after 30 days exposed to fracture fluid it is 4.87%.

Table 4.10 — TOC results for Marcellus Shale exposed to water and fracture fluid respectively

	Day 1	Day 5	Day 10	Day 30
Water	97.3	204.4	297.6	321.9
Fracture Fluid	4340	5250	5530	7140

The CEC of the Marcellus is 5.3 meq/100g and pH is 7.7.

4.3.3. Marcellus ICP-MS Results

Table 4.11 — ICP-MS results for Marcellus Shale sample exposed to water

PHYSICAL PROPERTIES	Day 1	Day 5	Day 10	Day 30
pH	8.1	7.9	8.2	8.1
TDS	2800	2500	3200	1500
Hardness as CaCO ₃	318	455	623	583
Hardness, Calcium in CaCO ₃	300	420	593	535
Hardness, Magnesium in CaCO ₃	19	35	30	48

MAJOR IONS				
Alkalinity, Total as CaCO ₃	180	90	267	200
Bicarbonate as HCO ₃	220	110	325	244
Carbonate as CO ₃	ND	ND	ND	ND
Chloride	87	107	155	97
Sulfate	514	801	995	884
Calcium	120	168	238	214
Magnesium	5	9	7	12
Potassium	14	16	13	13
Sodium	220	276	352	245
Boron	1.3	3.7	3.8	4.6
Silicon	65.2	104	32.2	37.5

METALS, DISSOLVED				
Aluminum	0.8	5.7	15.6	12.2
Barium	0.56	0.58	1.41	0.28
Iron	2.5	4.3	87.6	132
Strontium	0.35	0.56	1	1.3

BALANCE				
Anions	16.8	21.5	30.4	25.6
Cations	16.3	21.5	28.1	22.7
A/C Balance	-1.5	0.049	-3.9	-6

Table 4.12 — ICP-MS results for Marcellus Shale sample exposed to fracture fluid

	Marcellus			
PHYSICAL PROPERTIES	Day 1	Day 5	Day 10	Day 30
pH	9.7	8.2	7.6	7.8
TDS	10400	13100	12900	11600
Hardness as CaCO ₃	221	336	117	418
Hardness, Calcium in CaCO ₃	220	335	117	404
Hardness, Magnesium in CaCO ₃	ND	ND	ND	14

MAJOR IONS				
Alkalinity, Total as CaCO ₃	1760	1110	1500	879
Bicarbonate as HCO ₃	ND	1350	625	1071
Carbonate as CO ₃	568	ND	593	ND
Chloride	864	931	1240	804
Sulfate	716	1010	945	1140
Calcium	88	134	47	162
Magnesium	ND	ND	ND	ND
Potassium	18	20	19	25
Sodium	2140	2130	2630	1890
Boron	379	406	454	364

METALS, DISSOLVED				
Aluminum	3.5	2.3	6.8	4.3
Barium	0.8	0.53	0.51	0.48
Iron	1.9	8.4	22.5	29.8
Strontium	3.58	6.37	3.25	4.99

BALANCE				
Anions	75.1	71.4	85.2	111
Cations	98.1	99.8	117	91.2
A/C Balance	13.3	16.6	15.8	-9.7

4.4. Blank Fracture Fluid

The blank fracture fluid is used as a control in our experiment.

Table 4.13 — ICP-MS results for blank fracture fluid

PHYSICAL PROPERTIES	Blank			
	Day 1	Day 5	Day 10	Day 30
pH	10.35	9.4	8.6	7.95
TDS	12775	12825	13838	14950
Hardness as CaCO ₃	81.5	52.5	40.5	30.5
Hardness, Calcium in CaCO ₃	81.5	52	40.5	29.5
Hardness, Magnesium in CaCO ₃	ND	ND	ND	1

MAJOR IONS				
Alkalinity, Total as CaCO ₃	2420	1940	1430	608.5
Bicarbonate as HCO ₃	ND	ND	922.5	742
Carbonate as CO ₃	740	866	404	ND
Chloride	1090	1105	1159	903
Sulfate	376	822.5	1605	1341.5
Calcium	32.5	21	16.5	11.5
Magnesium	ND	ND	ND	ND
Potassium	14.5	15.5	19.5	12
Sodium	2645	2665	3010	2073.5
Boron	456.5	481	527.5	376

METALS, DISSOLVED				
Aluminum	ND	0.2	0.2	0.2
Barium	0.58	0.66	0.82	0.67
Iron	ND	ND	ND	ND
Strontium	7.37	6.38	6.76	3.30

BALANCE				
Anions	86.9	87.1	94.9	72.9
Cations	117	117.5	132	91.1
A/C Balance	14.75	15.05	16.85	9.6

Tables 4.14 — Total Organic Carbon (TOC) results for the Blank Fracture Fluid

Day 1	Day 5	Day 10	Day 30
4515	3955	5355	6510

** The TOC is measured in units of parts per million (ppm).

5. ANALYSES AND CONCLUSIONS

Tests were performed on 3 different outcrop samples; the Barnett, Eagle Ford and Marcellus shales. The results determined from the experiments with fracture fluid (FF) were repeated and the results averaged. However, the trends/patterns from rock/water experiments are preliminary observations because the tests were only carried out once.

The initial values of the water concentrations (base case) for the water/rock experiments were obtained from a water analysis report done by the Soil, Water and Forage Testing Laboratory of the Department of Soil and Crop Sciences, Texas A&M University. Table 5.1 shows the values of the tap water obtained from the lab where the experiments were carried out. For the base case of the fracture fluid/rock experiments, the total dissolved solids (TDS) value in the fracture fluid was computed by adding the TDS of tap water to the quantities of the solid components and the concentration of each element in the liquid components of the fracture fluid recipe. For the solids, a straightforward conversion to parts per million (ppm) was all that was required (i.e. a total of 26.5 lb/mgal (3.18 g/L) from the gelling agent and the breakers were converted to 3183.6 ppm). For the liquid constituents, more detailed calculations were employed using the information obtained from the MSDS sheets, atomic weight, density and mass of each element. The result of said calculations yielded ~8650 ppm of dissolved solids.

Similar calculations were utilized to calculate the concentrations of single elements such as iron, boron, sodium etc. Measurements such as alkalinity, bicarbonates

etc. were assumed to have the same values as the 24 hour broken fracture fluid that was analyzed in Energy laboratories (Table 5.1).

Table 5.1 — Results for the base cases for the water and fracture fluid experiments. (The Tap water results are from Soil, Water and Forage Laboratory’s Water analysis and the blank fracture fluid results are a combination of calculations and water analysis performed by Energy Laboratories, College Station.)

PHYSICAL PROPERTIES	A&M Tap Water	Blank fracture fluid
pH	7.88	10.35
TDS	820	8650
Hardness as CaCO ₃	11	81.5
Hardness, Calcium in CaCO ₃	NT	81.5
Hardness, Magnesium in CaCO ₃	NT	ND

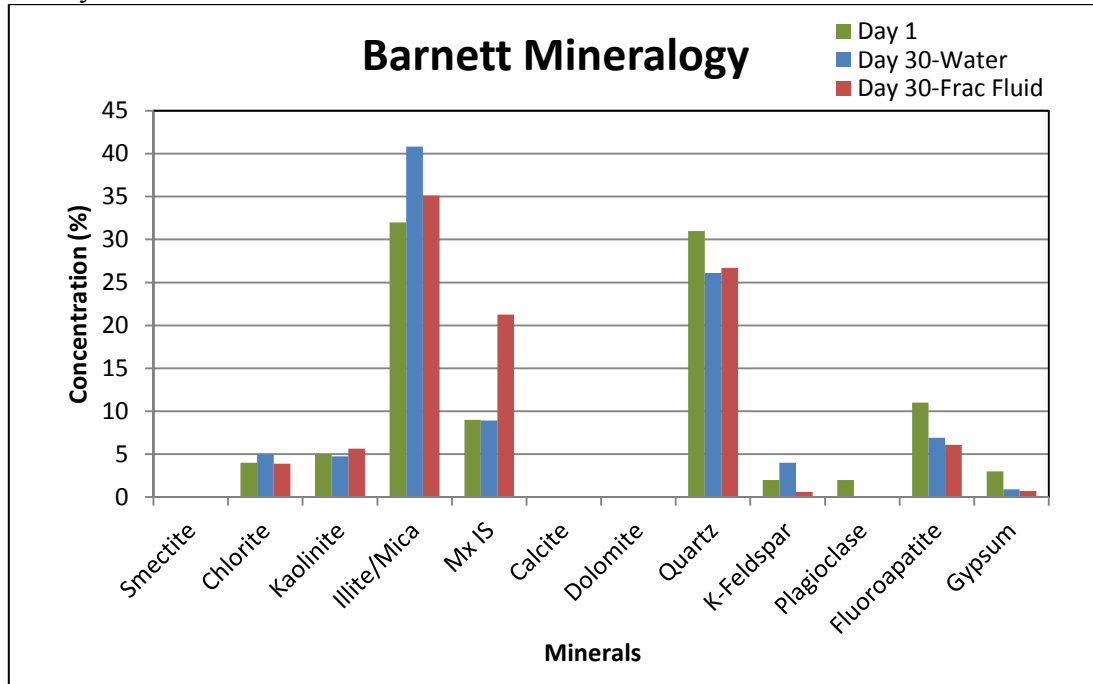
MAJOR IONS		
Alkalinity, Total as CaCO ₃	404	2420
Bicarbonate as HCO ₃	486	ND
Carbonate as CO ₃	3	740
Chloride	86	564.8
Sulfate	25	895.5
Calcium	3	32.5
Magnesium	0	ND
Potassium	3	14.5
Sodium	212	1360.75
Boron	0.3	256.95

METALS, DISSOLVED		
Aluminum	NT	ND
Barium	0.008	0.62
Iron	0	ND
Strontium	NT	7.16

ND: Not detected
 NT: Not tested

5.1. Barnett

Figure 5.1 – Barnett mineralogy results from XRD analyses. Both before the sample is exposed to the fluids and after it is exposed to water and hydraulic fracturing fluid after 30 days.



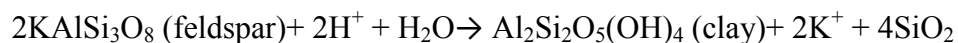
5.1.1. Observation from Mineralogy

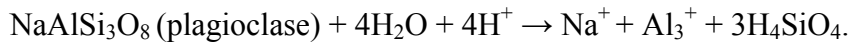
Increases in chlorite can be explained by the higher concentrations of magnesium and iron obtained from in the fluid analyses of the water flowback. Since chlorite is a hydrated aluminosilicate of magnesium and/or iron, the increased presence of iron and magnesium suggests chlorite is more reactive in water (Robinson, 2009; Gustafsson, 2002). Changes in the amount of chlorite measured either after exposure to water or fracture fluid although not statistically significant (Figure 5.1a), is not fully understood and is worth further investigation.

Similarly, a decrease in the amount of kaolinite (Figure 5.1a) is observed when the rock is exposed to water while an increase is noted after exposure to the fracture fluid. The difference in these concentrations, again since not significant is not fully understood. However, according to Curtis and Spears (1970), an increase in kaolinite could result from the silification of hydrated aluminum oxides. The concentrations of both illite/mica and mixed illite-smectite increase after exposure to fracture fluid. Assumptions can be made to suggest that the chemicals in fracture fluid, in addition to the raised temperature, create conditions that encourage conversion of kaolin to illite. (Gaudette, 1966; Colten-Bradley, 1987; Lanson et al., 2001).

Quartz is a very stable mineral at the temperatures and pressures simulated in the laboratory (Seki et al. 1964; Goldsmith, 1982), so changes in its concentration cannot be fully explained as a result of chemical reactions during the experiments. However, reactions can occur when the rock is ground to a fine powder. The decrease observed in the concentration of quartz could result from the etching that occurs on quartz grains, affecting the XRD pattern (Brantley, et al., 1986; White & Brantley, 2003).

Reduction in concentrations of k-feldspar and plagioclase are observed (See Figure 5.1). This may be because k-feldspar and plagioclase are susceptible to hydrolysis. In the presence of water and hydrogen, k-feldspar is chemically weathered and produces clay minerals, potassium ions and silicon dioxide while plagioclase produces kaolin and cations such as sodium, calcium and magnesium. (See equations below). (Lerman and Meybeck; 1988; Parsons, 1994).





The Barnett shale is devoid of carbonates.

5.1.2. *Observation from Fluid Analyses*

Physical properties

Fluids exposed to Barnett rock are buffered to a more acidic pH than that the original pH value of the base case. The pH value of the fracture fluid flowback is higher than that of the water because the fracture fluid contains a pH adjustor, sodium hydroxide, which raises the pH. The low pH of the Barnett could result from the lack of/absence of carbonates (calcite and dolomite)—see Figure 5.2. Alkalinity develops from water flowing through formations with limestone and/or marble (Mitchell et al., 2005), so the lack of carbonates in the Barnett sample not only explains the acidity of the flowback fluids collected but also clarifies the non-detectable concentrations of alkalinity and bicarbonates in the flowback analyses (Lerman and Meybeck, 1988).

As expected, TDS values are about 3 times more in fracture fluid flowback than just water flowback (9530 ppm vs. 3280 ppm). It is necessary to point out that the Energy laboratories use the evaporation method to measure TDS (EPA Method 2540). This means that the TDS values obtained from the water flowback would contain rock fragments and the value from the fracture fluid flowback could include rock fragments and broken polymers from the fracture fluid.

The measured value for TDS in the water flowback over 30 days is considerably larger than the TDS in its base case. For example, approximately 2500 – 4000 ppm (3 –

5 times more) after exposure to the rock compared to 820ppm in the base case. This indicates that minerals and solids are dissolved from the rock by water (Figure 5.3). These results are expected since the minerals and rock fragments dissolved/suspended are not adsorbed by the rock but remain in the solution.

In this Barnett sample, the TDS from the flowback after the fracture fluid is exposed to the rock (12400 ppm) for 24 hours is about the same as the TDS value obtained from the FF flowback base case (12775 ppm). Two different reasons exist for this observation. First, after 24 hours, the polymer gel is not completely broken and a clump of the gel is observed in the solution of the base case.

The second reason is due to adsorption. The CEC of the clay minerals in the rock attract the polymer fragments and cause them to attach to rock giving a lower TDS value than expected whereas in the base case, the broken polymer fragments are still in the solution, hence they are included in the measured TDS value. Over time, however, the TDS value of FF flowback exposed to rock is observed to be greater than that of the base case (which remains relatively the same) indicating that other minerals and salts are being dissolved from the rock.

Figure 5.2 – Barnett pH results obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

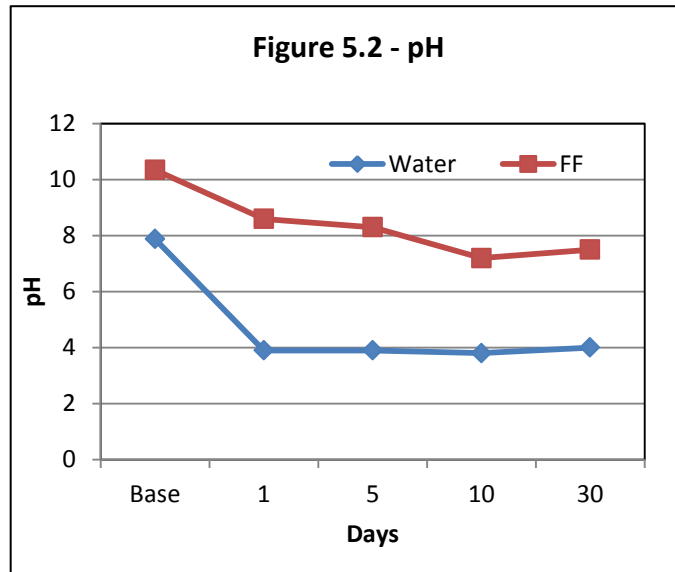
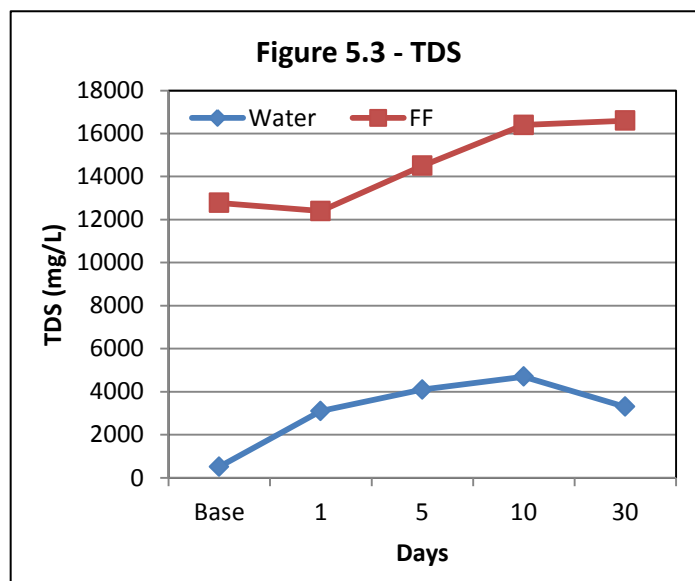


Figure 5.3 – Barnett TDS results obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



Cations

Concentrations of calcium and magnesium (Figures 5.1d & 5.1e) are higher in the water flowback than in the fracture fluid flowback. The lack of bicarbonates in the water flowback indicates that the calcium and magnesium concentrations may be coming from calcium sulfate and magnesium sulfate compounds (Rodriguez-Blanco, et al., 2008; Rodriguez-Blanco, et al., 2011). This can be backed up by the considerably high hardness values since hardness can be defined as the concentration of calcium and magnesium sulfates (Hurlbut, 1966; Hurlbut, Klein, 1985).

The increase in potassium concentrations in both flowback cases can be attributed to the dissolution of potassium (an element commonly found in soil and rock samples). (Deer et.al, 1992). (Figure 5.1f). Since potassium ions have a great affinity for clay particles, the Barnett shale (which is 50% clay) has the highest concentration of potassium ions in solution. Another possible source for the increased concentrations could occur as a result of the diagenesis of clay and reduction of plagioclase since potassium is a byproduct of both processes (Hanor, 2000, Hower, 1976).

Figure 5.4 – Barnett Calcium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

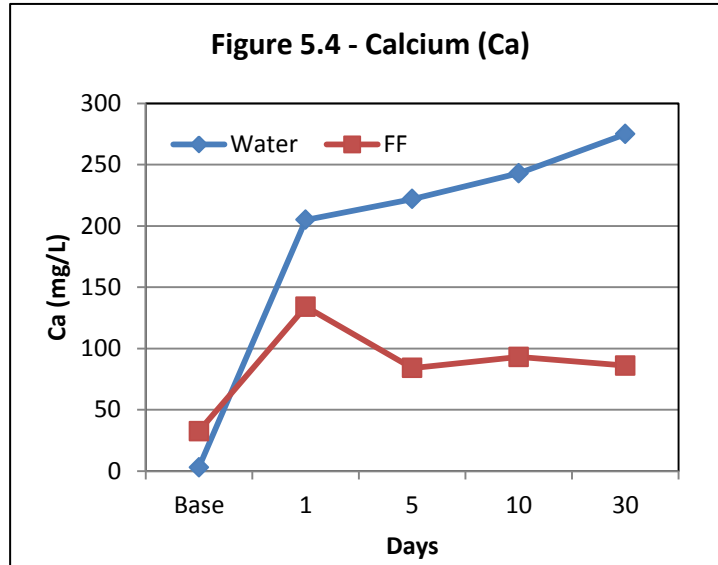
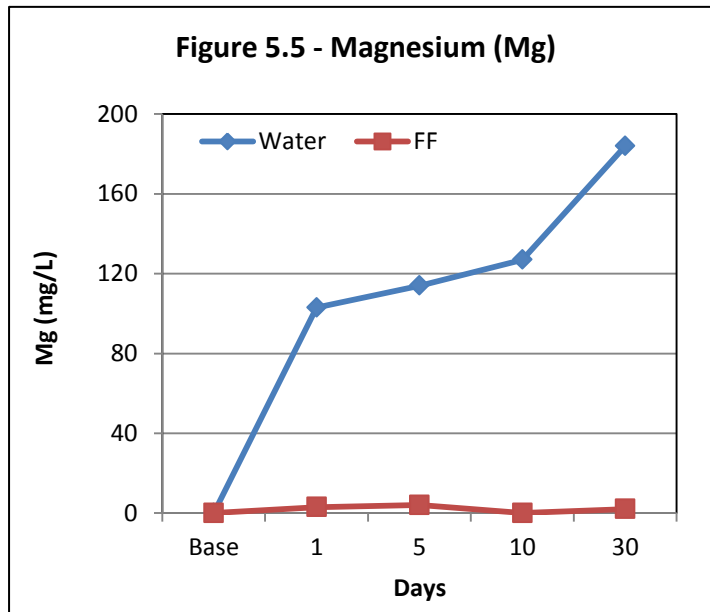


Figure 5.5 – Barnett Magnesium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



The sodium concentration does not change significantly in either case. The fact that weathered outcrop is used in the experiments suggests that the soluble salts/minerals in the rock have most likely been washed away.

Figure 5.6 – Barnett Potassium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

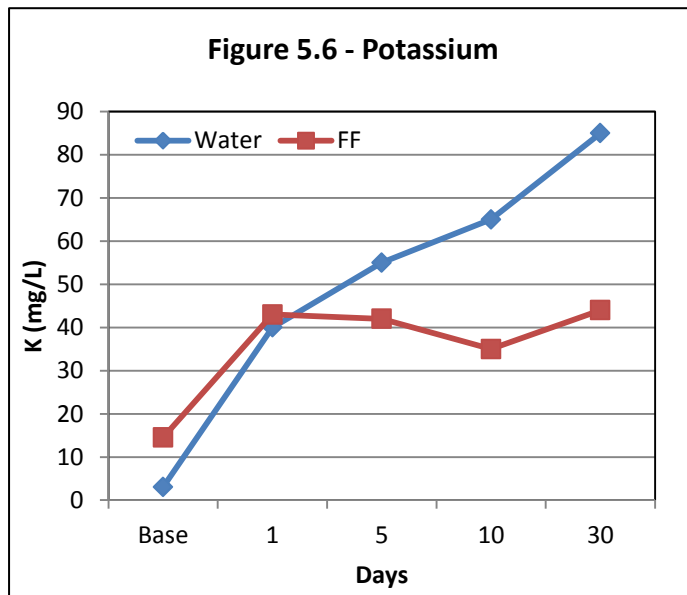
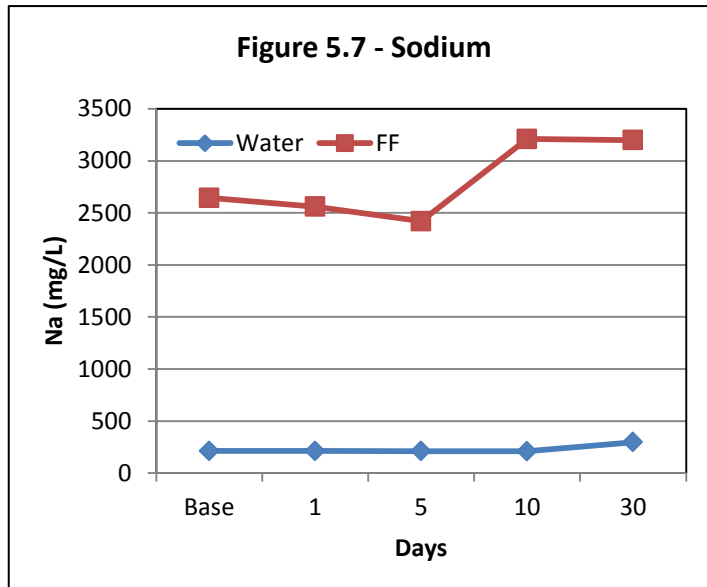


Figure 5.7 – Barnett Sodium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



Aluminum and iron concentrations in the water flowback are significantly greater than that of the fracture fluid flowback. This is due to the fact these cations are more soluble in acidic environments and the pH values of the water flowback are considerably lower than that of the fracture fluid. See Figures 5.1h & 5.1i.

