

THESIS

FLOWBACK QUALITY CHARACTERIZATION FOR HORIZONTAL WELLS IN
WATTENBERG FIELD

Submitted by

Xi Jiang

Department of Civil and Environmental Engineering

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Colorado State University

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Master's Committee:

Advisor: Kenneth H. Carlson

Pinar Omur-Ozbek
Thomas H. Bradley

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ABSTRACT

FLOWBACK QUALITY CHARACTERIZATION FOR HORIZONTAL WELLS IN WATTENBERG FIELD

The development of hydraulic fracturing has driven both the need for more fresh water, and also has increased the amount of flowback being produced. Faced with a shortage of usable water, transportation issues, strict environmental regulation and environmental concerns, flowback management is an important topic for oil and gas companies. Recycle and reuse flowback waste is a promising method, since it can simultaneously reduce the need of more fresh water for fracking and decrease the potential environmental issues. Understanding the quality characteristics of flowback is significant for implementing the required treatment of flowback water.

Flowback flows back to the surface during and after hydraulic fracturing and often flows for over a period of 3-4 weeks, though most wells finish in seven to 10 days. The fluid contains high total dissolved solids (TDS) and high salinity, and also contains some of the same chemicals that are pumped into wells. The volume of flowback can range from 10%-50% of initial injected fracturing fluid.

In our study, sampling time was from March to April 2013 and all the samples were taken separately from Wells Ranch State PC USX #AA16-69-1HNL and Wells Ranch State USX #AA16-68-1HNL. The results in this report used well #68 and well #69. Well #68 was injected with PermStim fracture fluid (injected pH 5.0) and well #69 was injected with SliverStim fracture fluid (injected pH 10.2). Wellhead pressure, temperature, pH, dissolved carbon dioxide (CO_2), bicarbonate (HCO_3) and dissolved hydrogen sulfide (H_2S) were tested in the field once samples

were collected. TDS, chloride, sulfate, bicarbonate, aluminum, barium, boron, calcium, iron, magnesium, potassium, silicon, strontium and zirconium were tested by E-Analytics Laboratory.

The objective of this paper is to analyze flowback water quality from two horizontal wells, located in the same place, which were injected with two different fracturing fluids. Based on the results of the temporal quality trend, this paper also intends to analyze the impact of different pH on water quality and the possible chemical reactions that occur during drilling and fracturing phases.

Keywords: flowback water, Wattenberg field, water quality, fracturing fluid

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Chapter 1 Introduction

In the past decades, unconventional natural gas has been an important energy supply for the United States. U.S. shale gas recoverable reserves are currently estimated at 500 to 1,000 trillion cubic feet. The development of horizontal drilling and hydraulic fracturing technology make the exploration of shale gas and oil available. During the hydraulic fracturing process, a large amount of water and chemical additives are injected underground to create fissures or cracks in the shale formation. A typical horizontal well utilizes 2-6 million gallons of fluid to finish the drilling and fracturing operation.

Generally, the portion of injected fluid that returns to the surface accounts for 10%-50% of initial fracturing fluid, and is called flowback water. This released water contains a significant amount of hardness, soil, heavy metals, chloride, salts, organic elements and also hydrocarbons and radionuclides from shale formation. Since the recent strict environmental regulation and concern produced multiple bans for flowback disposal, recycling and reusing flowback are increasingly attractive methods.

Additionally, a large amount of drilling and fracturing water comes from surface water, underground and municipal water. Due to world-wide water shortages, recycling and reusing flowback water is a promising management opportunity for oil and gas companies. Reusing flowback reduces the impact of community issues including less transportation, the demand for fresh water and the cost for disposal.

Flowback water quality is unstable and its composition depends on three categories: the composition of fluids used for hydraulic fracturing, the geology formation of the site and the amount of time during which the water has contact with the underground formation.¹ Furthermore,

the additives in fracturing fluids are not compatible with flowback water.² Therefore, in order to implement an effective treatment process, analysis of flowback water quality is critical.

Natural gas is called an energy game changer, which indicates that it contains low carbon compared to a common energy source like coal or oil. Even though drilling natural gas has a history of over 100 years, horizontal drilling technology has only been utilized for a few decades. Thus, there are few papers that talk about horizontal wells, and even fewer that talk about the quality of flowback from horizontal wells.

The three goals of this paper are to: 1) analyze flowback water quality from two horizontal wells that were injected with two different fracturing fluids, 2) to understand the temporal flowback quality for horizontal wells which are located at the same shale formation and 3) to use the collected data for the future prediction of flowback quality to make a better, instant and on-site treatment implementation.