Figure 5.8 – Barnett Iron concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

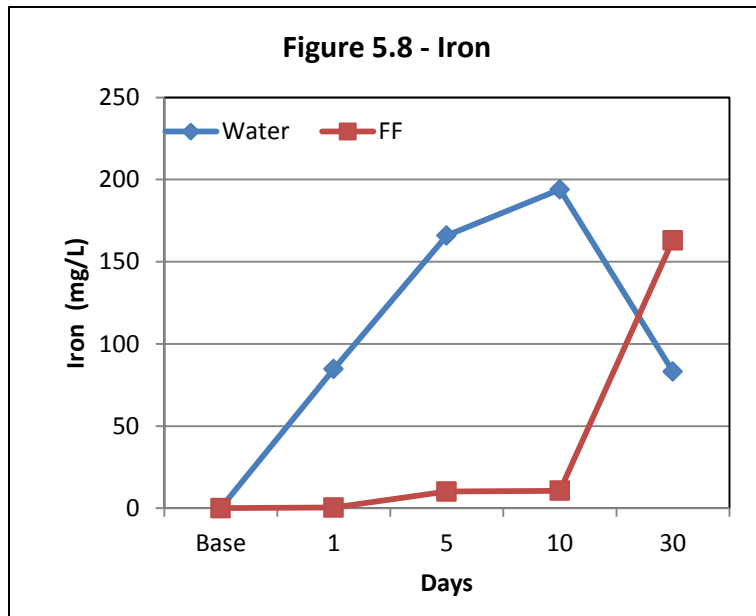
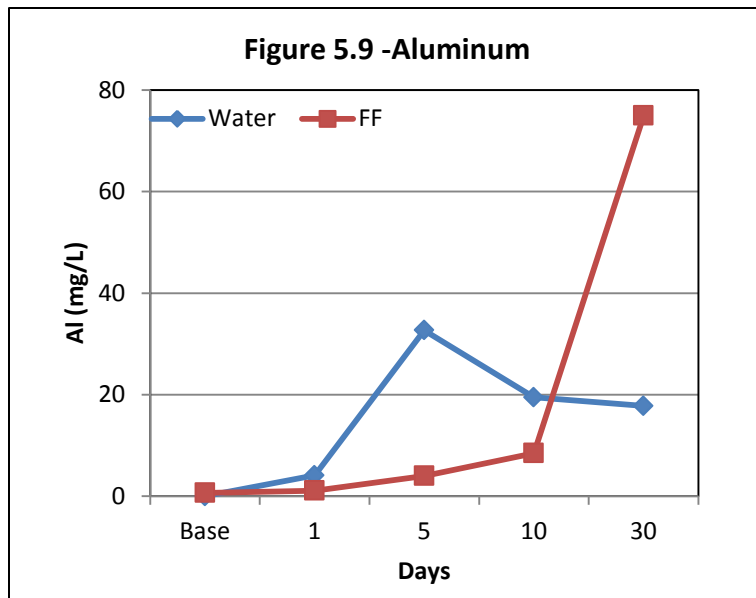


Figure 5.9 – Barnett Aluminum concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



Anions

Sulfate concentrations in the water flowback are over 60 times more than that in tap water. Generally, sulfates are soluble and form salts with cations where present. (Bock,, 1961). In this case, the high concentrations of sulfates can be attributed to the solubility of gypsum (which is a sulfate mineral). Decrease in the concentration of gypsum in the mineralogy after 30 days further supports this. For the fracture fluid flowback, additional concentrations of sulfates are introduced from the chemicals (breaker and gel stabilizer) used to create hydraulic fracturing fluids.

In the case of chlorides, the water flowback contains about twice as much chloride ions as tap water. Considering that outcrops are weathered, majority of the salinity that would be common in the subsurface is absent, explaining the low concentrations. The higher concentrations of chloride in the fracture fluid flowback could be introduced from the chemical components (clay stabilizers) in the fluid mixture.

Minimal amounts of boron are released from the rock when it is exposed to water. However, the much higher values in the fracture fluid flowback again, can be credited to the crosslinking agent in the fracture fluid.

Figure 5.10 – Barnett Chloride concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

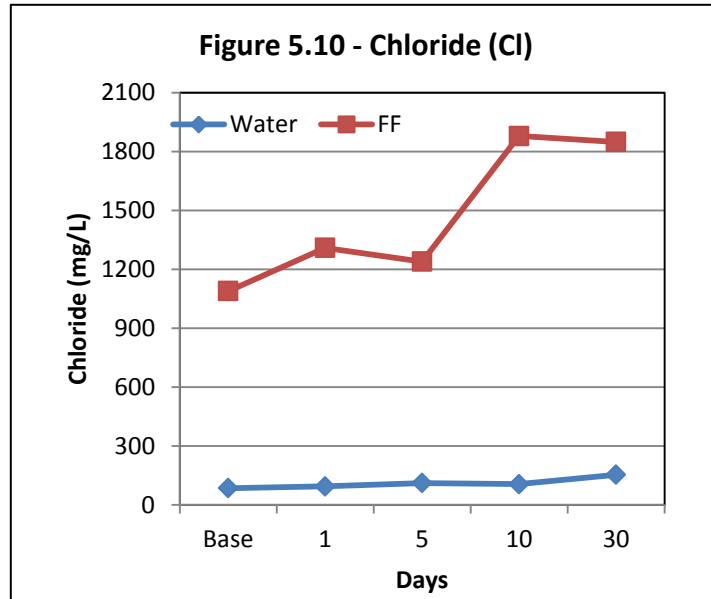


Figure 5.11 – Barnett Sulfate concentration obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

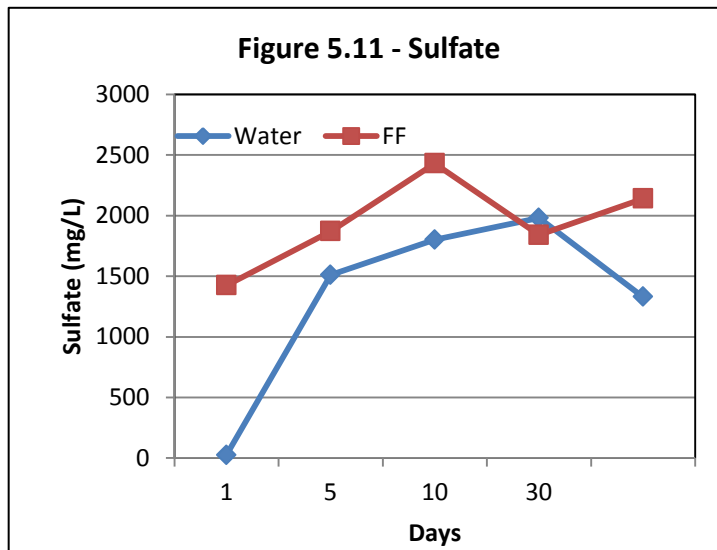
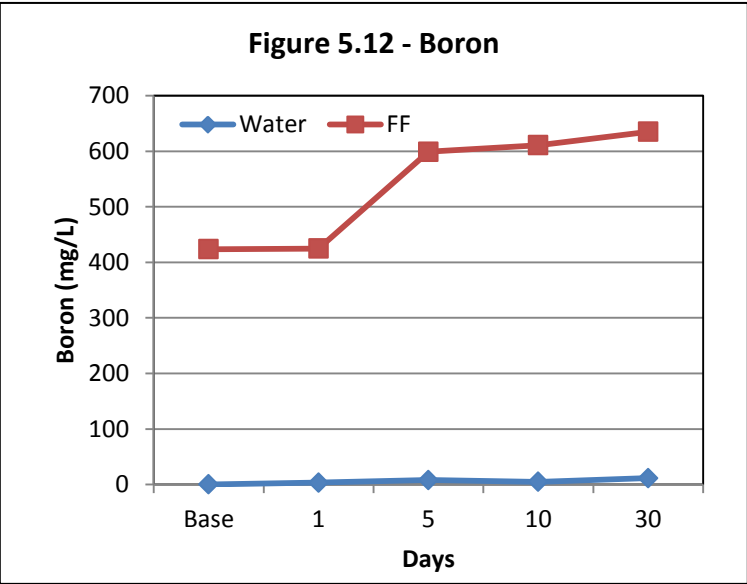
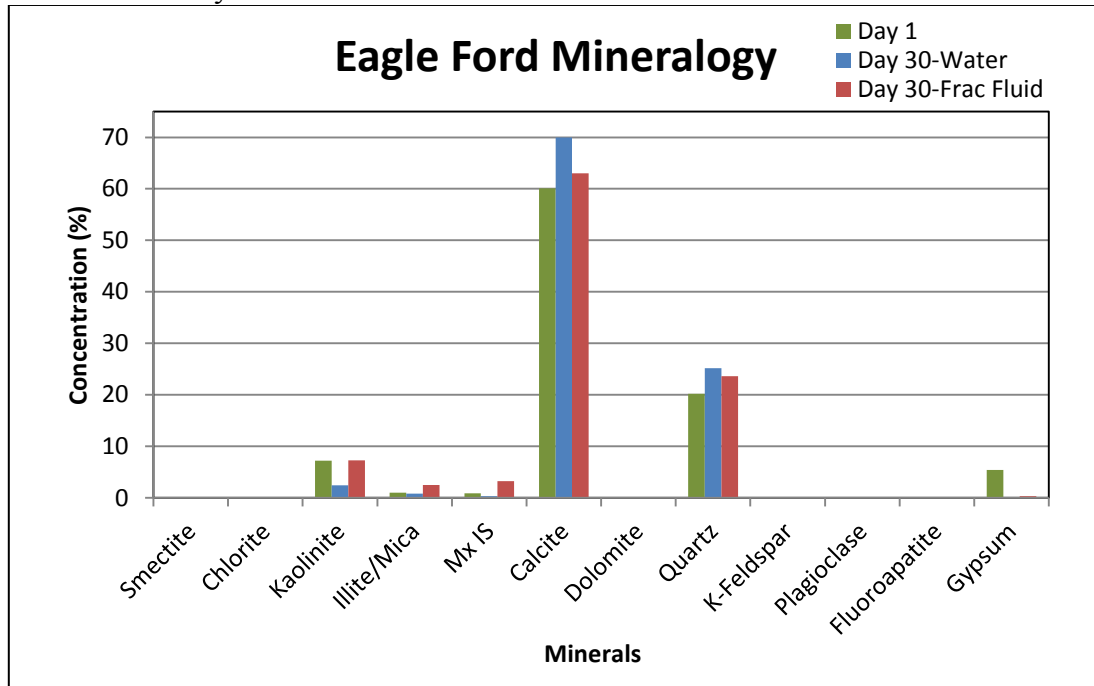


Figure 5.12 – Barnett Boron concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



5.2 Eagle Ford

Figure 5.13 – Eagle Ford mineralogy results from XRD analyses. Results before the sample is exposed to the fluids and after it is exposed to water and hydraulic fracturing fluid after 30 days.



5.2.1. Observation from Mineralogy

The kaolinite concentration remains relatively the same but the concentration of illite/mica is double the original amount after 30 days exposure to the fracture fluid. Considering the chemical composition of mica, it can be inferred that the cations (aluminum, calcium, iron, etc.) released into the solution combine with hydroxide and trace amounts of other clays to simulate illite/mica (Hower, 1981). In addition, the crystallinity of illite/mica could result in higher peaks on XRD mimicking an increase in its concentration (Jaboyedoff et al., 2001). The samples exposed to water, however,

showed a decrease in concentration of both types of clay after exposure for 30 days but there is not enough information to explain these phenomena.

From the equation, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{SO}_4^-$, gypsum dissolves in the presence of water to release byproducts of calcium and sulfate (Lerman and Meybeck; 1988). Gypsum concentrations are almost completely depleted after 30 days indicating that the calcium dissolved from the mineral may combine with carbonates in the fluids, precipitate out of solution and mimic calcite. This explanation is plausible for the increase in the calcite concentrations after 30 days in both flowback cases.

Although quartz is very stable, reactions can occur when rock samples are ground to a fine powder and a slight increase is observed in the results after exposure to the fluids for 30 days. During smectite to illite conversion, silica is one of the byproducts released during the reactions (SEPG, 2012). Therefore, the increase in quartz concentrations (Figure 5.13) could be from the silica released combining with oxygen when contacted by air and then precipitating out of the solution.

There are no k-feldspars or plagioclase minerals present in the Eagle Ford rock sample (Alder, 2009).

5.2.2. Observation from Fluid Analyses

Physical properties

The pH of the Eagle Ford is relatively constant (~8) during the 30 day time interval (rock plus water); see Figure 5.2b. The values measured in the fracture fluid

flowback are slightly higher due to the basic nature of the fracture fluid, also, the pH buffer keeps the pH elevated for at least the first 5 – 10 days.

Again, TDS values (See Figure 5.15) are higher in fracture fluid flowback than just water flowback. This explained above in the Barnett section. Similarly, the measured value of the TDS of water flowback is considerably larger than the dissolved solids found in the base tap water (approximately 5 – 9 times more solids are present in the flowback). Again, this is indicative of the rock's mineral dissolution by water.

For the Eagle Ford rock sample exposed to fracture fluid, the TDS value measured is generally lower than the other two rock samples. The CEC and the amount of clay present in the Eagle Ford sample is much lower than the other two rock samples (3.3 meq/100g vs. 18.33 meq/100g (Barnett) and 5.3meq/100g (Marcellus) —See Results in Chapter 4). This further supports the earlier hypothesis that the polymer fragments attach to the clay minerals, hence reducing measured TDS values.

Figure 5.14 – Eagle Ford TDS results obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

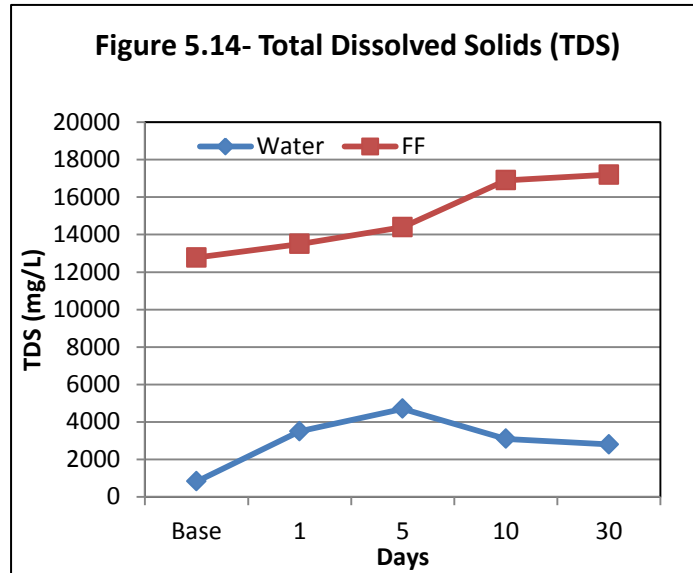
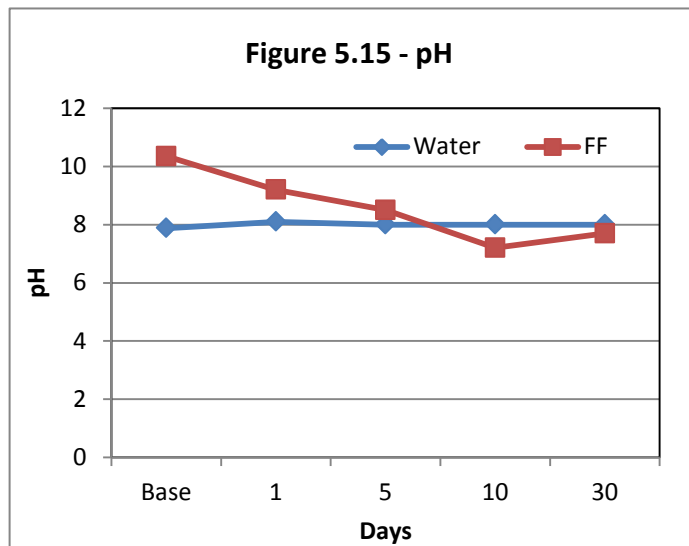


Figure 5.15 – Eagle Ford pH results obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



Cations

Concentration of calcium (Figure 5.16) in the Eagle Ford is much higher than the other two shale plays; up to twice as much as the Barnett's and four times that of Marcellus. This is understandable considering the very high amount of calcite (60%) in the Eagle Ford rock sample. On the other hand, the magnesium concentrations are very low. The XRF data indicates a low concentration of MgO, supporting also, the very low clay (illite/mica) concentrations; see Figure 5.17.

Analyses of the potassium and sodium concentrations (Figure 5.18 and 5.19) are very similar to the Barnett. However, lower concentrations of aluminum and iron (Figures 5.2h and 5.2i) are observed in the flowbacks from this rock sample (in comparison to the Barnett), is indicative of the much higher pH these systems have. In the fracture fluid flowback, concentrations of iron and aluminum exhibit a greater increase than water flowback after Day 10 as the pH of the former is lower after that time.

Figure 5.16 – Eagle Ford Calcium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

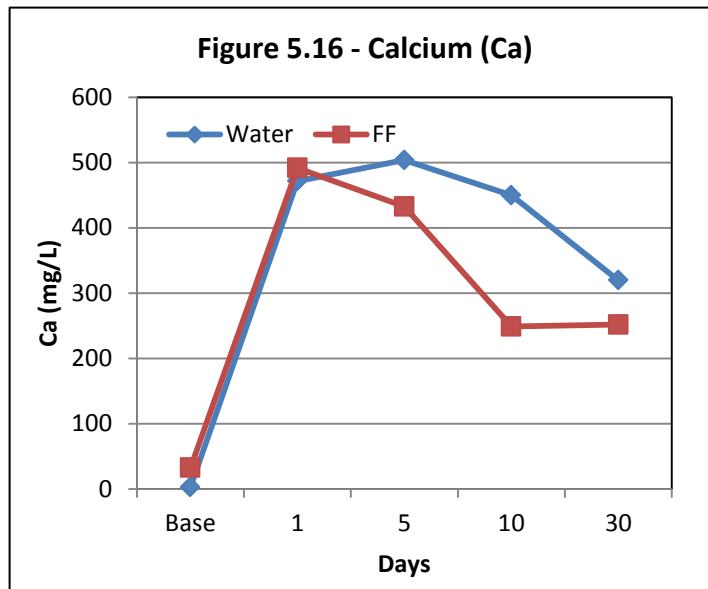


Figure 5.17 – Eagle Ford Magnesium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

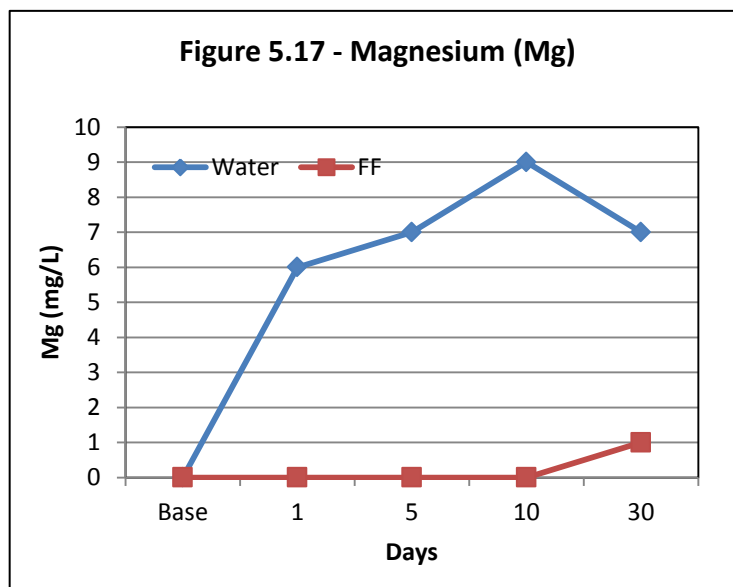


Figure 5.18 – Eagle Ford Potassium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

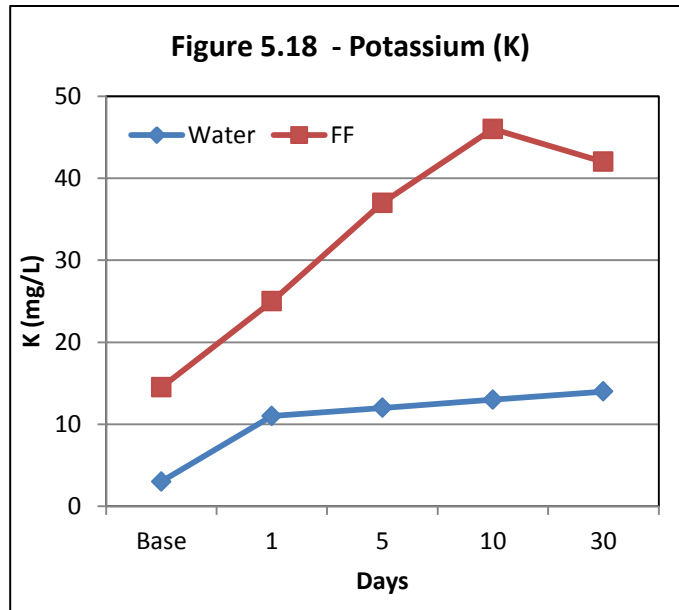


Figure 5.19 – Eagle Ford Sodium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

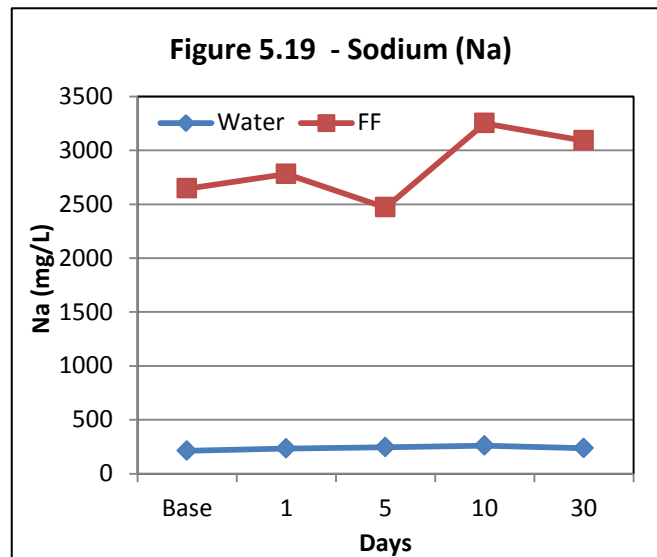


Figure 5.20 – Eagle Ford Aluminum concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

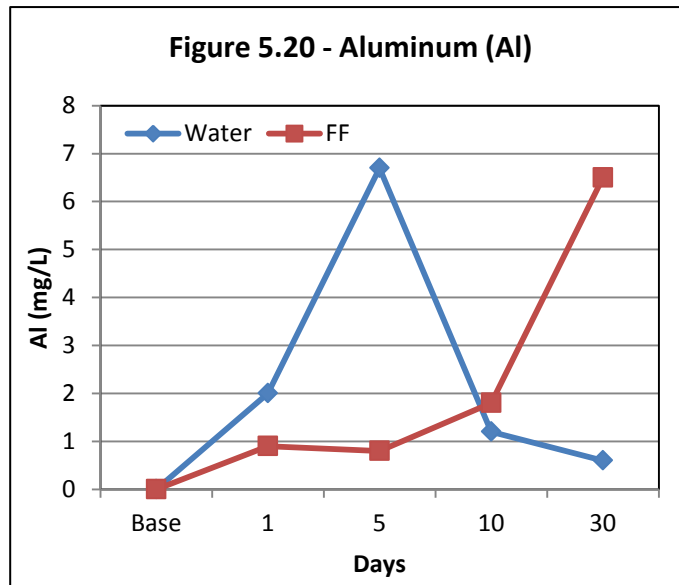
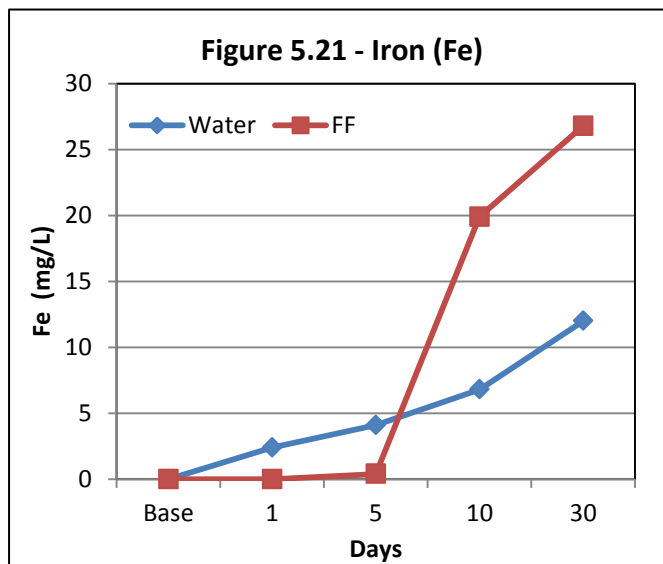


Figure 5.21 - Eagle Ford Iron concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



Anions

Similar results/explanation for chloride and sulfate concentrations as with the Barnett (See Figures 5.2j and 5.2k). This is also the case with boron concentrations (Figures 5.2l).

Figure 5.22 – Eagle Ford Chloride concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

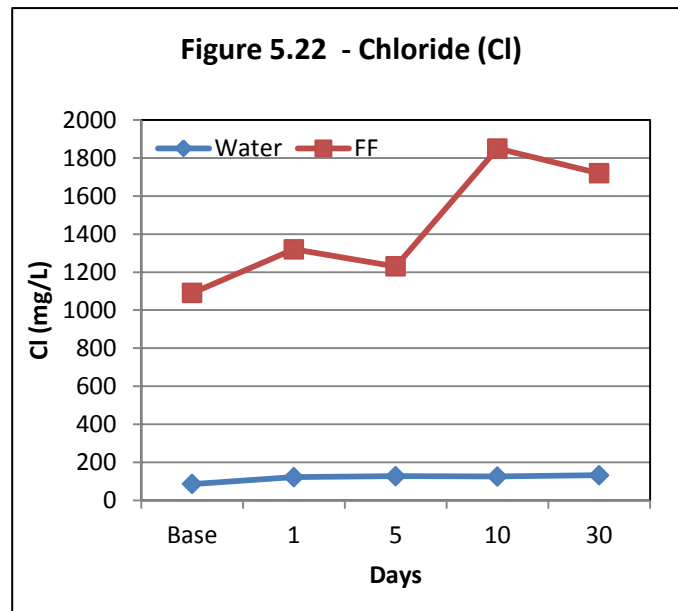


Figure 5.23 – Eagle Ford Sulfate concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

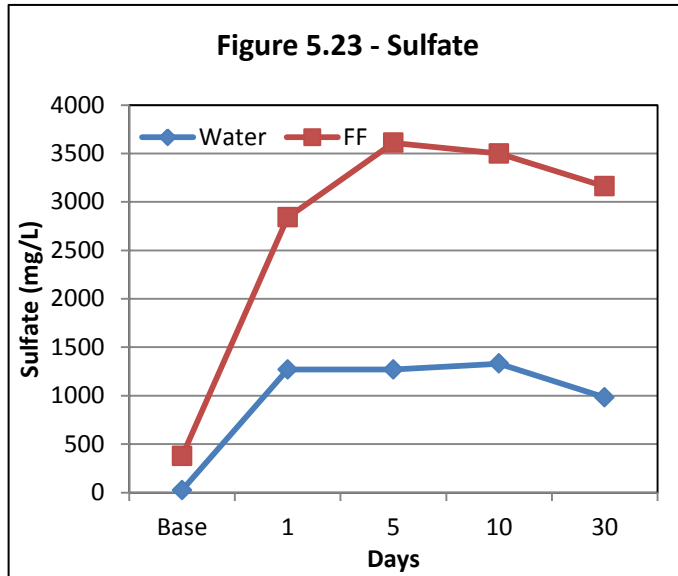
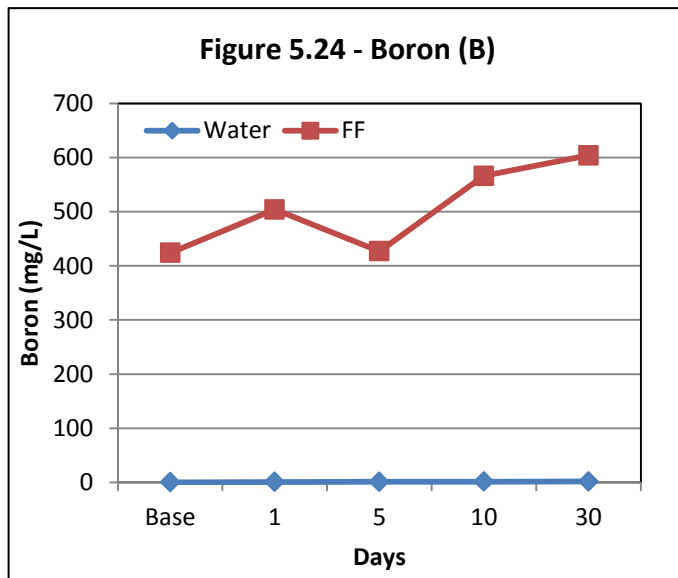
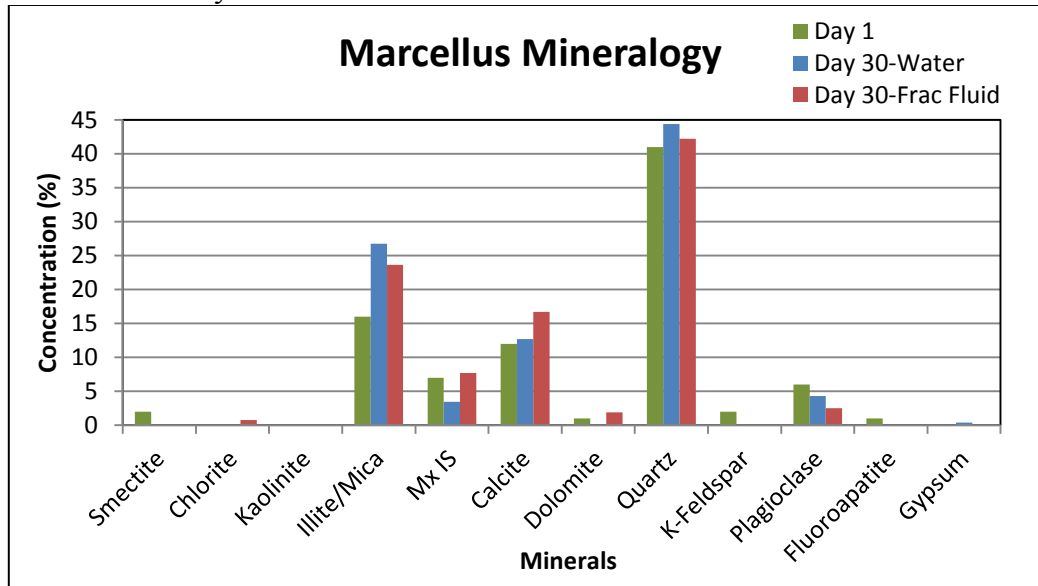


Figure 5.24 – Eagle Ford Boron concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



5.3 Marcellus

Figure 5.25 – Marcellus mineralogy results from XRD analyses. Results before the sample is exposed to the fluids and after it is exposed to water and hydraulic fracturing fluid after 30 days.



5.3.1. Observation from Mineralogy

This rock sample is the only one with smectite and after exposure to both fluids for 30 days, no smectite concentration is detected. The concentration of illite/mica increases after exposure to both fluids. According to Hower, et al. (1976), the most common diagenetic chemical change in shales is the progressive reaction of smectite to illite through a series of mixed illite/smectite (I/S) intermediate conversions. Water, silica and other ions are liberated during these reactions (Bethke and Altaner, 1986; Colten-Bradley, 1987).

The concentration of the mixed illite smectite clays reduces after exposed to water and increases after exposure to fracture fluid. This was also observed in the Eagle

Ford mineralogy analysis. This suggests that the chemicals in the fracture fluid may retard the conversion of mixed illite smectite to illite/mica.

Only trace concentrations of gypsum are measured in the Marcellus. However, there is a small amount of dolomite and fluoroapatite present and more pyrite than the previous two rock samples. According to Chan and Nancollas, 1991, fluoroapatite dissolves at relatively low temperatures in mildly acidic to neutral pHs. Hence, calcium dissolved from the fluoroapatite, like that from gypsum, may once again combine with carbonates in the fluids and precipitate out and mimic calcite. This explanation is plausible for the increase in the calcite concentrations after 30 day exposure to the fluids.

Finally, the changes to quartz, k-feldspar and plagioclase observed have been explained in the previous sections.

5.3.2. Observation from Fluid Analyses

Physical properties

Similar to the Eagle Ford sample, the pH of the Marcellus is relatively constant (~8) when exposed to water during the 30 day time interval (Figure 5.26). The values measured in the fracture fluid flowback are also slightly higher due to the basic nature of the fracture fluid and the pH buffer.

Similar trends as those explained in the Barnett are observed in the TDS values of the Marcellus. Again, TDS value are higher in fracture fluid flowback than just water flowback. Water flowback values are also considerably larger than the dissolved solids found in the tap water ; approximately 3 – 6 times more solids are dissolved from the

rock by water (Fig. 5.3c). Also, the same explanations for the initial low TDS values of FF flowback in the Barnett and Eagle Ford hold true for the Marcellus.

Figure 5.26 – Marcellus TDS results obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

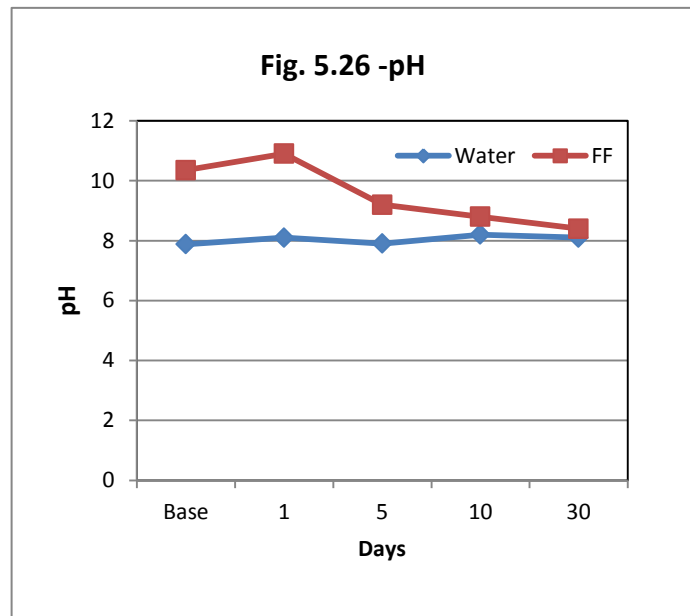
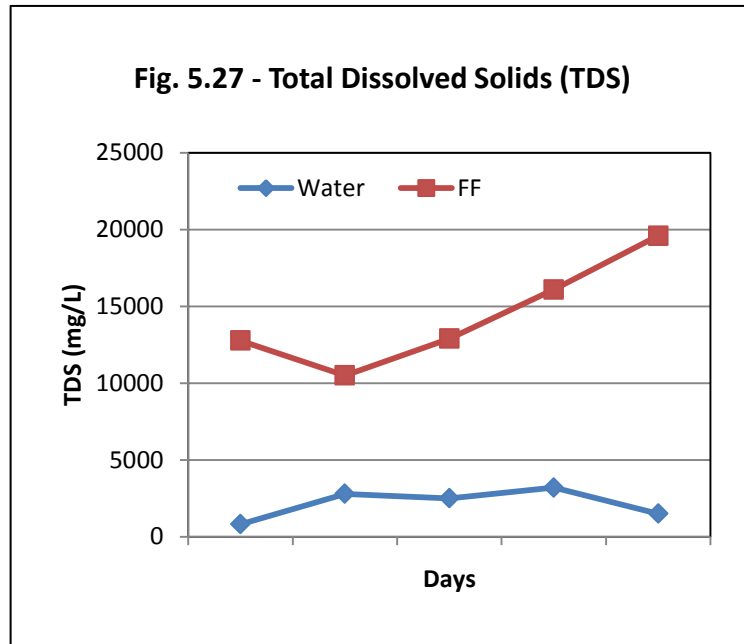


Figure 5.27 – Marcellus pH results obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



Cations

The magnesium concentrations are low when the rock is exposed to water and not detectable after exposure to fracture fluid. Mineralogy analysis indicates an almost 100% increase in the dolomite after the rock sample is exposed to fracture fluid after 30 days and a complete depletion of dolomite after exposure to water for the same time period. This could explain the concentrations of magnesium or lack thereof. Also, calcium concentrations are lower in the fracture fluid flowback (consequently, calcite concentrations are higher in mineralogy) than water flowback (calcite concentrations are lower). See Figures 5.3d & 5.3e.

Analyses of the sodium concentrations are very similar to the Barnett and Eagle Ford (Figures 5.3f & 5.3g). Potassium concentrations in these flowbacks, however, are different from the two previous samples. The concentrations of potassium decrease over time supporting the smectite to illite conversion that was discussed above in the observation from mineralogy section (SEPG, 2012). Aluminum and iron concentrations (Figures 5.3h & 5.3i) are generally much lower in the flowbacks from this rock in comparison to the Barnett since these systems have a much higher pH. Furthermore, the concentrations of both cations increase over time.

Figure 5.28 – Marcellus Magnesium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

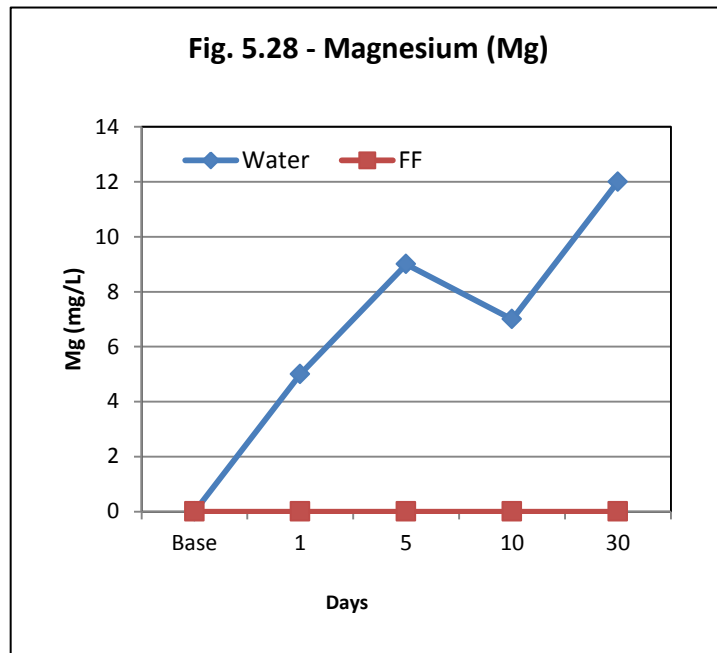


Figure 5.29 – Marcellus Calcium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

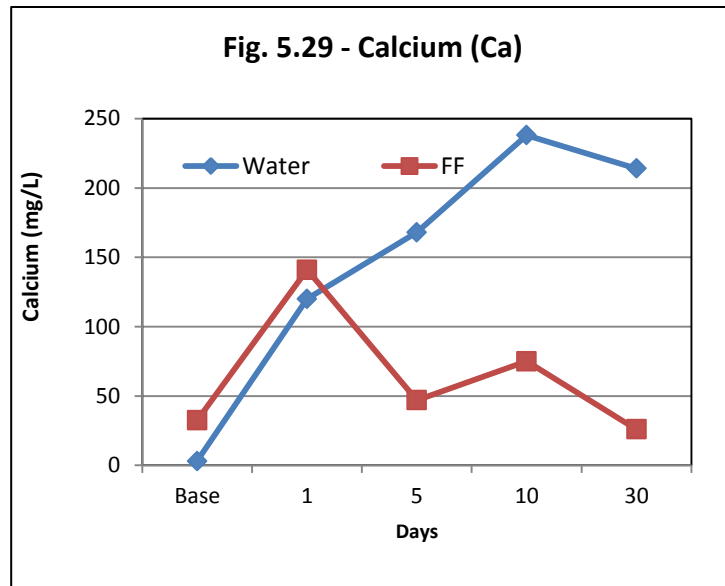


Figure 5.30 – Marcellus Potassium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

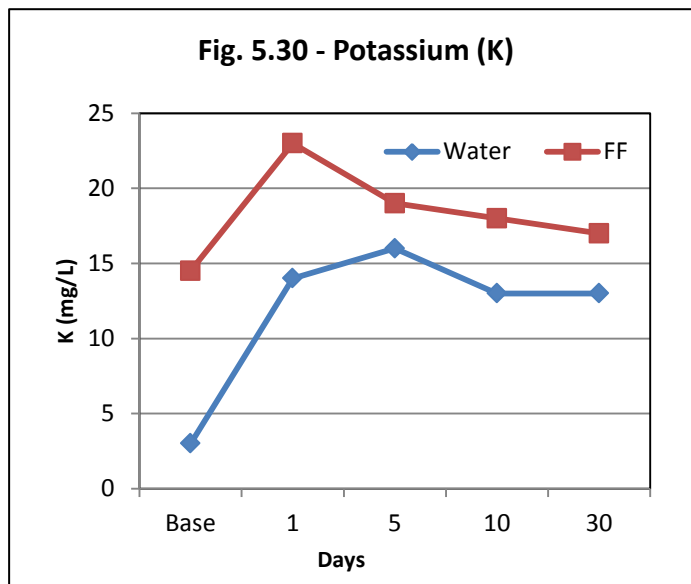


Figure 5.31 – Marcellus Sodium concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

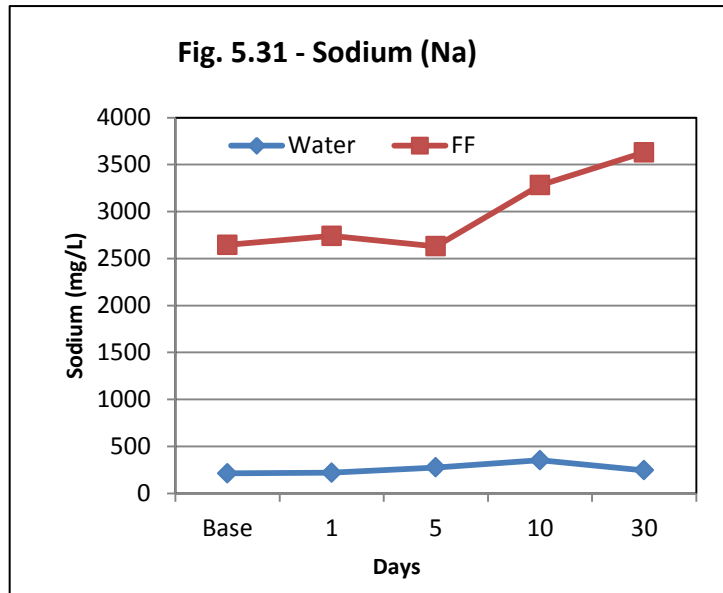


Figure 5.32 – Marcellus Aluminum concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

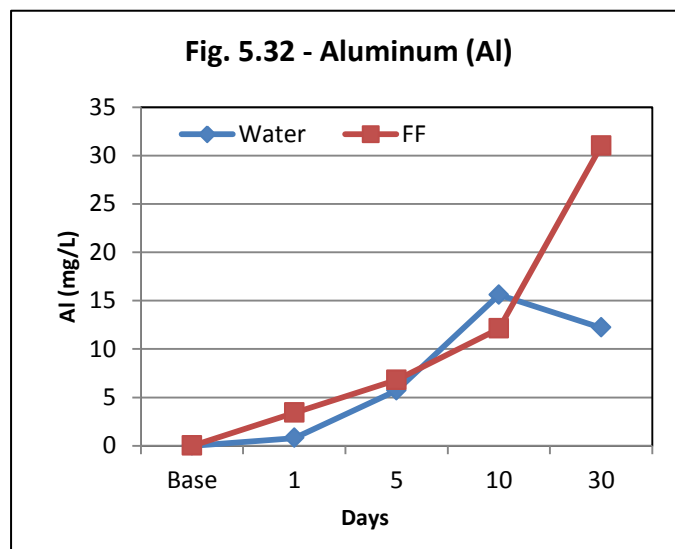
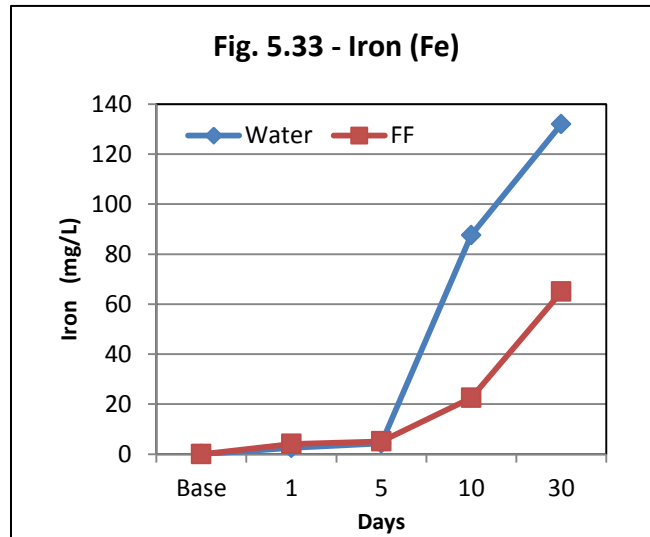


Figure 5.33 – Marcellus Iron concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.