The development of shale gas and advanced drilling techniques (horizontal drilling and hydraulic fracturing) will be presented in Chapter 2. Environmental concerns caused by shale gas development such as water contamination and land disturbance, flowback characteristics, and water management are discussed in Chapter 2 as well, along with a background of Wattenberg Field. Chapter 3 will discuss sampling schedule, sample method and sample measurement. Chapter 4 will include statistics and temporal analysis for two wells and also discuss correlation between different ions.

Chapter 2 Literature Review

Introduction

Since 2007, discoveries of unconventional gas—including shale gas—have more than doubled the estimate of North American reserves to 1,000 trillion cubic feet, enough to meet 100 years demand.³ At the same time, the demand for oil and gas is still increasing while the production from conventional reserves is decreasing sharply. Due to this deficiency, oil and gas from shale formations has become one of the most promising sources of energy sources in the United States.⁴

Low natural permeability of shale gas reservoirs produces mainly dry natural gas. Initially, the development of shale gas was treated as either technologically inaccessible or economically undesirable. Thanks to the advanced technology in horizontal drilling and hydraulic fracturing, shale gas availability is rapidly increasing.

During the hydraulic fracturing process, large amounts of fracturing fluid (fresh water and chemical additives) are injected into shale formations under high pressure. When the pressure is released, 10%-50% of the injected fluid will return to the surface as “flowback”. Due to the complex components of flowback, it is difficult to restore it to a condition that Environmental Protection Agency (EPA) and local government recommend. Additionally, the operators and service companies in an arid state such as Colorado are regularly faced with fresh water shortages. Therefore, recycling and reusing flowback is attractive as it can reduce the cost of transportation as well as minimize the impact on environment.

2.1 Shale Gas Development

With the increased demand for energy and the decline in conventional oil and gas reserves, more and more companies are turning to unconventional energy such as shale gas. The projects released by the U.S. Department of Energy estimate that the country holds around 482 trillion cubic feet (tcf) of recoverable natural gas from shale basins.⁵ Continually increasing gas prices are another reason for boosting development of shale gas. Over time, natural gas prices rise with the cost of developing incremental production capacity— after 2017, as seen in figure 2.1 specifically, natural gas prices are expected to rise significantly.

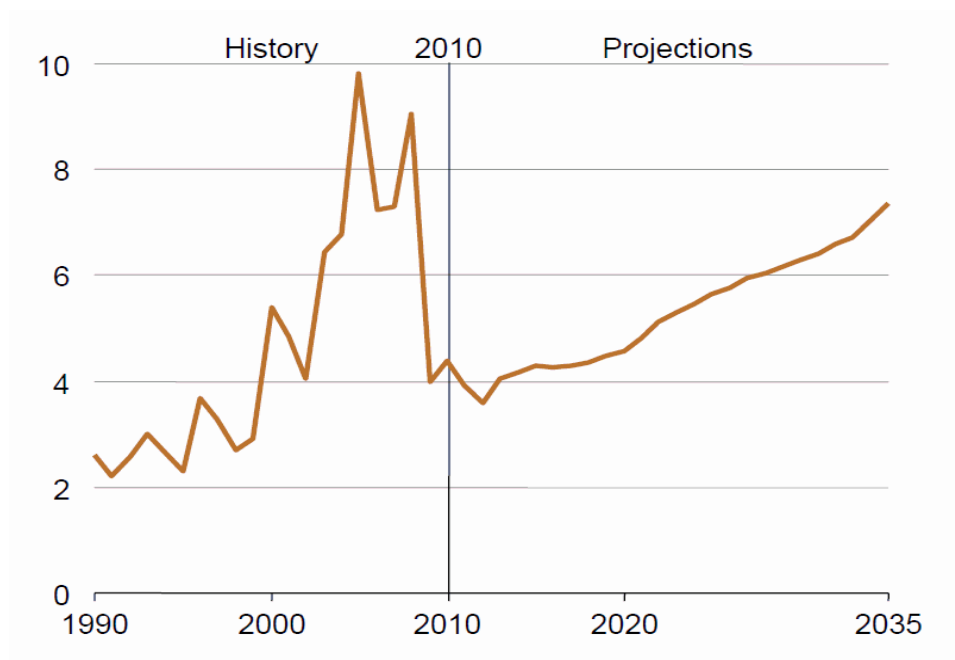


Figure 2.1. Annual average Henry Hub spot natural gas prices, 1990-2035 (2010 dollar per million Btu)⁶

Shale gas is the largest contributor to the unconventional gas growth. The U.S. Energy Information Administration (EIA) 2012 Annual Energy Outlook report asserts that the production of shale gas could account for 49% of total U.S. dry natural gas production in 2035, more than double its 23% in 2010.⁶

Shale gas is an unconventional gas reservoir contained in fine-grained, organic rich, sedimentary rocks including shale, but is composed of mud containing other minerals like quartz and calcite.⁷ The natural permeability and porosity of a shale formation is extremely low compared to conventional gas and oil formation. Additionally, every shale basin is different, even if they are located in the same field. Although exploration for shale gas is met with huge difficulties, recent advances in hydraulic fracturing and horizontal drilling have successfully unlocked these shale gas plays. The lower forty-eight states have a wide distribution of shale formation containing vast volume of natural gas (fig. 2.2). Shale gas plays are mainly located in the eastern and central parts of the United States, while the majority of shale oil plays are located in western United States.