Anions

Patterns in chloride concentrations (Figure 5.34) are similar to the other 2 rock samples (Barnett and Eagle Ford), but the sulfate concentrations (Figure 5.35) are much lower than the Barnett and Eagle Ford. The absence of gypsum could possibly justify the lower concentrations.

Boron concentrations are also analogous to both the Barnett and Eagle Ford (Figure 5.36).

Figure 5.34 – Marcellus Chloride concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

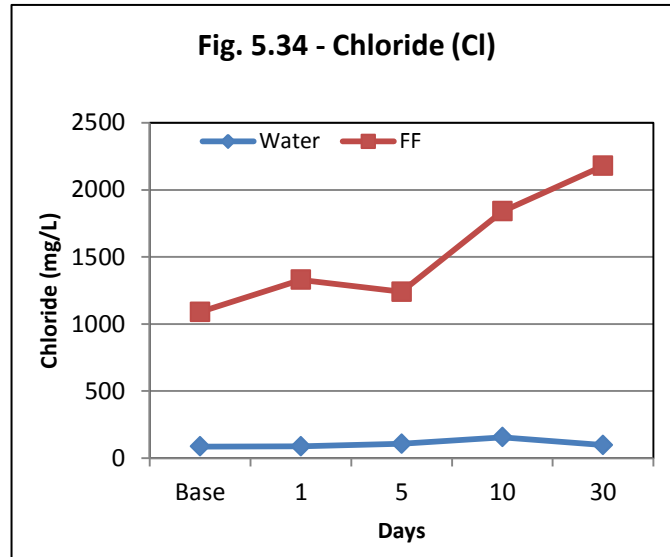


Figure 5.35 – Marcellus Sulfate concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

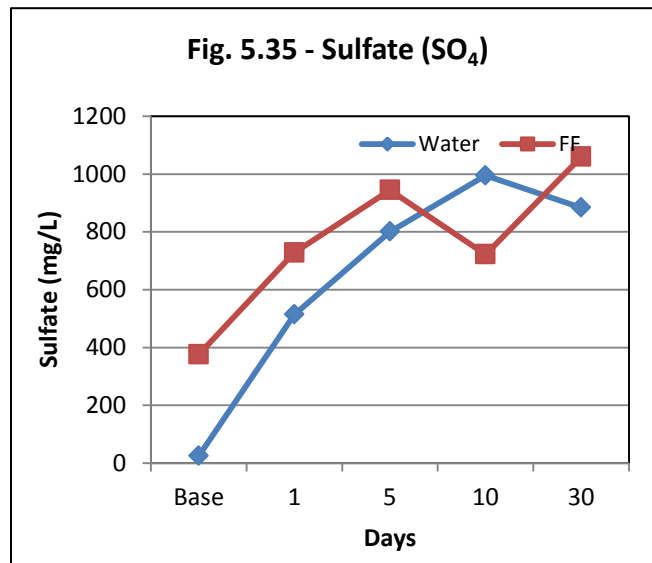
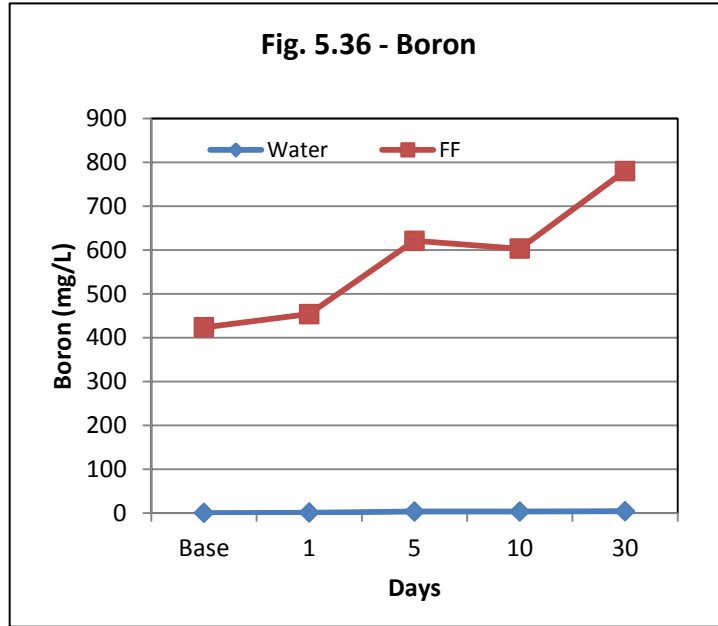


Figure 5.36 – Marcellus Boron concentrations obtained from water flowback and hydraulic fracturing fluid flowback over a period of 30 days.

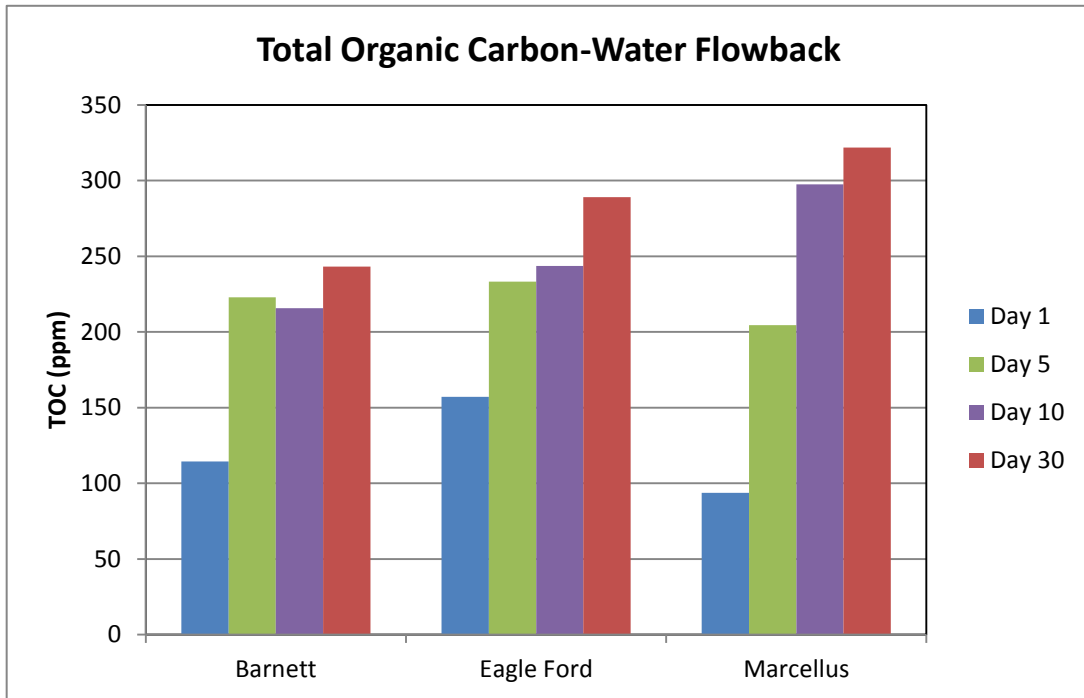


5.4. Total Organic Carbon (TOC)

5.4.1. Rock Sample Exposed to Water

The TOC of the flowback increases (Figure 5.37) while the TOC of the rock decreases in all three samples after 30 days of exposure. See Figure 5.39. These results indicate that there may be water soluble kerogen in the rock and this organic matter is leached out by the water.

Figure 5.37 – Results of the fluid analysis of the total organic carbon (TOC) after the rock was exposed to water over a period of 30 days.



5.4.2. Rock Sample Exposed to Fracture Fluid

The TOC of the fracture fluid flowback also increases over time and it is about 40 – 50 times higher than the water flowback. (Figure 5.38). Again, the broken polymers in the fracture fluid flowback could be responsible for these higher TOC values in the fracture fluid flowback.

Also as with the water flowback, an increase in the TOC is observed in all three rock samples after 30 days of exposure to fracture fluid. However, the measured value of TOC of the rock after being exposed to fracture fluid for 30 days is slightly higher than

that of the rocks exposed to water (Figure 5.39). So, although organic matter in the rock is still being leached out by the fluid, the high CEC of the clay particles causes the broken polymers attach to the rock samples thereby giving a slight increase in the TOC values obtained from the rock. See Figure 5.39.

Figure 5.38 – Results of the fluid analysis of the total organic carbon (TOC) after the rock was exposed to hydraulic fracturing fluid over a period of 30 days.

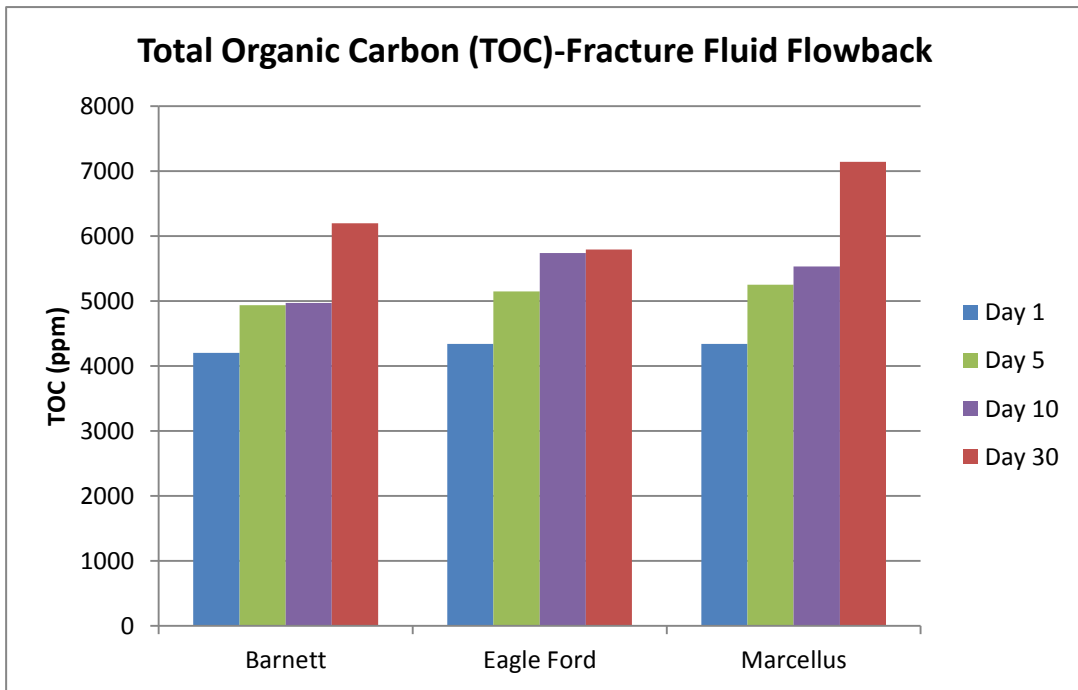
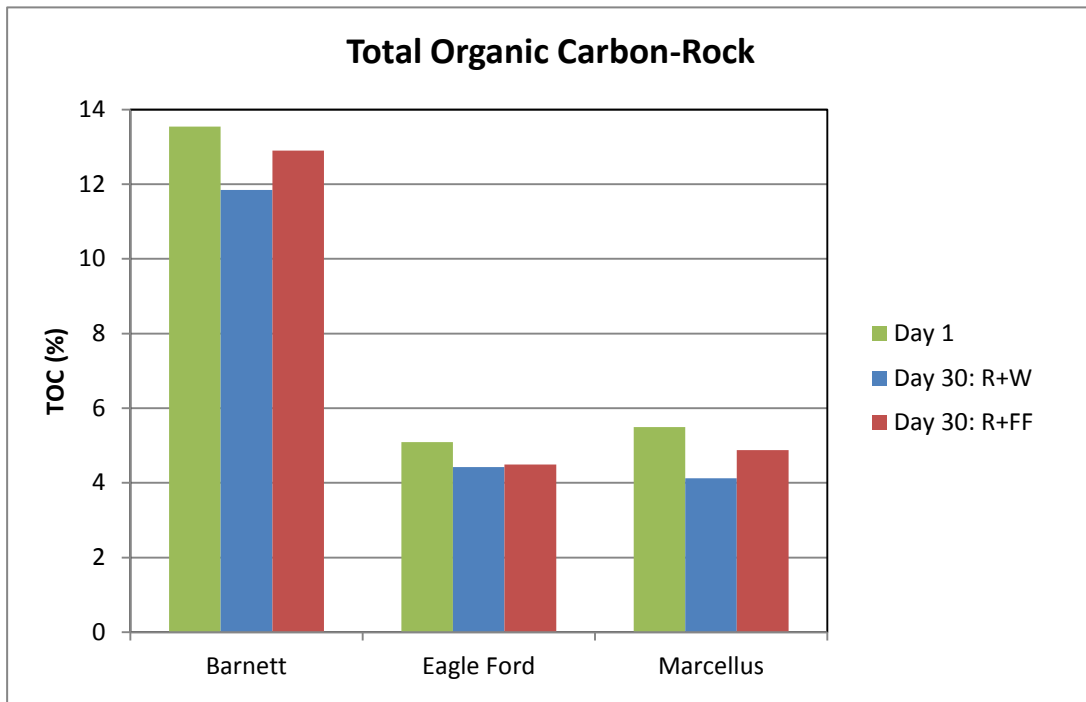


Figure 5.39 – XRD analysis results of the total organic carbon (TOC) prior to exposure to the fluids (water and hydraulic fracturing fluids) and 30 days after exposure.



5.5. Conclusions

Since clays are generally less stable and more reactive than other minerals such as quartz, feldspar, etc. reactions occur first in the clay minerals. Silica and aluminum are dissolved readily from clay mineral reactions (SEPG, 2012). In general, an increase is noted in the concentration of illite/mica and the mixed illite/smectite minerals after exposure to fracture fluids for 30 days in all three rock samples. Conclusions about kaolinite and chlorite concentrations cannot be made from the available data.

Increases in carbonates in also observed in both samples (Eagle Ford and Marcellus) suggesting calcium in the fluids combine with carbonates present and

precipitate out of solution, mimicking carbonates. Soluble minerals such as very fine k-feldspar, plagioclase, pyrite, gypsum etc. are dissolved when exposed to fluids. Changes in concentrations of quartz are a result of the size which the grains were ground to. This allowed reactions (etching of sand grains) that usually would not occur to happen.

pH and TDS follow the expected trends as in literature. Over time, pH values analyzed from the FF flowback decreases over time while the TDS increases (Blauch, 2009, LaFollette, 2010; Hayes, 2011). Similarly, an increase in the concentrations of sodium and chloride are evident in this work which is consistent with all reported work mentioned above.

Iron and aluminum are dissolved out of the rock when exposed to fluids and the results suggest that fracture fluid create an environment that allows for greater dissolution of said cations. Boron in fracture fluid flowback is present mainly as a function of the chemicals in the fraction fluid. From the results, it is clear that hardly any boron is dissolved from the rocks by fluid.

Part of the oxidative breaker (ammonium persulfate) is possibly lost to the breakdown of organic matter (Anderson, 1961). This could explain the substantial difference noted between the TOC analysis of water and FF flowback . For example, in the Barnett sample after 24 hours, the measured TOC value of water flowback is 114.5 ppm compared to 1120ppm from the fracture fluid flowback. After 30 days, the water flowback TOC is 243.2 ppm and the FF flowback TOC is 3115 ppm. This trend is similar for all tested samples. We can conclude that the presence of the breaker aids in

the dissolution and release of organic matter. More experimental work will be very helpful to completely understand this process.

Observations from the TOC analysis of the rock samples suggest that a fraction of the broken polymers from the fracture fluid stay attached to the rock (about 1%) since the rock exposed to fracture fluid exhibits a greater amount of TOC than that exposed to water despite the above mentioned findings.

5.6. Recommendations

Based on the results obtained from this work, more experiments should be carried out to understand the basic chemistry that occurs when shale rock samples are exposed to water. Armed with that knowledge, tests can then be expanded to include the analysis of slickwater fracture fluids chemistry.

Also, Scanning Electron Microscope (SEM) images of the rock samples should be taken before and after the rocks are exposed to fluids. This procedure will aid in understanding the possible development of zeolites and other types of clay minerals not easily measured by XRD techniques.

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APPENDIX A

BARNETT ROCK + WATER REPORT



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14050042-001
Client Sample ID: Lane BR1

Report Date: 05/30/14
Collection Date: 05/08/14 16:23
Date Received: 05/08/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	3.9	s.u.	H	0.1		A4500-H B	05/16/14 12:53 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	4100	mg/L		10		A2540 C	05/09/14 10:29 / rel
Hardness as CaCO3	937	mg/L		1		A2340 B	05/13/14 17:49 / ajm
Hardness, Calcium as CaCO3	512	mg/L		1		A2340 B	05/13/14 17:49 / ajm
Hardness, Magnesium as CaCO3	425	mg/L		1		A2340 B	05/13/14 17:49 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Carbonate as CO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Chloride	95	mg/L	D	10		E300.0	05/09/14 16:57 / rda
Sulfate	1510	mg/L	D	100		E300.0	05/12/14 23:29 / rda
Calcium	205	mg/L		1		E200.7	05/13/14 17:49 / jtr
Magnesium	103	mg/L		1		E200.7	05/13/14 17:49 / jtr
Potassium	40	mg/L		1		E200.7	05/13/14 17:49 / jtr
Sodium	212	mg/L		1		E200.7	05/13/14 17:49 / jtr
Boron	3.3	mg/L	D	0.2		E200.7	05/13/14 17:49 / jtr
Silica	111	mg/L	D	0.5		E200.7	05/13/14 17:49 / jtr
BALANCE							
Anions	34.1	meq/L				Calculation	05/28/14 12:33 / ajm
Cations	33.4	meq/L				Calculation	05/28/14 12:33 / ajm
A/C Balance	-1.0	%				Calculation	05/28/14 12:33 / ajm
Cation/Anion Balance includes selected metals							
METALS, DISSOLVED							
Aluminum	4.1	mg/L	D	0.2		E200.7	05/13/14 14:27 / jtr
Barium	0.45	mg/L	D	0.05		E200.7	05/13/14 14:27 / jtr
Iron	84.7	mg/L	D	0.2		E200.7	05/13/14 14:27 / jtr
Strontium	0.08	mg/L	D	0.05		E200.7	05/13/14 14:27 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

The results represented within this report relate only to the samples as submitted. This report may not be reproduced except in full.
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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14050057-001
Client Sample ID: Lane BR5

Report Date: 05/30/14
Collection Date: 05/12/14 17:29
Date Received: 05/12/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	3.9	s.u.	H	0.1		A4500-H B	05/16/14 13:53 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	3100	mg/L		10		A2540 C	05/14/14 16:30 / rel
Hardness as CaCO3	1020	mg/L		1		A2340 B	05/19/14 13:05 / ajm
Hardness, Calcium as CaCO3	555	mg/L		1		A2340 B	05/19/14 13:05 / ajm
Hardness, Magnesium as CaCO3	469	mg/L		1		A2340 B	05/19/14 13:05 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Carbonate as CO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Chloride	112	mg/L	D	10		E300.0	05/16/14 22:31 / kmh
Sulfate	1800	mg/L	D	50		E300.0	05/27/14 21:19 / rda
Calcium	222	mg/L	D	2		E200.7	05/19/14 13:05 / jtr
Magnesium	114	mg/L	D	2		E200.7	05/19/14 13:05 / jtr
Potassium	55	mg/L	D	2		E200.7	05/19/14 13:05 / jtr
Sodium	210	mg/L	D	2		E200.7	05/19/14 13:05 / jtr
Boron	8	mg/L	D	5		E200.7	05/13/14 18:08 / jtr
Silica	133	mg/L	D	1		E200.7	05/19/14 13:05 / jtr
BALANCE							
Anions	41.0	meq/L				Calculation	05/29/14 09:12 / ajm
Cations	31.0	meq/L				Calculation	05/29/14 09:12 / ajm
A/C Balance	-13.9	%				Calculation	05/29/14 09:12 / ajm
METALS, DISSOLVED							
Aluminum	32.7	mg/L	D	0.2		E200.7	05/13/14 14:39 / jtr
Barium	0.63	mg/L	D	0.05		E200.7	05/13/14 14:39 / jtr
Iron	166	mg/L	D	0.2		E200.7	05/13/14 14:39 / jtr
Strontium	0.21	mg/L	D	0.05		E200.7	05/13/14 14:39 / jtr

Report Definitions: RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University Petroleum Engineering
Project: LANE
Lab ID: T14050096-001
Client Sample ID: Lane BR10

Report Date: 06/18/14
Collection Date: 05/19/14 16:27
Date Received: 05/19/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	3.8	s.u.	H	0.1		A4500-H B	05/20/14 14:02 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	4700	mg/L		10		A2540 C	05/20/14 16:01 / rel
Hardness as CaCO ₃	1130	mg/L		1		A2340 B	05/21/14 17:27 / sas
Hardness, Calcium as CaCO ₃	607	mg/L		1		A2340 B	05/21/14 17:27 / sas
Hardness, Magnesium as CaCO ₃	521	mg/L		1		A2340 B	05/21/14 17:27 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	ND	mg/L		1		A2320 B	05/20/14 11:33 / rda
Bicarbonate as HCO ₃	ND	mg/L		1		A2320 B	05/20/14 11:33 / rda
Carbonate as CO ₃	ND	mg/L		1		A2320 B	05/20/14 11:33 / rda
Chloride	106	mg/L	D	10		E300.0	05/20/14 19:37 / rda
Sulfate	1980	mg/L	D	50		E300.0	05/28/14 14:24 / rda
Calcium	243	mg/L	D	10		E200.7	05/21/14 17:27 / jtr
Magnesium	127	mg/L	D	10		E200.7	05/21/14 17:27 / jtr
Potassium	65	mg/L	D	10		E200.7	05/21/14 17:27 / jtr
Sodium	209	mg/L	D	10		E200.7	05/21/14 17:27 / jtr
Boron	5	mg/L	D	2		E200.7	05/21/14 17:27 / jtr
Silicon	30.6	mg/L	D	0.2		E200.7	05/22/14 16:26 / jtr
Silica	65.5	mg/L	D	0.5		E200.7	05/22/14 16:26 / jtr
BALANCE							
Anions	44.5	meq/L				Calculation	06/03/14 14:54 / sas
Cations	33.3	meq/L				Calculation	06/03/14 14:54 / sas
A/C Balance	-14.5	%				Calculation	06/03/14 14:54 / sas
METALS, DISSOLVED							
Aluminum	19.5	mg/L	D	0.2		E200.7	05/28/14 16:38 / jtr
Barium	0.23	mg/L	D	0.05		E200.7	05/28/14 16:38 / jtr
Iron	194	mg/L	D	0.2		E200.7	05/28/14 16:38 / jtr
Strontium	0.30	mg/L	D	0.05		E200.7	05/28/14 16:38 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University Petroleum Engineering
Project: LANE
Lab ID: T14050134-001
Client Sample ID: Lane BR30

Report Date: 06/16/14
Collection Date: 05/28/14 16:32
Date Received: 05/28/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	4.0	s.u.	H	0.1		A4500-H B	06/02/14 11:00 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	3300	mg/L		1000		A2540 C	05/30/14 10:56 / rda
Hardness as CaCO ₃	1450	mg/L		1		A2340 B	05/30/14 17:13 / sas
Hardness, Calcium as CaCO ₃	688	mg/L		1		A2340 B	05/30/14 17:13 / sas
Hardness, Magnesium as CaCO ₃	758	mg/L		1		A2340 B	05/30/14 17:13 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	ND	mg/L		1		A2320 B	06/02/14 10:55 / rel
Bicarbonate as HCO ₃	ND	mg/L		1		A2320 B	06/02/14 10:55 / rel
Carbonate as CO ₃	ND	mg/L		1		A2320 B	06/02/14 10:55 / rel
Chloride	154	mg/L	D	50		E300.0	06/05/14 18:33 / rda
Sulfate	1330	mg/L	D	50		E300.0	06/05/14 18:33 / rda
Calcium	275	mg/L		1		E200.7	05/30/14 17:13 / jtr
Magnesium	184	mg/L		1		E200.7	05/30/14 17:13 / jtr
Potassium	85	mg/L	D	2		E200.7	06/04/14 16:54 / jtr
Sodium	297	mg/L		1		E200.7	05/30/14 17:13 / jtr
Boron	11.5	mg/L	D	0.5		E200.7	06/04/14 16:54 / jtr
Silicon	71.8	mg/L	D	0.5		E200.7	06/10/14 09:43 / jtr
BALANCE							
Anions	32.5	meq/L				Calculation	06/12/14 16:08 / sas
Cations	44.0	meq/L				Calculation	06/12/14 16:08 / sas
A/C Balance	14.9	%				Calculation	06/12/14 16:08 / sas
METALS, DISSOLVED							
Aluminum	17.8	mg/L	D	0.2		E200.7	06/04/14 13:24 / jtr
Barium	0.34	mg/L	D	0.05		E200.7	06/04/14 13:24 / jtr
Iron	83.2	mg/L	D	0.2		E200.7	06/04/14 13:24 / jtr
Strontium	0.16	mg/L	D	0.05		E200.7	06/04/14 13:24 / jtr

Report Definitions: RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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APPENDIX B

BARNETT ROCK + FRACTURE FLUID REPORT



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14020023-001
Client Sample ID: Lane B1

Report Date: 02/19/14
Collection Date: 02/06/14 17:12
Date Received: 02/06/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	6.9	s.u.	H	0.1		A4500-H B	02/12/14 11:30 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	14000	mg/L		10		A2540 C	02/07/14 16:10 / rel
Hardness as CaCO3	297	mg/L		1		A2340 B	02/10/14 13:26 / sas
Hardness, Calcium as CaCO3	182	mg/L		1		A2340 B	02/10/14 13:26 / sas
Hardness, Magnesium as CaCO3	114	mg/L		1		A2340 B	02/10/14 13:26 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	242	mg/L		1		A2320 B	02/12/14 10:59 / rel
Bicarbonate as HCO3	295	mg/L		1		A2320 B	02/12/14 10:59 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	02/12/14 10:59 / rel
Chloride	871	mg/L	D	50		E300.0	02/08/14 02:19 / rda
Sulfate	1780	mg/L	D	50		E300.0	02/08/14 02:19 / rda
Calcium	73	mg/L	D	10		E200.7	02/10/14 13:26 / jtr
Magnesium	28	mg/L	D	10		E200.7	02/10/14 13:26 / jtr
Potassium	37	mg/L	D	10		E200.7	02/10/14 13:26 / jtr
Sodium	1940	mg/L	D	10		E200.7	02/10/14 13:26 / jtr
Boron	387	mg/L	D	2		E200.7	02/10/14 13:26 / jtr
BALANCE							
Anions	67.0	meq/L				Calculation	02/18/14 08:51 / sas
Cations	91.3	meq/L				Calculation	02/18/14 08:51 / sas
A/C Balance	15.3	%				Calculation	02/18/14 08:51 / sas
METALS, DISSOLVED							
Aluminum	6.3	mg/L	D	0.2		E200.7	02/13/14 18:22 / jtr
Barium	0.17	mg/L	D	0.05		E200.7	02/13/14 18:22 / jtr
Iron	10.3	mg/L	D	0.2		E200.7	02/13/14 18:22 / jtr
Strontium	2.01	mg/L	D	0.05		E200.7	02/13/14 18:22 / jtr

Report Definitions: RL - Analyte reporting limit. MCL - Maximum contaminant level.
QCL - Quality control limit. ND - Not detected at the reporting limit.
D - RL increased due to sample matrix. H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14040117-001
Client Sample ID: Lane B1B

Report Date: 05/08/14
Collection Date: 04/28/14 11:44
Date Received: 04/28/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.6	s.u.	H	0.1		A4500-H B	04/28/14 15:09 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	12400	mg/L		10		A2540 C	04/29/14 10:49 / rel
Hardness as CaCO ₃	345	mg/L		1		A2340 B	04/30/14 14:07 / sas
Hardness, Calcium as CaCO ₃	334	mg/L		1		A2340 B	04/30/14 14:07 / sas
Hardness, Magnesium as CaCO ₃	12	mg/L		1		A2340 B	04/30/14 14:07 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	1120	mg/L		1		A2320 B	04/28/14 11:30 / rel
Bicarbonate as HCO ₃	468	mg/L		1		A2320 B	04/28/14 11:30 / rel
Carbonate as CO ₃	440	mg/L		1		A2320 B	04/28/14 11:30 / rel
Chloride	1310	mg/L	D	50		E300.0	04/29/14 13:37 / rda
Sulfate	1870	mg/L	D	50		E300.0	04/29/14 13:37 / rda
Calcium	134	mg/L	D	20		E200.7	04/29/14 11:54 / jtr
Magnesium	3	mg/L		1		E200.7	04/30/14 14:07 / jtr
Potassium	43	mg/L	D	20		E200.7	04/29/14 11:54 / jtr
Sodium	2560	mg/L	D	20		E200.7	04/29/14 11:54 / jtr
Boron	599	mg/L	D	5		E200.7	04/29/14 11:54 / jtr
BALANCE							
Anions	98.6	meq/L				Calculation	05/08/14 13:53 / sas
Cations	120	meq/L				Calculation	05/08/14 13:53 / sas
A/C Balance	9.6	%				Calculation	05/08/14 13:53 / sas
METALS, DISSOLVED							
Aluminum	1.1	mg/L	D	0.2		E200.7	05/01/14 10:46 / jtr
Barium	0.55	mg/L	D	0.05		E200.7	05/01/14 10:46 / jtr
Iron	0.4	mg/L	D	0.2		E200.7	05/01/14 10:46 / jtr
Strontium	6.42	mg/L	D	0.05		E200.7	05/01/14 10:46 / jtr

Report Definitions: RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14010059-001
Client Sample ID: Lane B5

Report Date: 02/03/14
Collection Date: 01/21/14 16:58
Date Received: 01/21/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	6.8	s.u.	H	0.1		A4500-H B	01/23/14 15:52 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	12500	mg/L		10		A2540 C	01/22/14 17:21 / rel
Hardness as CaCO ₃	414	mg/L		1		A2340 B	02/01/14 09:23 / sas
Hardness, Calcium as CaCO ₃	224	mg/L		1		A2340 B	02/01/14 09:23 / sas
Hardness, Magnesium as CaCO ₃	190	mg/L		1		A2340 B	02/01/14 09:23 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	282	mg/L		1		A2320 B	01/23/14 11:53 / rel
Bicarbonate as HCO ₃	344	mg/L		1		A2320 B	01/23/14 11:53 / rel
Carbonate as CO ₃	ND	mg/L		1		A2320 B	01/23/14 11:53 / rel
Chloride	926	mg/L	D	50		E300.0	01/28/14 13:22 / rda
Sulfate	2150	mg/L	D	50		E300.0	01/28/14 13:22 / rda
Calcium	90	mg/L	D	2		E200.7	02/01/14 09:23 / jtr
Magnesium	46	mg/L	D	2		E200.7	02/01/14 09:23 / jtr
Potassium	48	mg/L	D	2		E200.7	02/01/14 09:23 / jtr
Sodium	2020	mg/L	D	20		E200.7	01/28/14 12:42 / jtr
Boron	373	mg/L	D	5		E200.7	01/28/14 12:42 / jtr
- Sample diluted according to sample matrix.							
BALANCE							
Anions	77.4	meq/L				Calculation	02/03/14 11:42 / sas
Cations	97.5	meq/L				Calculation	02/03/14 11:42 / sas
A/C Balance	11.5	%				Calculation	02/03/14 11:42 / sas
METALS, DISSOLVED							
Aluminum	6.7	mg/L	D	0.2		E200.7	01/27/14 13:18 / jtr
Barium	0.42	mg/L	D	0.05		E200.7	01/27/14 13:18 / jtr
Iron	23.5	mg/L	D	0.2		E200.7	01/27/14 13:18 / jtr
Strontium	2.20	mg/L	D	0.05		E200.7	01/27/14 13:18 / jtr
- Sample diluted due to lack of sample received.							

Report RL - Analyte reporting limit.

Definitions: QCL - Quality control limit.

D - RL increased due to sample matrix.

MCL - Maximum contaminant level.

ND - Not detected at the reporting limit.

H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14040020-001
Client Sample ID: Lane B56

Report Date: 04/16/14
Collection Date: 04/04/14 14:45
Date Received: 04/04/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.3	s.u.	H	0.1		A4500-H B	04/09/14 12:58 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	16400	mg/L		10		A2540 C	04/07/14 13:31 / rel
Hardness as CaCO ₃	237	mg/L		1		A2340 B	04/08/14 13:33 / sas
Hardness, Calcium as CaCO ₃	232	mg/L		1		A2340 B	04/08/14 13:33 / sas
Hardness, Magnesium as CaCO ₃	5	mg/L		1		A2340 B	04/08/14 13:33 / sas
-TDS: High TDS to conductivity ratio. Not able to re-analyze due to insufficient sample amount.							
MAJOR IONS							
Alkalinity, Total as CaCO ₃	1080	mg/L		1		A2320 B	04/09/14 11:01 / rel
Bicarbonate as HCO ₃	1320	mg/L		1		A2320 B	04/09/14 11:01 / rel
Carbonate as CO ₃	ND	mg/L		1		A2320 B	04/09/14 11:01 / rel
Chloride	1880	mg/L	D	50		E300.0	04/08/14 20:36 / rda
Sulfate	1840	mg/L	D	50		E300.0	04/08/14 20:36 / rda
Calcium	93	mg/L	D	20		E200.7	04/08/14 13:33 / jtr
Magnesium	ND	mg/L	D	20		E200.7	04/08/14 13:33 / jtr
Potassium	35	mg/L	D	20		E200.7	04/08/14 13:33 / jtr
Sodium	3210	mg/L	D	20		E200.7	04/08/14 13:33 / jtr
Boron	611	mg/L	D	5		E200.7	04/08/14 13:33 / jtr
BALANCE							
Anions	116	meq/L				Calculation	04/14/14 08:32 / sas
Cations	145	meq/L				Calculation	04/14/14 08:32 / sas
A/C Balance	11.1	%				Calculation	04/14/14 08:32 / sas
METALS, DISSOLVED							
Aluminum	8.5	mg/L	D	0.2		E200.7	04/08/14 12:13 / jtr
Barium	0.47	mg/L	D	0.05		E200.7	04/08/14 12:13 / jtr
Iron	10.6	mg/L	D	0.2		E200.7	04/08/14 12:13 / jtr
Strontium	6.54	mg/L	D	0.05		E200.7	04/08/14 12:13 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14020046-001
Client Sample ID: Lane B10

Report Date: 03/15/14
Collection Date: 02/18/14 13:44
Date Received: 02/18/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	6.7	s.u.	H	0.1		A4500-H B	02/19/14 16:12 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	12800	mg/L		10		A2540 C	02/19/14 13:04 / rel
Hardness as CaCO3	229	mg/L		1		A2340 B	02/24/14 14:06 / sas
Hardness, Calcium as CaCO3	95	mg/L		1		A2340 B	02/24/14 14:06 / sas
Hardness, Magnesium as CaCO3	134	mg/L		1		A2340 B	02/24/14 14:06 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	311	mg/L		1		A2320 B	02/19/14 10:04 / rda
Bicarbonate as HCO3	379	mg/L		1		A2320 B	02/19/14 10:04 / rda
Carbonate as CO3	ND	mg/L		1		A2320 B	02/19/14 10:04 / rda
Chloride	926	mg/L	D	50		E300.0	02/20/14 00:34 / rda
Sulfate	1950	mg/L	D	50		E300.0	02/20/14 00:34 / rda
Calcium	38	mg/L	D	10		E200.7	02/24/14 14:06 / jtr
Magnesium	32	mg/L	D	10		E200.7	02/24/14 14:06 / jtr
Potassium	51	mg/L	D	10		E200.7	02/24/14 14:06 / jtr
Sodium	1920	mg/L	D	10		E200.7	02/24/14 14:06 / jtr
Boron	399	mg/L	D	2		E200.7	02/24/14 14:06 / jtr
BALANCE							
Anions	75.0	meq/L				Calculation	03/04/14 11:45 / sas
Cations	89.5	meq/L				Calculation	03/04/14 11:45 / sas
A/C Balance	8.8	%				Calculation	03/04/14 11:45 / sas
- Cation / Anion Balance is outside of normal acceptance limits. Unable to re-analyze samples due to limited volume.							
METALS, DISSOLVED							
Aluminum	24.8	mg/L	D	0.2		E200.7	02/28/14 16:00 / jtr
Barium	0.34	mg/L	D	0.05		E200.7	02/28/14 16:00 / jtr
Iron	65.0	mg/L	D	0.2		E200.7	02/28/14 16:00 / jtr
Strontium	0.85	mg/L	D	0.05		E200.7	02/28/14 16:00 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: TAMU Flowback Chemical Analysis
Lab ID: T14030001-001
Client Sample ID: LANE B10b

Report Date: 03/28/14
Collection Date: 03/03/14 16:09
Date Received: 03/03/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.2	s.u.	H	0.1		A4500-H B	03/06/14 15:03 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	14500	mg/L		10		A2540 C	03/05/14 10:08 / rel
Hardness as CaCO3	372	mg/L		1		A2340 B	03/10/14 14:19 / ajm
Hardness, Calcium as CaCO3	209	mg/L		1		A2340 B	03/10/14 14:19 / ajm
Hardness, Magnesium as CaCO3	163	mg/L		1		A2340 B	03/10/14 14:19 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	622	mg/L		1		A2320 B	03/06/14 09:13 / rda
Bicarbonate as HCO3	759	mg/L		1		A2320 B	03/06/14 09:13 / rda
Carbonate as CO3	ND	mg/L		1		A2320 B	03/06/14 09:13 / rda
Chloride	1240	mg/L	D	50		E300.0	03/08/14 05:13 / rda
Sulfate	2430	mg/L	D	50		E300.0	03/08/14 05:13 / rda
Calcium	84	mg/L	D	20		E200.7	03/10/14 14:19 / jtr
Magnesium	40	mg/L	D	20		E200.7	03/10/14 14:19 / jtr
Potassium	42	mg/L	D	20		E200.7	03/10/14 14:19 / jtr
Sodium	2420	mg/L	D	20		E200.7	03/10/14 14:19 / jtr
Boron	425	mg/L	D	5		E200.7	03/10/14 14:19 / jtr
BALANCE							
Anions	98.5	meq/L				Calculation	03/25/14 16:53 / ajm
Cations	114	meq/L				Calculation	03/25/14 16:53 / ajm
A/C Balance	7.3	%				Calculation	03/25/14 16:53 / ajm
METALS, DISSOLVED							
Aluminum	4.0	mg/L	D	0.2		E200.7	03/21/14 13:11 / sas
Barium	0.58	mg/L	D	0.05		E200.7	03/21/14 13:11 / sas
Iron	10.2	mg/L	D	0.2		E200.7	03/21/14 13:11 / sas
Strontium	2.55	mg/L	D	0.05		E200.7	03/21/14 13:11 / sas

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE C1090
Lab ID: T14010050-001
Client Sample ID: Lane B30

Report Date: 01/28/14
Collection Date: 01/16/14 16:44
Date Received: 01/16/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	4.6	s.u.	H	0.1		A4500-H B	01/23/14 15:04 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	11600	mg/L		10		A2540 C	01/17/14 10:47 / rel
Hardness as CaCO3	908	mg/L		1		A2340 B	01/22/14 19:46 / sas
Hardness, Calcium as CaCO3	400	mg/L		1		A2340 B	01/22/14 19:46 / sas
Hardness, Magnesium as CaCO3	507	mg/L		1		A2340 B	01/22/14 19:46 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	30	mg/L		1		A2320 B	01/23/14 11:53 / rel
Bicarbonate as HCO3	37	mg/L		1		A2320 B	01/23/14 11:53 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	01/23/14 11:53 / rel
Chloride	864	mg/L	D	50		E300.0	01/22/14 20:48 / rda
Sulfate	3370	mg/L	D	50		E300.0	01/22/14 20:48 / rda
Calcium	160	mg/L	D	20		E200.7	01/22/14 19:46 / jtr
Magnesium	123	mg/L	D	20		E200.7	01/22/14 19:46 / jtr
Potassium	70	mg/L	D	20		E200.7	01/22/14 19:46 / jtr
Sodium	1790	mg/L	D	20		E200.7	01/22/14 19:46 / jtr
Boron	355	mg/L	D	5		E200.7	01/23/14 11:56 / jtr
BALANCE							
Anions	98.1	meq/L				Calculation	01/27/14 11:03 / sas
Cations	98.0	meq/L				Calculation	01/27/14 11:03 / sas
A/C Balance	-0.040	%				Calculation	01/27/14 11:03 / sas
METALS, DISSOLVED							
Aluminum	26.1	mg/L	D	0.2		E200.7	01/22/14 10:50 / jtr
Barium	0.54	mg/L	D	0.05		E200.7	01/22/14 10:50 / jtr
Iron	150	mg/L	D	0.2		E200.7	01/22/14 10:50 / jtr
Strontium	0.36	mg/L	D	0.05		E200.7	01/22/14 10:50 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14040115-001
Client Sample ID: B30b

Report Date: 05/08/14
Collection Date: 04/25/14 11:11
Date Received: 04/25/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.5	s.u.	H	0.1		A4500-H B	04/28/14 14:23 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	16600	mg/L		10		A2540 C	04/29/14 10:48 / rel
Hardness as CaCO3	222	mg/L		1		A2340 B	04/30/14 13:55 / sas
Hardness, Calcium as CaCO3	215	mg/L		1		A2340 B	04/30/14 13:55 / sas
Hardness, Magnesium as CaCO3	7	mg/L		1		A2340 B	04/30/14 13:55 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	801	mg/L		1		A2320 B	04/28/14 11:30 / rel
Bicarbonate as HCO3	976	mg/L		1		A2320 B	04/28/14 11:30 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	04/28/14 11:30 / rel
Chloride	1850	mg/L	D	50		E300.0	04/26/14 14:11 / rda
Sulfate	2140	mg/L	D	50		E300.0	04/26/14 14:11 / rda
Calcium	86	mg/L	D	2		E200.7	04/28/14 14:56 / jtr
Magnesium	2	mg/L		1		E200.7	04/30/14 13:55 / jtr
Potassium	44	mg/L	D	2		E200.7	04/28/14 14:56 / jtr
Sodium	3200	mg/L	D	2		E200.7	04/28/14 14:56 / jtr
Boron	635	mg/L	D	5		E200.7	04/29/14 11:47 / jtr
BALANCE							
Anions	118	meq/L				Calculation	05/08/14 13:52 / sas
Cations	145	meq/L				Calculation	05/08/14 13:52 / sas
A/C Balance	10.1	%				Calculation	05/08/14 13:52 / sas
METALS, DISSOLVED							
Aluminum	75.0	mg/L	D	0.3		E200.7	05/01/14 10:25 / jtr
Barium	0.9	mg/L	D	0.1		E200.7	05/01/14 10:25 / jtr
Iron	163	mg/L	D	0.5		E200.7	05/01/14 10:25 / jtr
Strontium	8.1	mg/L	D	0.1		E200.7	05/01/14 10:25 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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APPENDIX C

EAGLE FORD ROCK + WATER LABORATORY REPORT



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14050042-002
Client Sample ID: Lane ER1

Report Date: 05/30/14
Collection Date: 05/08/14 16:23
Date Received: 05/08/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.1	s.u.	H	0.1		A4500-H B	05/16/14 13:00 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	3500	mg/L		10		A2540 C	05/09/14 10:29 / rel
Hardness as CaCO3	1210	mg/L		1		A2340 B	05/13/14 17:51 / ajm
Hardness, Calcium as CaCO3	1180	mg/L		1		A2340 B	05/13/14 17:51 / ajm
Hardness, Magnesium as CaCO3	26	mg/L		1		A2340 B	05/13/14 17:51 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	170	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Bicarbonate as HCO3	207	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Carbonate as CO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Chloride	122	mg/L	D	10		E300.0	05/09/14 17:32 / rda
Sulfate	1270	mg/L	D	10		E300.0	05/09/14 17:32 / rda
Calcium	472	mg/L		1		E200.7	05/13/14 17:51 / jtr
Magnesium	6	mg/L		1		E200.7	05/13/14 17:51 / jtr
Potassium	11	mg/L		1		E200.7	05/13/14 17:51 / jtr
Sodium	233	mg/L		1		E200.7	05/13/14 17:51 / jtr
Boron	0.7	mg/L	D	0.2		E200.7	05/13/14 17:51 / jtr
Silica	65.5	mg/L	D	0.5		E200.7	05/13/14 17:51 / jtr
BALANCE							
Anions	33.3	meq/L				Calculation	05/28/14 12:25 / ajm
Cations	34.5	meq/L				Calculation	05/28/14 12:25 / ajm
A/C Balance	1.7	%				Calculation	05/28/14 12:25 / ajm
METALS, DISSOLVED							
Aluminum	2.0	mg/L	D	0.2		E200.7	05/13/14 14:30 / jtr
Barium	0.60	mg/L	D	0.05		E200.7	05/13/14 14:30 / jtr
Iron	12.0	mg/L	D	0.2		E200.7	05/13/14 14:30 / jtr
Strontium	2.81	mg/L	D	0.05		E200.7	05/13/14 14:30 / jtr