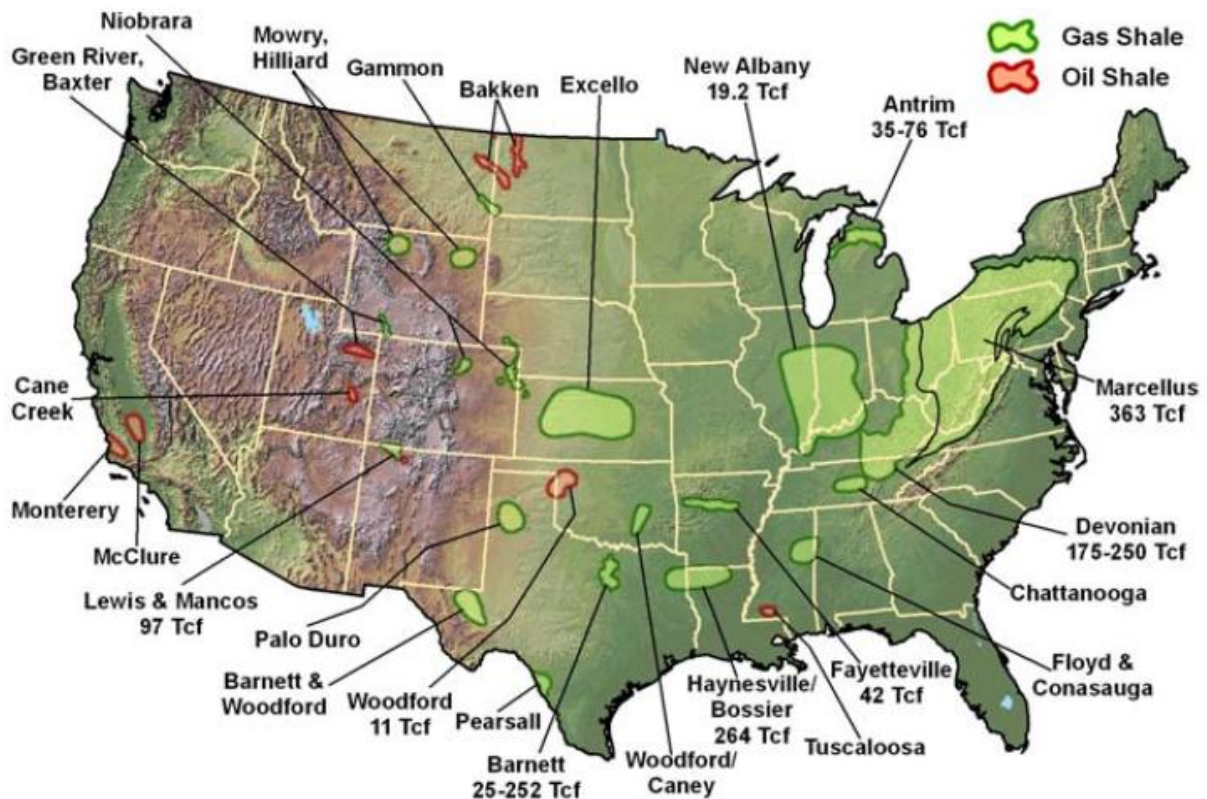


Figure 2.2. Gas shale basins of the United States with estimated reserves⁸

Even though there are vast amounts of shale gas in the United States, from the west coast to the eastern mountains, shale basins characteristics vary both vertically and spatially. Because of these differences, developing the “best” exploration technique criteria primarily depends on main geologic parameters such as total organic carbon (TOC), average gas content, reservoir pressure, permeability, porosity and thickness. TOC indicates the amount of organic material, which is available to be stored as hydrocarbon in the rock formation and is usually expressed as weight percent. The average gas content and reservoir pressure play a key role in determining gas recovery. Permeability and porosity control gas quantity and gas-flow rate. Thickness is another significant parameter. Commonly, thin layer (less than 50ft) shale is treated as uneconomic, since it would be too difficult to determine production layer if the shale were too thick. The comparison among different shale gas plays (table 2.1) provides invaluable information for determining economic drilling and exploration technique.