Report Definitions: RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14050057-002
Client Sample ID: Lane ER5

Report Date: 05/30/14
Collection Date: 05/12/14 17:29
Date Received: 05/12/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.0	s.u.	H	0.1		A4500-H B	05/16/14 13:57 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	4700	mg/L		10		A2540 C	05/16/14 11:48 / rel
Hardness as CaCO3	1150	mg/L		1		A2340 B	05/14/14 14:14 / ajm
Hardness, Calcium as CaCO3	1120	mg/L		1		A2340 B	05/14/14 14:14 / ajm
Hardness, Magnesium as CaCO3	29	mg/L		1		A2340 B	05/14/14 14:14 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	163	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Bicarbonate as HCO3	199	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Carbonate as CO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Chloride	127	mg/L	D	10		E300.0	05/16/14 22:49 / kmh
Sulfate	1270	mg/L	D	10		E300.0	05/16/14 22:49 / kmh
Calcium	450	mg/L		1		E200.7	05/14/14 14:14 / jtr
Magnesium	7	mg/L		1		E200.7	05/14/14 14:14 / jtr
Potassium	12	mg/L		1		E200.7	05/14/14 14:14 / jtr
Sodium	245	mg/L		1		E200.7	05/14/14 14:14 / jtr
Boron	1.2	mg/L	D	0.2		E200.7	05/14/14 14:14 / jtr
Silica	102	mg/L	D	1		E200.7	05/19/14 13:36 / jtr
BALANCE							
Anions	33.3	meq/L				Calculation	05/28/14 12:28 / ajm
Cations	34.0	meq/L				Calculation	05/28/14 12:28 / ajm
A/C Balance	1.1	%				Calculation	05/28/14 12:28 / ajm
METALS, DISSOLVED							
Aluminum	6.7	mg/L	D	0.2		E200.7	05/13/14 14:45 / jtr
Barium	0.56	mg/L	D	0.05		E200.7	05/13/14 14:45 / jtr
Iron	6.8	mg/L	D	0.2		E200.7	05/13/14 14:45 / jtr
Strontium	2.31	mg/L	D	0.05		E200.7	05/13/14 14:45 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University Petroleum Engineering
Project: LANE
Lab ID: T14050096-002
Client Sample ID: Lane ER10

Report Date: 06/18/14
Collection Date: 05/19/14 16:27
Date Received: 05/19/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.0	s.u.	H	0.1		A4500-H B	05/20/14 14:14 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	3100	mg/L		10		A2540 C	05/20/14 16:01 / rel
Hardness as CaCO3	1290	mg/L		1		A2340 B	05/22/14 16:38 / sas
Hardness, Calcium as CaCO3	1260	mg/L		1		A2340 B	05/22/14 16:38 / sas
Hardness, Magnesium as CaCO3	36	mg/L		1		A2340 B	05/22/14 16:38 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	460	mg/L		1		A2320 B	05/20/14 11:33 / rda
Bicarbonate as HCO3	561	mg/L		1		A2320 B	05/20/14 11:33 / rda
Carbonate as CO3	ND	mg/L		1		A2320 B	05/20/14 11:33 / rda
Chloride	125	mg/L	D	10		E300.0	05/20/14 20:12 / rda
Sulfate	1330	mg/L	D	10		E300.0	05/20/14 20:12 / rda
Calcium	504	mg/L		1		E200.7	05/22/14 16:38 / jtr
Magnesium	9	mg/L		1		E200.7	05/22/14 16:38 / jtr
Potassium	13	mg/L		1		E200.7	05/22/14 16:38 / jtr
Sodium	259	mg/L		1		E200.7	05/22/14 16:38 / jtr
Boron	1.3	mg/L	D	0.2		E200.7	05/22/14 16:38 / jtr
Silicon	42.4	mg/L	D	0.2		E200.7	05/22/14 16:38 / jtr
Silica	90.7	mg/L	D	0.5		E200.7	05/22/14 16:38 / jtr
BALANCE							
Anions	40.5	meq/L				Calculation	06/03/14 14:03 / sas
Cations	37.5	meq/L				Calculation	06/03/14 14:03 / sas
A/C Balance	-3.9	%				Calculation	06/03/14 14:03 / sas
METALS, DISSOLVED							
Aluminum	1.2	mg/L	D	0.2		E200.7	05/28/14 16:40 / jtr
Barium	0.55	mg/L	D	0.05		E200.7	05/28/14 16:40 / jtr
Iron	4.1	mg/L	D	0.2		E200.7	05/28/14 16:40 / jtr
Strontium	1.86	mg/L	D	0.05		E200.7	05/28/14 16:40 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University Petroleum Engineering
Project: LANE
Lab ID: T14050134-002
Client Sample ID: Lane ER30

Report Date: 06/16/14
Collection Date: 05/28/14 16:32
Date Received: 05/28/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.0	s.u.	H	0.1		A4500-H B	06/02/14 11:00 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	2800	mg/L		1000		A2540 C	05/30/14 10:56 / rda
Hardness as CaCO3	827	mg/L		1		A2340 B	05/30/14 17:29 / sas
Hardness, Calcium as CaCO3	800	mg/L		1		A2340 B	05/30/14 17:29 / sas
Hardness, Magnesium as CaCO3	27	mg/L		1		A2340 B	05/30/14 17:29 / sas
- TDS: TDS to Conductivity ratio outside of acceptable limits. There was not a sufficient amount of sample to re-analyze.							
MAJOR IONS							
Alkalinity, Total as CaCO3	267	mg/L		1		A2320 B	06/02/14 10:55 / rel
Bicarbonate as HCO3	325	mg/L		1		A2320 B	06/02/14 10:55 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	06/02/14 10:55 / rel
Chloride	132	mg/L	D	10		E300.0	06/05/14 18:50 / rda
Sulfate	982	mg/L	D	10		E300.0	06/05/14 18:50 / rda
Calcium	320	mg/L		1		E200.7	05/30/14 17:29 / jtr
Magnesium	7	mg/L		1		E200.7	05/30/14 17:29 / jtr
Potassium	14	mg/L		1		E200.7	06/04/14 17:09 / jtr
Sodium	236	mg/L		1		E200.7	05/30/14 17:29 / jtr
Boron	1.8	mg/L	D	0.2		E200.7	06/04/14 17:09 / jtr
Silicon	47.6	mg/L	D	0.5		E200.7	06/10/14 09:45 / jtr
BALANCE							
Anions	29.7	meq/L				Calculation	06/12/14 16:03 / sas
Cations	27.2	meq/L				Calculation	06/12/14 16:03 / sas
A/C Balance	-4.5	%				Calculation	06/12/14 16:03 / sas
METALS, DISSOLVED							
Aluminum	0.6	mg/L	D	0.2		E200.7	06/04/14 13:34 / jtr
Barium	0.31	mg/L	D	0.05		E200.7	06/04/14 13:34 / jtr
Iron	2.4	mg/L	D	0.2		E200.7	06/04/14 13:34 / jtr
Strontium	2.18	mg/L	D	0.05		E200.7	06/04/14 13:34 / jtr

Report RL - Analyte reporting limit. MCL - Maximum contaminant level.
Definitions: QCL - Quality control limit. ND - Not detected at the reporting limit.
D - RL increased due to sample matrix. H - Analysis performed past recommended holding time.

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APPENDIX D

EAGLE FORD ROCK + FRACTURE FLUID LABORATORY REPORT



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14020023-002
Client Sample ID: Lane E1

Report Date: 02/19/14
Collection Date: 02/06/14 17:12
Date Received: 02/06/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.2	s.u.	H	0.1		A4500-H B	02/12/14 11:35 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	12800	mg/L		10		A2540 C	02/07/14 16:10 / rel
Hardness as CaCO ₃	1360	mg/L		1		A2340 B	02/14/14 09:26 / sas
Hardness, Calcium as CaCO ₃	1360	mg/L		1		A2340 B	02/14/14 09:26 / sas
Hardness, Magnesium as CaCO ₃	ND	mg/L		1		A2340 B	02/14/14 09:26 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	1260	mg/L		1		A2320 B	02/12/14 10:59 / rel
Bicarbonate as HCO ₃	ND	mg/L		1		A2320 B	02/12/14 10:59 / rel
Carbonate as CO ₃	532	mg/L		1		A2320 B	02/12/14 10:59 / rel
Chloride	845	mg/L	D	50		E300.0	02/08/14 02:58 / rda
Sulfate	2650	mg/L	D	50		E300.0	02/08/14 02:58 / rda
Calcium	545	mg/L	D	10		E200.7	02/10/14 13:29 / jtr
Magnesium	ND	mg/L		1		E200.7	02/14/14 09:26 / jtr
Potassium	19	mg/L	D	10		E200.7	02/10/14 13:29 / jtr
Sodium	2220	mg/L	D	10		E200.7	02/10/14 13:29 / jtr
Boron	350	mg/L	D	2		E200.7	02/10/14 13:29 / jtr
BALANCE							
Anions	104	meq/L				Calculation	02/18/14 08:51 / sas
Cations	124	meq/L				Calculation	02/18/14 08:51 / sas
A/C Balance	8.7	%				Calculation	02/18/14 08:51 / sas
METALS, DISSOLVED							
Aluminum	0.9	mg/L	D	0.2		E200.7	02/13/14 18:31 / jtr
Barium	0.22	mg/L	D	0.05		E200.7	02/13/14 18:31 / jtr
Iron	0.5	mg/L	D	0.2		E200.7	02/13/14 18:31 / jtr
Strontium	9.77	mg/L	D	0.05		E200.7	02/13/14 18:31 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14040117-002
Client Sample ID: Lane E1B

Report Date: 05/08/14
Collection Date: 04/28/14 11:44
Date Received: 04/28/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.2	s.u.	H	0.1		A4500-H B	04/28/14 15:16 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	13500	mg/L		10		A2540 C	04/29/14 10:50 / rel
Hardness as CaCO3	1230	mg/L		1		A2340 B	04/30/14 14:20 / sas
Hardness, Calcium as CaCO3	1230	mg/L		1		A2340 B	04/30/14 14:20 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	04/30/14 14:20 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	1680	mg/L		1		A2320 B	04/28/14 11:30 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	04/28/14 11:30 / rel
Carbonate as CO3	760	mg/L		1		A2320 B	04/28/14 11:30 / rel
Chloride	1320	mg/L	D	50		E300.0	04/29/14 14:12 / rda
Sulfate	2840	mg/L	D	50		E300.0	04/29/14 14:12 / rda
Calcium	492	mg/L	D	20		E200.7	04/29/14 12:06 / jtr
Magnesium	ND	mg/L		1		E200.7	04/30/14 14:20 / jtr
Potassium	25	mg/L	D	20		E200.7	04/29/14 12:06 / jtr
Sodium	2780	mg/L	D	20		E200.7	04/29/14 12:06 / jtr
Boron	504	mg/L	D	5		E200.7	04/29/14 12:06 / jtr
BALANCE							
Anions	130	meq/L				Calculation	05/08/14 13:53 / sas
Cations	146	meq/L				Calculation	05/08/14 13:53 / sas
A/C Balance	5.7	%				Calculation	05/08/14 13:53 / sas
METALS, DISSOLVED							
Aluminum	1.1	mg/L	D	0.2		E200.7	05/01/14 10:48 / jtr
Barium	0.66	mg/L	D	0.05		E200.7	05/01/14 10:48 / jtr
Iron	ND	mg/L	D	0.2		E200.7	05/01/14 10:48 / jtr
Strontium	9.48	mg/L	D	0.05		E200.7	05/01/14 10:48 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14010059-002
Client Sample ID: Lane E5

Report Date: 02/03/14
Collection Date: 01/21/14 16:58
Date Received: 01/21/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.5	s.u.	H	0.1		A4500-H B	01/23/14 16:00 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	13100	mg/L		10		A2540 C	01/22/14 17:21 / rel
Hardness as CaCO3	954	mg/L		1		A2340 B	02/01/14 09:37 / sas
Hardness, Calcium as CaCO3	951	mg/L		1		A2340 B	02/01/14 09:37 / sas
Hardness, Magnesium as CaCO3	3	mg/L		1		A2340 B	02/01/14 09:37 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	907	mg/L		1		A2320 B	01/23/14 11:53 / rel
Bicarbonate as HCO3	688	mg/L		1		A2320 B	01/23/14 11:53 / rel
Carbonate as CO3	206	mg/L		1		A2320 B	01/23/14 11:53 / rel
Chloride	908	mg/L	D	50		E300.0	01/28/14 16:44 / rda
Sulfate	2200	mg/L	D	50		E300.0	01/28/14 16:44 / rda
Calcium	381	mg/L	D	2		E200.7	02/01/14 09:37 / jtr
Magnesium	ND	mg/L	D	2		E200.7	02/01/14 09:37 / jtr
Potassium	20	mg/L	D	2		E200.7	02/01/14 09:37 / jtr
Sodium	2140	mg/L	D	20		E200.7	01/28/14 12:50 / jtr
Boron	358	mg/L	D	5		E200.7	01/28/14 12:50 / jtr
- Sample diluted according to sample matrix.							
BALANCE							
Anions	90.9	meq/L				Calculation	02/03/14 11:42 / sas
Cations	113	meq/L				Calculation	02/03/14 11:42 / sas
A/C Balance	10.7	%				Calculation	02/03/14 11:42 / sas
METALS, DISSOLVED							
Aluminum	0.8	mg/L	D	0.2		E200.7	01/27/14 13:20 / jtr
Barium	0.39	mg/L	D	0.05		E200.7	01/27/14 13:20 / jtr
Iron	2.1	mg/L	D	0.2		E200.7	01/27/14 13:20 / jtr
Strontium	8.04	mg/L	D	0.05		E200.7	01/27/14 13:20 / jtr
- Sample diluted due to lack of sample received.							

Report Definitions: RL - Analyte reporting limit. MCL - Maximum contaminant level.
QCL - Quality control limit. ND - Not detected at the reporting limit.
D - RL increased due to sample matrix. H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14040020-002
Client Sample ID: Lane E56

Report Date: 04/16/14
Collection Date: 04/04/14 14:45
Date Received: 04/04/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.5	s.u.	H	0.1		A4500-H B	04/09/14 13:06 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	16900	mg/L		10		A2540 C	04/07/14 13:31 / rel
Hardness as CaCO3	1080	mg/L		1		A2340 B	04/08/14 13:48 / sas
Hardness, Calcium as CaCO3	1080	mg/L		1		A2340 B	04/08/14 13:48 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	04/08/14 13:48 / sas
-TDS: High TDS to conductivity ratio. Not able to re-analyze due to insufficient sample amount.							
MAJOR IONS							
Alkalinity, Total as CaCO3	1200	mg/L		1		A2320 B	04/09/14 11:01 / rel
Bicarbonate as HCO3	976	mg/L		1		A2320 B	04/09/14 11:01 / rel
Carbonate as CO3	240	mg/L		1		A2320 B	04/09/14 11:01 / rel
Chloride	1850	mg/L	D	50		E300.0	04/08/14 21:12 / rda
Sulfate	3500	mg/L	D	50		E300.0	04/08/14 21:12 / rda
Calcium	433	mg/L	D	20		E200.7	04/08/14 13:48 / jtr
Magnesium	ND	mg/L	D	20		E200.7	04/08/14 13:48 / jtr
Potassium	37	mg/L	D	20		E200.7	04/08/14 13:48 / jtr
Sodium	3250	mg/L	D	20		E200.7	04/08/14 13:48 / jtr
Boron	566	mg/L	D	5		E200.7	04/08/14 13:48 / jtr
BALANCE							
Anions	150	meq/L				Calculation	04/14/14 08:32 / sas
Cations	164	meq/L				Calculation	04/14/14 08:32 / sas
A/C Balance	4.6	%				Calculation	04/14/14 08:32 / sas
METALS, DISSOLVED							
Aluminum	0.6	mg/L	D	0.2		E200.7	04/08/14 12:26 / jtr
Barium	0.39	mg/L	D	0.05		E200.7	04/08/14 12:26 / jtr
Iron	0.4	mg/L	D	0.2		E200.7	04/08/14 12:26 / jtr
Strontium	9.42	mg/L	D	0.05		E200.7	04/08/14 12:26 / jtr

Report RL - Analyte reporting limit. MCL - Maximum contaminant level.
Definitions: QCL - Quality control limit. ND - Not detected at the reporting limit.
D - RL increased due to sample matrix. H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T13120125-002
Client Sample ID: Lane E10

Report Date: 01/16/14
Collection Date: 12/27/13 11:07
Date Received: 12/27/13
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.2	s.u.	H	0.1		A4500-H B	12/30/13 17:59 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	10400	mg/L		10		A2540 C	12/27/13 12:42 / kmh
Hardness as CaCO3	1020	mg/L		1		A2340 B	01/09/14 16:16 / sas
Hardness, Calcium as CaCO3	1010	mg/L		1		A2340 B	01/09/14 16:16 / sas
Hardness, Magnesium as CaCO3	4	mg/L		1		A2340 B	01/09/14 16:16 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	736	mg/L		1		A2320 B	12/30/13 12:30 / rda
Bicarbonate as HCO3	897	mg/L		1		A2320 B	12/30/13 12:30 / rda
Carbonate as CO3	ND	mg/L		1		A2320 B	12/30/13 12:30 / rda
Chloride	746	mg/L	D	100		E300.0	01/09/14 21:19 / rda
Sulfate	1770	mg/L	D	100		E300.0	01/09/14 21:19 / rda
Calcium	405	mg/L	D	2		E200.7	01/09/14 16:16 / jtr
Magnesium	ND	mg/L	D	2		E200.7	01/09/14 16:16 / jtr
Potassium	20	mg/L	D	2		E200.7	01/09/14 16:16 / jtr
Sodium	1820	mg/L	D	2		E200.7	01/09/14 16:16 / jtr
Boron	310	mg/L	D	5		E200.7	01/14/14 12:15 / jtr
BALANCE							
Anions	72.5	meq/L				Calculation	01/16/14 08:51 / sas
Cations	99.9	meq/L				Calculation	01/16/14 08:51 / sas
A/C Balance	15.9	%				Calculation	01/16/14 08:51 / sas
- Individual components were not re-run due to sample volume.							
METALS, DISSOLVED							
Aluminum	1.8	mg/L	D	0.3		E200.7	01/09/14 18:05 / jtr
Barium	0.1	mg/L	D	0.1		E200.7	01/09/14 18:05 / jtr
Iron	5.2	mg/L	D	0.5		E200.7	01/09/14 18:05 / jtr
Strontium	5.5	mg/L	D	0.1		E200.7	01/09/14 18:05 / jtr

Report Definitions: RL - Analyte reporting limit. MCL - Maximum contaminant level.
QCL - Quality control limit. ND - Not detected at the reporting limit.
D - RL increased due to sample matrix. H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: TAMU Flowback Chemical Analysis
Lab ID: T14030001-002
Client Sample ID: LANE E10b

Report Date: 03/28/14
Collection Date: 03/03/14 16:09
Date Received: 03/03/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.2	s.u.	H	0.1		A4500-H B	03/06/14 15:03 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	14400	mg/L		10		A2540 C	03/05/14 10:08 / rel
Hardness as CaCO3	783	mg/L		1		A2340 B	03/10/14 14:34 / sas
Hardness, Calcium as CaCO3	622	mg/L		1		A2340 B	03/10/14 14:34 / sas
Hardness, Magnesium as CaCO3	161	mg/L		1		A2340 B	03/10/14 14:34 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	436	mg/L		1		A2320 B	03/06/14 09:13 / rda
Bicarbonate as HCO3	531	mg/L		1		A2320 B	03/06/14 09:13 / rda
Carbonate as CO3	ND	mg/L		1		A2320 B	03/06/14 09:13 / rda
Chloride	1230	mg/L	D	50		E300.0	03/08/14 07:09 / rda
Sulfate	3610	mg/L	D	50		E300.0	03/08/14 07:09 / rda
Calcium	249	mg/L	D	20		E200.7	03/10/14 14:34 / jtr
Magnesium	39	mg/L	D	20		E200.7	03/10/14 14:34 / jtr
Potassium	46	mg/L	D	20		E200.7	03/10/14 14:34 / jtr
Sodium	2470	mg/L	D	20		E200.7	03/10/14 14:34 / jtr
Boron	427	mg/L	D	5		E200.7	03/10/14 14:34 / jtr
BALANCE							
Anions	119	meq/L				Calculation	03/13/14 17:07 / sas
Cations	124	meq/L				Calculation	03/13/14 17:07 / sas
A/C Balance	2.1	%				Calculation	03/13/14 17:07 / sas
METALS, DISSOLVED							
Aluminum	4.7	mg/L	D	0.2		E200.7	03/21/14 13:17 / sas
Barium	0.53	mg/L	D	0.05		E200.7	03/21/14 13:17 / sas
Iron	19.9	mg/L	D	0.2		E200.7	03/21/14 13:17 / sas
Strontium	2.83	mg/L	D	0.05		E200.7	03/21/14 13:17 / sas

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE C1090
Lab ID: T14010050-002
Client Sample ID: Lane E30

Report Date: 01/28/14
Collection Date: 01/16/14 16:44
Date Received: 01/16/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.7	s.u.	H	0.1		A4500-H B	01/23/14 15:31 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	11600	mg/L		10		A2540 C	01/17/14 10:47 / rel
Hardness as CaCO3	710	mg/L		1		A2340 B	01/22/14 19:57 / sas
Hardness, Calcium as CaCO3	696	mg/L		1		A2340 B	01/22/14 19:57 / sas
Hardness, Magnesium as CaCO3	14	mg/L		1		A2340 B	01/22/14 19:57 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	857	mg/L		1		A2320 B	01/23/14 11:53 / rel
Bicarbonate as HCO3	1040	mg/L		1		A2320 B	01/23/14 11:53 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	01/23/14 11:53 / rel
Chloride	838	mg/L	D	50		E300.0	01/22/14 21:27 / rda
Sulfate	1640	mg/L	D	50		E300.0	01/22/14 21:27 / rda
Calcium	279	mg/L	D	20		E200.7	01/22/14 19:57 / jtr
Magnesium	ND	mg/L	D	20		E200.7	01/22/14 19:57 / jtr
Potassium	25	mg/L	D	20		E200.7	01/22/14 19:57 / jtr
Sodium	2010	mg/L	D	20		E200.7	01/22/14 19:57 / jtr
Boron	354	mg/L	D	5		E200.7	01/23/14 12:12 / jtr
- Sample diluted according to sample matrix.							
BALANCE							
Anions	77.2	meq/L				Calculation	01/27/14 11:06 / sas
Cations	102	meq/L				Calculation	01/27/14 11:06 / sas
A/C Balance	13.9	%				Calculation	01/27/14 11:06 / sas
METALS, DISSOLVED							
Aluminum	6.5	mg/L	D	0.2		E200.7	01/22/14 10:59 / jtr
Barium	0.32	mg/L	D	0.05		E200.7	01/22/14 10:59 / jtr
Iron	50.2	mg/L	D	0.2		E200.7	01/22/14 10:59 / jtr
Strontium	12.3	mg/L	D	0.05		E200.7	01/22/14 10:59 / jtr

Report Definitions: RL - Analyte reporting limit. MCL - Maximum contaminant level.
QCL - Quality control limit. ND - Not detected at the reporting limit.
D - RL increased due to sample matrix. H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14040115-002
Client Sample ID: E30b

Report Date: 05/08/14
Collection Date: 04/25/14 11:11
Date Received: 04/25/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.7	s.u.	H	0.1		A4500-H B	04/28/14 14:31 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	17200	mg/L		10		A2540 C	04/29/14 10:48 / rel
Hardness as CaCO3	635	mg/L		1		A2340 B	04/30/14 13:59 / sas
Hardness, Calcium as CaCO3	630	mg/L		1		A2340 B	04/30/14 13:59 / sas
Hardness, Magnesium as CaCO3	5	mg/L		1		A2340 B	04/30/14 13:59 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	817	mg/L		1		A2320 B	04/28/14 11:30 / rel
Bicarbonate as HCO3	996	mg/L		1		A2320 B	04/28/14 11:30 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	04/28/14 11:30 / rel
Chloride	1720	mg/L	D	50		E300.0	04/26/14 14:48 / rda
Sulfate	3160	mg/L	D	50		E300.0	04/26/14 14:48 / rda
Calcium	252	mg/L	D	2		E200.7	04/28/14 15:01 / jtr
Magnesium	1	mg/L		1		E200.7	04/30/14 13:59 / jtr
Potassium	42	mg/L	D	2		E200.7	04/28/14 15:01 / jtr
Sodium	3090	mg/L	D	2		E200.7	04/28/14 15:01 / jtr
Boron	604	mg/L	D	5		E200.7	04/29/14 11:48 / jtr
BALANCE							
Anions	131	meq/L				Calculation	05/08/14 13:52 / sas
Cations	148	meq/L				Calculation	05/08/14 13:52 / sas
A/C Balance	6.3	%				Calculation	05/08/14 13:52 / sas
METALS, DISSOLVED							
Aluminum	5.0	mg/L	D	0.2		E200.7	05/01/14 10:34 / jtr
Barium	0.38	mg/L	D	0.05		E200.7	05/01/14 10:34 / jtr
Iron	26.8	mg/L	D	0.2		E200.7	05/01/14 10:34 / jtr
Strontium	5.36	mg/L	D	0.05		E200.7	05/01/14 10:34 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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APPENDIX E

MARCELLUS ROCK + WATER LABORATORY REPORT



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14050042-003
Client Sample ID: Lane MR1

Report Date: 05/30/14
Collection Date: 05/08/14 16:23
Date Received: 05/08/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.1	s.u.	H	0.1		A4500-H B	05/16/14 13:23 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	2800	mg/L		10		A2540 C	05/09/14 10:30 / rel
Hardness as CaCO ₃	318	mg/L		1		A2340 B	05/13/14 17:53 / ajm
Hardness, Calcium as CaCO ₃	300	mg/L		1		A2340 B	05/13/14 17:53 / ajm
Hardness, Magnesium as CaCO ₃	19	mg/L		1		A2340 B	05/13/14 17:53 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO ₃	180	mg/L		1		A2320 B	05/20/14 11:33 / rda
Bicarbonate as HCO ₃	220	mg/L		1		A2320 B	05/20/14 11:33 / rda
Carbonate as CO ₃	ND	mg/L		1		A2320 B	05/20/14 11:33 / rda
Chloride	87	mg/L	D	10		E300.0	05/09/14 18:06 / rda
Sulfate	514	mg/L	D	10		E300.0	05/09/14 18:06 / rda
Calcium	120	mg/L		1		E200.7	05/13/14 17:53 / jtr
Magnesium	5	mg/L		1		E200.7	05/13/14 17:53 / jtr
Potassium	14	mg/L		1		E200.7	05/13/14 17:53 / jtr
Sodium	220	mg/L		1		E200.7	05/13/14 17:53 / jtr
Boron	1.2	mg/L	D	0.2		E200.7	05/13/14 17:53 / jtr
Silica	65.2	mg/L	D	0.5		E200.7	05/13/14 17:53 / jtr
BALANCE							
Anions	16.8	meq/L				Calculation	05/28/14 12:26 / ajm
Cations	16.3	meq/L				Calculation	05/28/14 12:26 / ajm
A/C Balance	-1.5	%				Calculation	05/28/14 12:26 / ajm
METALS, DISSOLVED							
Aluminum	0.8	mg/L	D	0.2		E200.7	05/13/14 14:32 / jtr
Barium	0.56	mg/L	D	0.05		E200.7	05/13/14 14:32 / jtr
Iron	2.5	mg/L	D	0.2		E200.7	05/13/14 14:32 / jtr
Strontium	0.35	mg/L	D	0.05		E200.7	05/13/14 14:32 / jtr

Report Definitions:
 RL - Analyte reporting limit.
 QCL - Quality control limit.
 D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
 ND - Not detected at the reporting limit.
 H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14050057-003
Client Sample ID: Lane MR5

Report Date: 05/30/14
Collection Date: 05/12/14 17:29
Date Received: 05/12/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.9	s.u.	H	0.1		A4500-H B	05/16/14 14:10 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	2500	mg/L		10		A2540 C	05/16/14 11:49 / rel
Hardness as CaCO3	455	mg/L		1		A2340 B	05/14/14 14:16 / ajm
Hardness, Calcium as CaCO3	420	mg/L		1		A2340 B	05/14/14 14:16 / ajm
Hardness, Magnesium as CaCO3	35	mg/L		1		A2340 B	05/14/14 14:16 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	90	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Bicarbonate as HCO3	110	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Carbonate as CO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Chloride	107	mg/L	D	10		E300.0	05/16/14 23:06 / kmh
Sulfate	801	mg/L	D	10		E300.0	05/16/14 23:06 / kmh
Calcium	168	mg/L		1		E200.7	05/14/14 14:16 / jtr
Magnesium	9	mg/L		1		E200.7	05/14/14 14:16 / jtr
Potassium	16	mg/L		1		E200.7	05/14/14 14:16 / jtr
Sodium	276	mg/L		1		E200.7	05/14/14 14:16 / jtr
Boron	3.7	mg/L	D	0.2		E200.7	05/14/14 14:16 / jtr
Silica	104	mg/L	D	1		E200.7	05/19/14 13:38 / jtr
BALANCE							
Anions	21.5	meq/L				Calculation	05/28/14 12:28 / ajm
Cations	21.5	meq/L				Calculation	05/28/14 12:28 / ajm
A/C Balance	0.049	%				Calculation	05/28/14 12:28 / ajm
METALS, DISSOLVED							
Aluminum	5.7	mg/L	D	0.2		E200.7	05/13/14 14:48 / jtr
Barium	0.58	mg/L	D	0.05		E200.7	05/13/14 14:48 / jtr
Iron	4.3	mg/L	D	0.2		E200.7	05/13/14 14:48 / jtr
Strontium	0.56	mg/L	D	0.05		E200.7	05/13/14 14:48 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University Petroleum Engineering
Project: LANE
Lab ID: T14050096-003
Client Sample ID: Lane MR10

Report Date: 06/18/14
Collection Date: 05/19/14 16:27
Date Received: 05/19/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.2	s.u.	H	0.1		A4500-H B	05/20/14 14:24 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	3200	mg/L		10		A2540 C	05/20/14 16:01 / rel
Hardness as CaCO ₃	623	mg/L		1		A2340 B	05/22/14 16:40 / sas
Hardness, Calcium as CaCO ₃	593	mg/L		1		A2340 B	05/22/14 16:40 / sas
Hardness, Magnesium as CaCO ₃	30	mg/L		1		A2340 B	05/22/14 16:40 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	267	mg/L		1		A2320 B	05/20/14 11:33 / rda
Bicarbonate as HCO ₃	325	mg/L		1		A2320 B	05/20/14 11:33 / rda
Carbonate as CO ₃	ND	mg/L		1		A2320 B	05/20/14 11:33 / rda
Chloride	155	mg/L	D	10		E300.0	05/20/14 20:46 / rda
Sulfate	995	mg/L	D	10		E300.0	05/20/14 20:46 / rda
Calcium	238	mg/L		1		E200.7	05/22/14 16:40 / jtr
Magnesium	7	mg/L		1		E200.7	05/22/14 16:40 / jtr
Potassium	13	mg/L		1		E200.7	05/22/14 16:40 / jtr
Sodium	352	mg/L		1		E200.7	05/22/14 16:40 / jtr
Boron	3.8	mg/L	D	0.2		E200.7	05/22/14 16:40 / jtr
Silicon	32.2	mg/L	D	0.2		E200.7	05/22/14 16:40 / jtr
Silica	69.0	mg/L	D	0.5		E200.7	05/22/14 16:40 / jtr
BALANCE							
Anions	30.4	meq/L				Calculation	06/03/14 14:03 / sas
Cations	28.1	meq/L				Calculation	06/03/14 14:03 / sas
A/C Balance	-3.9	%				Calculation	06/03/14 14:03 / sas
METALS, DISSOLVED							
Aluminum	15.6	mg/L	D	0.2		E200.7	05/28/14 16:42 / jtr
Barium	1.41	mg/L	D	0.05		E200.7	05/28/14 16:42 / jtr
Iron	87.6	mg/L	D	0.2		E200.7	05/28/14 16:42 / jtr
Strontium	1.00	mg/L	D	0.05		E200.7	05/28/14 16:42 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University Petroleum Engineering
Project: LANE
Lab ID: T14050134-003
Client Sample ID: Lane MR30

Report Date: 06/16/14
Collection Date: 05/28/14 16:32
Date Received: 05/28/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.1	s.u.	H	0.1		A4500-H B	06/02/14 11:00 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	1500	mg/L		1000		A2540 C	05/30/14 10:56 / rda
Hardness as CaCO3	583	mg/L		1		A2340 B	05/30/14 17:32 / sas
Hardness, Calcium as CaCO3	535	mg/L		1		A2340 B	05/30/14 17:32 / sas
Hardness, Magnesium as CaCO3	48	mg/L		1		A2340 B	05/30/14 17:32 / sas
- TDS: Sample residue below acceptable limits. Unable to run at higher volume due to insufficient amount of sample.							
MAJOR IONS							
Alkalinity, Total as CaCO3	200	mg/L		1		A2320 B	06/02/14 10:55 / rel
Bicarbonate as HCO3	244	mg/L		1		A2320 B	06/02/14 10:55 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	06/02/14 10:55 / rel
Chloride	97	mg/L	D	10		E300.0	06/05/14 19:08 / rda
Sulfate	884	mg/L	D	10		E300.0	06/05/14 19:08 / rda
Calcium	214	mg/L		1		E200.7	05/30/14 17:32 / jtr
Magnesium	12	mg/L		1		E200.7	05/30/14 17:32 / jtr
Potassium	13	mg/L		1		E200.7	06/04/14 17:13 / jtr
Sodium	245	mg/L		1		E200.7	05/30/14 17:32 / jtr
Boron	4.6	mg/L	D	0.2		E200.7	06/04/14 17:13 / jtr
Silicon	37.5	mg/L	D	0.5		E200.7	06/10/14 09:56 / jtr
BALANCE							
Anions	25.6	meq/L				Calculation	06/12/14 16:08 / sas
Cations	22.7	meq/L				Calculation	06/12/14 16:08 / sas
A/C Balance	-6.0	%				Calculation	06/12/14 16:08 / sas
METALS, DISSOLVED							
Aluminum	12.2	mg/L	D	0.2		E200.7	06/04/14 13:36 / jtr
Barium	0.28	mg/L	D	0.05		E200.7	06/04/14 13:36 / jtr
Iron	132	mg/L	D	0.2		E200.7	06/04/14 13:36 / jtr
Strontium	1.30	mg/L	D	0.05		E200.7	06/04/14 13:36 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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APPENDIX F

MARCELLUS ROCK + FRACTURE FLUID LABORATORY REPORT



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14020023-003
Client Sample ID: Lane M1

Report Date: 02/19/14
Collection Date: 02/06/14 17:12
Date Received: 02/06/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.7	s.u.	H	0.1		A4500-H B	02/12/14 11:40 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	10400	mg/L		10		A2540 C	02/07/14 16:11 / rel
Hardness as CaCO3	221	mg/L		1		A2340 B	02/14/14 09:35 / sas
Hardness, Calcium as CaCO3	220	mg/L		1		A2340 B	02/14/14 09:35 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	02/14/14 09:35 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	1760	mg/L		1		A2320 B	02/12/14 10:59 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	02/12/14 10:59 / rel
Carbonate as CO3	568	mg/L		1		A2320 B	02/12/14 10:59 / rel
Chloride	864	mg/L	D	50		E300.0	02/08/14 04:16 / rda
Sulfate	716	mg/L	D	50		E300.0	02/08/14 04:16 / rda
Calcium	88	mg/L	D	10		E200.7	02/10/14 13:33 / jtr
Magnesium	ND	mg/L		1		E200.7	02/14/14 09:35 / jtr
Potassium	18	mg/L	D	10		E200.7	02/10/14 13:33 / jtr
Sodium	2140	mg/L	D	10		E200.7	02/10/14 13:33 / jtr
Boron	379	mg/L	D	2		E200.7	02/10/14 13:33 / jtr
BALANCE							
Anions	75.1	meq/L				Calculation	02/18/14 08:52 / sas
Cations	98.1	meq/L				Calculation	02/18/14 08:52 / sas
A/C Balance	13.3	%				Calculation	02/18/14 08:52 / sas
METALS, DISSOLVED							
Aluminum	3.5	mg/L	D	0.2		E200.7	02/13/14 18:34 / jtr
Barium	0.80	mg/L	D	0.05		E200.7	02/13/14 18:34 / jtr
Iron	1.9	mg/L	D	0.2		E200.7	02/13/14 18:34 / jtr
Strontium	3.58	mg/L	D	0.05		E200.7	02/13/14 18:34 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14040117-003
Client Sample ID: Lane M1B

Report Date: 05/08/14
Collection Date: 04/28/14 11:44
Date Received: 04/28/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	10.9	s.u.	H	0.1		A4500-H B	04/28/14 15:22 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	10500	mg/L		10		A2540 C	04/29/14 10:50 / rel
Hardness as CaCO3	353	mg/L		1		A2340 B	04/29/14 12:07 / sas
Hardness, Calcium as CaCO3	353	mg/L		1		A2340 B	04/29/14 12:07 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	04/29/14 12:07 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	3390	mg/L		1		A2320 B	04/28/14 11:30 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	04/28/14 11:30 / rel
Carbonate as CO3	880	mg/L		1		A2320 B	04/28/14 11:30 / rel
Chloride	1330	mg/L	D	50		E300.0	04/29/14 14:47 / rda
Sulfate	728	mg/L	D	50		E300.0	04/29/14 14:47 / rda
Calcium	141	mg/L	D	20		E200.7	04/29/14 12:07 / jtr
Magnesium	ND	mg/L	D	20		E200.7	04/29/14 12:07 / jtr
Potassium	23	mg/L		1		E200.7	04/30/14 14:23 / jtr
Sodium	2740	mg/L	D	20		E200.7	04/29/14 12:07 / jtr
Boron	621	mg/L	D	5		E200.7	04/29/14 12:07 / jtr
BALANCE							
Anions	121	meq/L				Calculation	05/08/14 13:45 / sas
Cations	127	meq/L				Calculation	05/08/14 13:45 / sas
A/C Balance	2.5	%				Calculation	05/08/14 13:45 / sas
METALS, DISSOLVED							
Aluminum	3.4	mg/L	D	0.2		E200.7	05/01/14 10:50 / jtr
Barium	0.81	mg/L	D	0.05		E200.7	05/01/14 10:50 / jtr
Iron	4.1	mg/L	D	0.2		E200.7	05/01/14 10:50 / jtr
Strontium	8.15	mg/L	D	0.05		E200.7	05/01/14 10:50 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14010059-003
Client Sample ID: Lane M5

Report Date: 02/03/14
Collection Date: 01/21/14 16:58
Date Received: 01/21/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.2	s.u.	H	0.1		A4500-H B	01/23/14 16:17 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	13100	mg/L		10		A2540 C	01/22/14 17:22 / rel
Hardness as CaCO3	336	mg/L		1		A2340 B	02/01/14 09:41 / sas
Hardness, Calcium as CaCO3	335	mg/L		1		A2340 B	02/01/14 09:41 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	02/01/14 09:41 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	1110	mg/L		1		A2320 B	01/23/14 11:53 / rel
Bicarbonate as HCO3	1350	mg/L		1		A2320 B	01/23/14 11:53 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	01/23/14 11:53 / rel
Chloride	931	mg/L	D	50		E300.0	01/28/14 17:23 / rda
Sulfate	1010	mg/L	D	50		E300.0	01/28/14 17:23 / rda
Calcium	134	mg/L	D	2		E200.7	02/01/14 09:41 / jtr
Magnesium	ND	mg/L	D	2		E200.7	02/01/14 09:41 / jtr
Potassium	20	mg/L	D	2		E200.7	02/01/14 09:41 / jtr
Sodium	2130	mg/L	D	20		E200.7	01/28/14 12:59 / jtr
Boron	406	mg/L	D	5		E200.7	01/28/14 12:59 / jtr
- Sample diluted according to sample matrix.							
BALANCE							
Anions	71.4	meq/L				Calculation	02/03/14 11:42 / sas
Cations	99.8	meq/L				Calculation	02/03/14 11:42 / sas
A/C Balance	16.6	%				Calculation	02/03/14 11:42 / sas
METALS, DISSOLVED							
Aluminum	2.3	mg/L	D	0.2		E200.7	01/27/14 13:23 / jtr
Barium	0.53	mg/L	D	0.05		E200.7	01/27/14 13:23 / jtr
Iron	8.4	mg/L	D	0.2		E200.7	01/27/14 13:23 / jtr
Strontium	6.37	mg/L	D	0.05		E200.7	01/27/14 13:23 / jtr
- Sample diluted due to lack of sample received.							

Report Definitions: RL - Analyte reporting limit. MCL - Maximum contaminant level.
QCL - Quality control limit. ND - Not detected at the reporting limit.
D - RL increased due to sample matrix. H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14040020-003
Client Sample ID: Lane M56

Report Date: 04/16/14
Collection Date: 04/04/14 14:45
Date Received: 04/04/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.2	s.u.	H	0.1		A4500-H B	04/09/14 13:32 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	16100	mg/L		10		A2540 C	04/07/14 13:31 / rel
Hardness as CaCO3	186	mg/L		1		A2340 B	04/08/14 13:51 / sas
Hardness, Calcium as CaCO3	186	mg/L		1		A2340 B	04/08/14 13:51 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	04/08/14 13:51 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	2440	mg/L		1		A2320 B	04/09/14 11:01 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	04/09/14 11:01 / rel
Carbonate as CO3	1360	mg/L		1		A2320 B	04/09/14 11:01 / rel
Chloride	1840	mg/L	D	50		E300.0	04/08/14 21:49 / rda
Sulfate	722	mg/L	D	50		E300.0	04/08/14 21:49 / rda
Calcium	75	mg/L	D	20		E200.7	04/08/14 13:51 / jtr
Magnesium	ND	mg/L	D	20		E200.7	04/08/14 13:51 / jtr
Potassium	ND	mg/L	D	20		E200.7	04/08/14 13:51 / jtr
Sodium	3280	mg/L	D	20		E200.7	04/08/14 13:51 / jtr
Boron	603	mg/L	D	5		E200.7	04/08/14 13:51 / jtr
BALANCE							
Anions	118	meq/L				Calculation	04/14/14 08:32 / sas
Cations	147	meq/L				Calculation	04/14/14 08:32 / sas
A/C Balance	10.9	%				Calculation	04/14/14 08:32 / sas
METALS, DISSOLVED							
Aluminum	2.1	mg/L	D	0.2		E200.7	04/08/14 12:29 / jtr
Barium	0.73	mg/L	D	0.05		E200.7	04/08/14 12:29 / jtr
Iron	5.1	mg/L	D	0.2		E200.7	04/08/14 12:29 / jtr
Strontium	5.73	mg/L	D	0.05		E200.7	04/08/14 12:29 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T13120125-001
Client Sample ID: Lane M10

Report Date: 01/16/14
Collection Date: 12/27/13 11:07
Date Received: 12/27/13
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.6	s.u.	H	0.1		A4500-H B	12/30/13 17:53 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	10300	mg/L		10		A2540 C	12/27/13 12:42 / kmh
Hardness as CaCO3	239	mg/L		1		A2340 B	01/09/14 15:57 / sas
Hardness, Calcium as CaCO3	231	mg/L		1		A2340 B	01/09/14 15:57 / sas
Hardness, Magnesium as CaCO3	8	mg/L		1		A2340 B	01/09/14 15:57 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	605	mg/L		1		A2320 B	12/30/13 12:30 / rda
Bicarbonate as HCO3	737	mg/L		1		A2320 B	12/30/13 12:30 / rda
Carbonate as CO3	ND	mg/L		1		A2320 B	12/30/13 12:30 / rda
Chloride	784	mg/L	D	200		E300.0	01/09/14 20:40 / rda
Sulfate	1070	mg/L	D	200		E300.0	01/09/14 20:40 / rda
Calcium	92	mg/L	D	2		E200.7	01/09/14 15:57 / jtr
Magnesium	ND	mg/L	D	2		E200.7	01/09/14 15:57 / jtr
Potassium	25	mg/L	D	2		E200.7	01/09/14 15:57 / jtr
Sodium	1750	mg/L	D	2		E200.7	01/09/14 15:57 / jtr
Boron	339	mg/L	D	5		E200.7	01/14/14 12:03 / jtr
BALANCE							
Anions	56.4	meq/L				Calculation	01/16/14 08:50 / sas
Cations	81.5	meq/L				Calculation	01/16/14 08:50 / sas
A/C Balance	18.2	%				Calculation	01/16/14 08:50 / sas
- Individual components were not re-run due to sample volume.							
METALS, DISSOLVED							
Aluminum	2.4	mg/L	D	0.3		E200.7	01/09/14 17:56 / jtr
Barium	0.3	mg/L	D	0.1		E200.7	01/09/14 17:56 / jtr
Iron	4.8	mg/L	D	0.5		E200.7	01/09/14 17:56 / jtr
Strontium	3.1	mg/L	D	0.1		E200.7	01/09/14 17:56 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: TAMU Flowback Chemical Analysis
Lab ID: T14030001-003
Client Sample ID: LANE M10b

Report Date: 03/28/14
Collection Date: 03/03/14 16:09
Date Received: 03/03/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.8	s.u.	H	0.1		A4500-H B	03/06/14 15:09 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	12900	mg/L		10		A2540 C	03/05/14 10:08 / rel
Hardness as CaCO3	117	mg/L		1		A2340 B	03/13/14 10:26 / ajm
Hardness, Calcium as CaCO3	117	mg/L		1		A2340 B	03/13/14 10:26 / ajm
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	03/13/14 10:26 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	1500	mg/L		1		A2320 B	03/06/14 09:13 / rda
Bicarbonate as HCO3	625	mg/L		1		A2320 B	03/06/14 09:13 / rda
Carbonate as CO3	593	mg/L		1		A2320 B	03/06/14 09:13 / rda
Chloride	1240	mg/L	D	50		E300.0	03/08/14 07:48 / rda
Sulfate	945	mg/L	D	50		E300.0	03/08/14 07:48 / rda
Calcium	47	mg/L	D	20		E200.7	03/10/14 14:37 / jtr
Magnesium	ND	mg/L		1		E200.7	03/13/14 10:26 / jtr
Potassium	19	mg/L		1		E200.7	03/13/14 10:26 / jtr
Sodium	2630	mg/L	D	20		E200.7	03/10/14 14:37 / jtr
Boron	454	mg/L	D	5		E200.7	03/10/14 14:37 / jtr
BALANCE							
Anions	85.2	meq/L				Calculation	03/25/14 16:53 / ajm
Cations	117	meq/L				Calculation	03/25/14 16:53 / ajm
A/C Balance	15.8	%				Calculation	03/25/14 16:53 / ajm
METALS, DISSOLVED							
Aluminum	6.8	mg/L	D	0.2		E200.7	03/21/14 13:20 / sas
Barium	0.51	mg/L	D	0.05		E200.7	03/21/14 13:20 / sas
Iron	22.5	mg/L	D	0.2		E200.7	03/21/14 13:20 / sas
Strontium	3.25	mg/L	D	0.05		E200.7	03/21/14 13:20 / sas

Report Definitions: RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE C1090
Lab ID: T14010050-003
Client Sample ID: Lane M30

Report Date: 01/28/14
Collection Date: 01/16/14 16:44
Date Received: 01/16/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	7.8	s.u.	H	0.1		A4500-H B	01/23/14 15:31 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	11600	mg/L		10		A2540 C	01/17/14 10:47 / rel
Hardness as CaCO3	418	mg/L		1		A2340 B	01/22/14 19:58 / sas
Hardness, Calcium as CaCO3	404	mg/L		1		A2340 B	01/22/14 19:58 / sas
Hardness, Magnesium as CaCO3	14	mg/L		1		A2340 B	01/22/14 19:58 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	3130	mg/L		1		A2320 B	01/23/14 11:53 / rel
Bicarbonate as HCO3	3810	mg/L		1		A2320 B	01/23/14 11:53 / rel
Carbonate as CO3	ND	mg/L		1		A2320 B	01/23/14 11:53 / rel
Chloride	804	mg/L	D	50		E300.0	01/22/14 22:06 / rda
Sulfate	1140	mg/L	D	50		E300.0	01/22/14 22:06 / rda
Calcium	162	mg/L	D	20		E200.7	01/22/14 19:58 / jtr
Magnesium	ND	mg/L	D	20		E200.7	01/22/14 19:58 / jtr
Potassium	25	mg/L	D	20		E200.7	01/22/14 19:58 / jtr
Sodium	1890	mg/L	D	20		E200.7	01/22/14 19:58 / jtr
Boron	364	mg/L	D	5		E200.7	01/23/14 12:15 / jtr
- Sample diluted according to sample matrix.							
BALANCE							
Anions	111	meq/L				Calculation	01/27/14 11:06 / sas
Cations	91.2	meq/L				Calculation	01/27/14 11:06 / sas
A/C Balance	-9.7	%				Calculation	01/27/14 11:06 / sas
METALS, DISSOLVED							
Aluminum	4.3	mg/L	D	0.2		E200.7	01/22/14 11:08 / jtr
Barium	0.48	mg/L	D	0.05		E200.7	01/22/14 11:08 / jtr
Iron	29.8	mg/L	D	0.2		E200.7	01/22/14 11:08 / jtr
Strontium	4.99	mg/L	D	0.05		E200.7	01/22/14 11:08 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14040115-003
Client Sample ID: M30b

Report Date: 05/08/14
Collection Date: 04/25/14 11:11
Date Received: 04/25/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	8.4	s.u.	H	0.1		A4500-H B	04/28/14 14:36 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	19600	mg/L		10		A2540 C	04/29/14 10:48 / rel
Hardness as CaCO ₃	68	mg/L		1		A2340 B	04/30/14 14:03 / sas
Hardness, Calcium as CaCO ₃	65	mg/L		1		A2340 B	04/30/14 14:03 / sas
Hardness, Magnesium as CaCO ₃	3	mg/L		1		A2340 B	04/30/14 14:03 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	2090	mg/L		1		A2320 B	04/28/14 11:30 / rel
Bicarbonate as HCO ₃	2260	mg/L		1		A2320 B	04/28/14 11:30 / rel
Carbonate as CO ₃	140	mg/L		1		A2320 B	04/28/14 11:30 / rel
Chloride	2180	mg/L	D	50		E300.0	04/26/14 15:25 / rda
Sulfate	1060	mg/L	D	50		E300.0	04/26/14 15:25 / rda
Calcium	26	mg/L	D	2		E200.7	04/28/14 15:05 / jtr
Magnesium	ND	mg/L		1		E200.7	04/30/14 14:03 / jtr
Potassium	17	mg/L	D	2		E200.7	04/28/14 15:05 / jtr
Sodium	3630	mg/L	D	2		E200.7	04/28/14 15:05 / jtr
Boron	780	mg/L	D	5		E200.7	04/29/14 11:50 / jtr
BALANCE							
Anions	132	meq/L				Calculation	05/08/14 13:52 / sas
Cations	160	meq/L				Calculation	05/08/14 13:52 / sas
A/C Balance	9.4	%				Calculation	05/08/14 13:52 / sas
METALS, DISSOLVED							
Aluminum	31.0	mg/L	D	0.2		E200.7	05/01/14 10:37 / jtr
Barium	1.20	mg/L	D	0.05		E200.7	05/01/14 10:37 / jtr
Iron	65.0	mg/L	D	0.2		E200.7	05/01/14 10:37 / jtr
Strontium	6.51	mg/L	D	0.05		E200.7	05/01/14 10:37 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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APPENDIX G

BLANK FRACTURE FLUID REPORT



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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14020023-004
Client Sample ID: Lane N1

Report Date: 02/19/14
Collection Date: 02/06/14 17:12
Date Received: 02/06/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	10.5	s.u.	H	0.1		A4500-H B	02/12/14 11:45 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	12500	mg/L		10		A2540 C	02/07/14 16:11 / rel
Hardness as CaCO3	41	mg/L		1		A2340 B	02/14/14 09:39 / sas
Hardness, Calcium as CaCO3	39	mg/L		1		A2340 B	02/14/14 09:39 / sas
Hardness, Magnesium as CaCO3	2	mg/L		1		A2340 B	02/14/14 09:39 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	2300	mg/L		1		A2320 B	02/12/14 10:59 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	02/12/14 10:59 / rel
Carbonate as CO3	665	mg/L		1		A2320 B	02/12/14 10:59 / rel
Chloride	846	mg/L	D	50		E300.0	02/08/14 06:13 / rda
Sulfate	289	mg/L	D	50		E300.0	02/08/14 06:13 / rda
Calcium	16	mg/L	D	10		E200.7	02/10/14 13:50 / jtr
Magnesium	ND	mg/L		1		E200.7	02/14/14 09:39 / jtr
Potassium	12	mg/L	D	10		E200.7	02/10/14 13:50 / jtr
Sodium	2210	mg/L	D	10		E200.7	02/10/14 13:50 / jtr
Boron	391	mg/L	D	2		E200.7	02/10/14 13:50 / jtr
BALANCE							
Anions	76.5	meq/L				Calculation	02/18/14 08:52 / sas
Cations	97.2	meq/L				Calculation	02/18/14 08:52 / sas
A/C Balance	12.0	%				Calculation	02/18/14 08:52 / sas
METALS, DISSOLVED							
Aluminum	0.2	mg/L	D	0.2		E200.7	02/13/14 18:41 / jtr
Barium	0.74	mg/L	D	0.05		E200.7	02/13/14 18:41 / jtr
Iron	ND	mg/L	D	0.2		E200.7	02/13/14 18:41 / jtr
Strontium	6.53	mg/L	D	0.05		E200.7	02/13/14 18:41 / jtr

Report Definitions:
RL - Analyte reporting limit.
QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14040117-004
Client Sample ID: Lane N1B

Report Date: 05/08/14
Collection Date: 04/28/14 11:44
Date Received: 04/28/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.6	s.u.	H	0.1		A4500-H B	04/28/14 15:30 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	11400	mg/L		10		A2540 C	04/29/14 10:50 / rel
Hardness as CaCO3	377	mg/L		1		A2340 B	04/30/14 14:40 / sas
Hardness, Calcium as CaCO3	377	mg/L		1		A2340 B	04/30/14 14:40 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	04/30/14 14:40 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	2590	mg/L		1		A2320 B	04/28/14 11:30 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	04/28/14 11:30 / rel
Carbonate as CO3	900	mg/L		1		A2320 B	04/28/14 11:30 / rel
Chloride	1300	mg/L	D	50		E300.0	04/29/14 15:22 / rda
Sulfate	306	mg/L	D	50		E300.0	04/29/14 15:22 / rda
Calcium	151	mg/L	D	20		E200.7	04/29/14 12:09 / jtr
Magnesium	ND	mg/L		1		E200.7	04/30/14 14:40 / jtr
Potassium	17	mg/L		1		E200.7	04/30/14 14:40 / jtr
Sodium	2750	mg/L	D	20		E200.7	04/29/14 12:09 / jtr
Boron	613	mg/L	D	5		E200.7	04/29/14 12:09 / jtr
BALANCE							
Anions	94.8	meq/L				Calculation	05/08/14 13:53 / sas
Cations	128	meq/L				Calculation	05/08/14 13:53 / sas
A/C Balance	14.8	%				Calculation	05/08/14 13:53 / sas
METALS, DISSOLVED							
Aluminum	0.6	mg/L	D	0.2		E200.7	05/01/14 10:53 / jtr
Barium	0.72	mg/L	D	0.05		E200.7	05/01/14 10:53 / jtr
Iron	ND	mg/L	D	0.2		E200.7	05/01/14 10:53 / jtr
Strontium	12.8	mg/L	D	0.05		E200.7	05/01/14 10:53 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: Lane
Lab ID: T14050050-001
Client Sample ID: Lane N1c

Report Date: 05/30/14
Collection Date: 05/09/14 16:05
Date Received: 05/09/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	10.4	s.u.	H	0.1		A4500-H B	05/16/14 13:24 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	13600	mg/L		10		A2540 C	05/14/14 16:30 / rel
Hardness as CaCO3	103	mg/L		1		A2340 B	05/14/14 13:52 / ajm
Hardness, Calcium as CaCO3	103	mg/L		1		A2340 B	05/14/14 13:52 / ajm
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	05/14/14 13:52 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO3	2430	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Carbonate as CO3	760	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Chloride	970	mg/L	D	50		E300.0	05/13/14 01:13 / rda
Sulfate	355	mg/L	D	50		E300.0	05/13/14 01:13 / rda
Calcium	41	mg/L	D	10		E200.7	05/14/14 13:52 / jtr
Magnesium	ND	mg/L	D	10		E200.7	05/14/14 13:52 / jtr
Potassium	14	mg/L	D	10		E200.7	05/14/14 13:52 / jtr
Sodium	2680	mg/L	D	10		E200.7	05/14/14 13:52 / jtr
Boron	456	mg/L	D	2		E200.7	05/14/14 13:52 / jtr
BALANCE							
Anions	83.4	meq/L				Calculation	05/29/14 09:13 / ajm
Cations	119	meq/L				Calculation	05/29/14 09:13 / ajm
A/C Balance	17.6	%				Calculation	05/29/14 09:13 / ajm
METALS, DISSOLVED							
Aluminum	ND	mg/L	D	0.2		E200.7	05/13/14 14:34 / jtr
Barium	0.59	mg/L	D	0.05		E200.7	05/13/14 14:34 / jtr
Iron	ND	mg/L	D	0.2		E200.7	05/13/14 14:34 / jtr
Strontium	7.38	mg/L	D	0.05		E200.7	05/13/14 14:34 / jtr

Report Definitions:
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D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14010059-004
Client Sample ID: Lane N5

Report Date: 02/03/14
Collection Date: 01/21/14 16:58
Date Received: 01/21/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.5	s.u.	H	0.1		A4500-H B	01/23/14 16:24 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	11800	mg/L		10		A2540 C	01/22/14 17:22 / rel
Hardness as CaCO3	187	mg/L		1		A2340 B	02/01/14 09:46 / sas
Hardness, Calcium as CaCO3	187	mg/L		1		A2340 B	02/01/14 09:46 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	02/01/14 09:46 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	1790	mg/L		1		A2320 B	01/23/14 11:53 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	01/23/14 11:53 / rel
Carbonate as CO3	677	mg/L		1		A2320 B	01/23/14 11:53 / rel
Chloride	908	mg/L	D	50		E300.0	01/28/14 18:02 / rda
Sulfate	418	mg/L	D	50		E300.0	01/28/14 18:02 / rda
Calcium	75	mg/L	D	2		E200.7	02/01/14 09:46 / jtr
Magnesium	ND	mg/L	D	2		E200.7	02/01/14 09:46 / jtr
Potassium	13	mg/L	D	2		E200.7	02/01/14 09:46 / jtr
Sodium	2230	mg/L	D	20		E200.7	01/28/14 13:01 / jtr
Boron	385	mg/L	D	5		E200.7	01/28/14 13:01 / jtr
- Sample diluted according to sample matrix.							
BALANCE							
Anions	71.6	meq/L				Calculation	02/03/14 11:42 / sas
Cations	101	meq/L				Calculation	02/03/14 11:42 / sas
A/C Balance	17.0	%				Calculation	02/03/14 11:42 / sas
METALS, DISSOLVED							
Aluminum	0.2	mg/L	D	0.2		E200.7	01/27/14 13:25 / jtr
Barium	0.45	mg/L	D	0.05		E200.7	01/27/14 13:25 / jtr
Iron	ND	mg/L	D	0.2		E200.7	01/27/14 13:25 / jtr
Strontium	9.94	mg/L	D	0.05		E200.7	01/27/14 13:25 / jtr
- Sample diluted due to lack of sample received.							

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

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H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14040020-004
Client Sample ID: Lane N56

Report Date: 04/16/14
Collection Date: 04/04/14 14:45
Date Received: 04/04/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	11.5	s.u.	H	0.1		A4500-H B	04/09/14 13:46 / rel
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	14600	mg/L		10		A2540 C	04/07/14 13:32 / rel
Hardness as CaCO3	293	mg/L		1		A2340 B	04/08/14 13:54 / sas
Hardness, Calcium as CaCO3	293	mg/L		1		A2340 B	04/08/14 13:54 / sas
Hardness, Magnesium as CaCO3	ND	mg/L		1		A2340 B	04/08/14 13:54 / sas
MAJOR IONS							
Alkalinity, Total as CaCO3	3840	mg/L		1		A2320 B	04/09/14 11:01 / rel
Bicarbonate as HCO3	ND	mg/L		1		A2320 B	04/09/14 11:01 / rel
Carbonate as CO3	1180	mg/L		1		A2320 B	04/09/14 11:01 / rel
Chloride	1840	mg/L	D	50		E300.0	04/08/14 22:26 / rda
Sulfate	370	mg/L	D	50		E300.0	04/08/14 22:26 / rda
Calcium	117	mg/L	D	20		E200.7	04/08/14 13:54 / jtr
Magnesium	ND	mg/L	D	20		E200.7	04/08/14 13:54 / jtr
Potassium	ND	mg/L	D	20		E200.7	04/08/14 13:54 / jtr
Sodium	3260	mg/L	D	20		E200.7	04/08/14 13:54 / jtr
Boron	580	mg/L	D	5		E200.7	04/08/14 13:54 / jtr
BALANCE							
Anions	139	meq/L				Calculation	04/14/14 08:33 / sas
Cations	148	meq/L				Calculation	04/14/14 08:33 / sas
A/C Balance	3.1	%				Calculation	04/14/14 08:33 / sas
METALS, DISSOLVED							
Aluminum	0.2	mg/L	D	0.2		E200.7	04/08/14 12:31 / jtr
Barium	0.39	mg/L	D	0.05		E200.7	04/08/14 12:31 / jtr
Iron	ND	mg/L	D	0.2		E200.7	04/08/14 12:31 / jtr
Strontium	13.9	mg/L	D	0.05		E200.7	04/08/14 12:31 / jtr

Report RL - Analyte reporting limit.
Definitions: QCL - Quality control limit.
D - RL increased due to sample matrix.

MCL - Maximum contaminant level.
ND - Not detected at the reporting limit.
H - Analysis performed past recommended holding time.

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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T14050057-004
Client Sample ID: Lane N5C

Report Date: 05/30/14
Collection Date: 05/12/14 17:29
Date Received: 05/12/14
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.5	s.u.	H	0.1		A4500-H B	05/16/14 14:15 / kmh
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	12500	mg/L		10		A2540 C	05/16/14 11:49 / rel
Hardness as CaCO ₃	39	mg/L		1		A2340 B	05/14/14 14:18 / ajm
Hardness, Calcium as CaCO ₃	39	mg/L		1		A2340 B	05/14/14 14:18 / ajm
Hardness, Magnesium as CaCO ₃	ND	mg/L		1		A2340 B	05/14/14 14:18 / ajm
MAJOR IONS							
Alkalinity, Total as CaCO ₃	2040	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Bicarbonate as HCO ₃	ND	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Carbonate as CO ₃	880	mg/L		1		A2320 B	05/16/14 09:30 / kmh
Chloride	1060	mg/L	D	50		E300.0	05/16/14 23:23 / kmh
Sulfate	365	mg/L	D	50		E300.0	05/16/14 23:23 / kmh
Calcium	16	mg/L	D	2		E200.7	05/14/14 14:18 / jtr
Magnesium	ND	mg/L	D	2		E200.7	05/14/14 14:18 / jtr
Potassium	16	mg/L	D	2		E200.7	05/14/14 14:18 / jtr
Sodium	2640	mg/L	D	2		E200.7	05/14/14 14:18 / jtr
Boron	481	mg/L	D	5		E200.7	05/13/14 18:18 / jtr
Silica	50	mg/L	D	1		E200.7	05/19/14 13:39 / jtr
BALANCE							
Anions	78.3	meq/L				Calculation	05/29/14 09:12 / ajm
Cations	116	meq/L				Calculation	05/29/14 09:12 / ajm
A/C Balance	19.5	%				Calculation	05/29/14 09:12 / ajm
METALS, DISSOLVED							
Aluminum	0.4	mg/L	D	0.2		E200.7	05/13/14 14:50 / jtr
Barium	0.67	mg/L	D	0.05		E200.7	05/13/14 14:50 / jtr
Iron	0.4	mg/L	D	0.2		E200.7	05/13/14 14:50 / jtr
Strontium	7.07	mg/L	D	0.05		E200.7	05/13/14 14:50 / jtr

Report Definitions:
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MCL - Maximum contaminant level.
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LABORATORY ANALYTICAL REPORT

Prepared by College Station, TX Branch

Client: Texas A and M University
Project: LANE
Lab ID: T13120125-003
Client Sample ID: Lane N10

Report Date: 01/16/14
Collection Date: 12/27/13 11:07
Date Received: 12/27/13
Matrix: Aqueous

Analyses	Result	Units	Qualifiers	RL	MCL/ QCL	Method	Analysis Date / By
AGRONOMIC PROPERTIES							
pH	9.2	s.u.	H	0.1		A4500-H B	12/30/13 17:59 / rda
PHYSICAL PROPERTIES							
Solids, Total Dissolved TDS @ 180 C	9150	mg/L		10		A2540 C	12/27/13 12:42 / kmh
Hardness as CaCO ₃	47	mg/L		1		A2340 B	01/09/14 16:19 / sas
Hardness, Calcium as CaCO ₃	45	mg/L		1		A2340 B	01/09/14 16:19 / sas
Hardness, Magnesium as CaCO ₃	2	mg/L		1		A2340 B	01/09/14 16:19 / sas
MAJOR IONS							
Alkalinity, Total as CaCO ₃	1440	mg/L		1		A2320 B	12/30/13 12:30 / rda
Bicarbonate as HCO ₃	ND	mg/L		1		A2320 B	12/30/13 12:30 / rda
Carbonate as CO ₃	834	mg/L		1		A2320 B	12/30/13 12:30 / rda
Chloride	812	mg/L	D	100		E300.0	01/09/14 21:58 / rda
Sulfate	376	mg/L	D	100		E300.0	01/09/14 21:58 / rda
Calcium	18	mg/L	D	2		E200.7	01/09/14 16:19 / jtr
Magnesium	ND	mg/L	D	2		E200.7	01/09/14 16:19 / jtr
Potassium	11	mg/L	D	2		E200.7	01/09/14 16:19 / jtr
Sodium	1810	mg/L	D	2		E200.7	01/09/14 16:19 / jtr
Boron	315	mg/L	D	5		E200.7	01/14/14 12:16 / jtr
BALANCE							
Anions	59.5	meq/L				Calculation	01/16/14 08:51 / sas
Cations	79.9	meq/L				Calculation	01/16/14 08:51 / sas
A/C Balance	14.6	%				Calculation	01/16/14 08:51 / sas
- Individual components were not re-run due to sample volume.							
METALS, DISSOLVED							
Aluminum	ND	mg/L	D	0.3		E200.7	01/09/14 18:07 / jtr
Barium	0.2	mg/L	D	0.1		E200.7	01/09/14 18:07 / jtr
Iron	ND	mg/L	D	0.5		E200.7	01/09/14 18:07 / jtr
Strontium	2.4	mg/L	D	0.1		E200.7	01/09/14 18:07 / jtr

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