Table 2.1. Summary of key properties from five shale gas basins in the United States⁹

Property	Antrim Shale	Barnett Shale	Haynesville Shale	Marcellus Shale	Woodford Shale
Basin	Michigan	Fort Worth	North Louisiana Salt	Appalachian	Arkoma
Fairway depth (ft)	600 to 2,200	6,500 to 8,500	9,900 to 16,500	4,000 to 8,000	6,000 to 11,000
Thickness (ft)	120 to 200 (net 70 to 120)	200 to 300 (net 50 to 100)	270 (net 100 to 200)	40 to 900 (varies between states)	50 to 220 (net-100)
TOC (%)	up to 20	up to 12 (average 4.5)	0.5 to 4	0.3 to 11	up to 20 (average 3 to 10)
Total porosity (%)	3 to 10	3 to 8	7 to 15	9 to 13	7.5 to 14
Gas-filled porosity (%)	2 to 6	2 to 6	5 to 11	3 to 6	3 to 6.5
Gas content (scf/ton)	40 to 100	300 to 350	350 to 475	275 to 325	60 to 115
Quartz content (%)	50 to 60	40 to 45	28 to 33	18 to 24	55 to 87
Clay content (%)	20 to 35	20 to 40	25 to 33	40 to 60	8 to 34
Reservoir pressure (psi)	400	3,000 to 4,000	8,000 to 10,000	1,600 to 5,000	3,100 to 5,800
Reservoir pressure gradient (psi/ft)	0.33 to 0.38	0.42 to 0.46	0.7 to 0.92	0.4 to 0.7	0.48 to 0.55
Adsorbed gas (%)	60 to 70	15 to 30	20 to 30	20 to 40	20 to 40
Well spacing (acre as of 1/1/09)	40 to 160	80 to 160	40 to 160	40 to 80	40 to 80
Gas-In-Place (TCF as of 1/1/09)	35 to 75	25 to 30	250 to 320	1,300 to 1,650	45 to 60

Shale formation produces a small amount of gas, but the shale itself is available in continuous volumes across the United States. The first horizontal well in the Barnett Shale Basin was drilled in 1992¹⁰ using hydraulic fracturing, a process first developed in Texas. Due to the successful drilling activity in Barnett Shale Basin, industry operators began to put more attention to exploration and production in shale gas and expanded the drilling technology to Marcellus shale, Fayetteville shale and Woodford shale plays, to name a few. Five emerging shale gas plays are gaining considerable attention due to their potential production (fig. 2.2): the Antrim shale in western and eastern Michigan, the Barnett shale in western Texas, the Haynesville shale in Northern Louisiana and Eastern Texas, the Marcellus shale located in the Northeastern states of West Virginia, Pennsylvania, Ohio and New York and Woodford shale in Oklahoma state of south-central United States.

2.2 Advancements (Hydraulic Fracturing and Horizontal Drilling) in Shale Gas Exploration

Although unconventional shale gas exploration has already gained more and more attention from gas and oil operators, challenges still exist during drilling and production processes. Thanks to the advanced techniques in both hydraulic fracturing and horizontal drilling the exploration of shale gas has become possible. Additionally, both techniques also increase the recovery of shale gas, which means that drilling shale gas has become more economical.

Table 2.2. Comparison between injected water and flowback water from seven horizontal wells¹¹

	Concentrations in mg/L		
	Injected fluid median, day 0	Flowback median, day 14	Flowback range, day14
pH	7.0	6.2	5.8-6.6
Alkalinity as CaCO₃	126	71	26-95
Total dissolved solids	735	157,000	3010-228,000
Total organic carbon	205	14	1.2-509
Chemical oxygen demand	734	8370	228-128,000
Cl	82	98,300	1070-151,000
Br	<10 (<0.2-19)	872	16-1190
SO₄	59	<50*	0.8-89
NH₃-N	16	193	4-359
P	0.36	0.55*	0.04-2.2
Al	0.3*	0.5	0.15-0.91
Ba	0.6	1,990	76-13,600
B	0.5	20	2.7-3880
Ca	32	11200	204-14,800
Fe	0.68	47	14-59
K	<50 (3-57)	281	8-1,010
Zn	0.08	0.09	0.07-0.14
Mg	3.7	875	22-1,800
Mn	0.074	5.6	1.2-8.4
Na	80	36,400	1100-44,100
Sr	0.82	2330	46-5350

*Approximated because some <values. For an even number of samples, the two middle values are averaged to obtain the median.

Since flowback water contains very complex chemical and physical compositions, it is tough to implement an on-site flowback treatment facility. Another reason is that while one treatment might meet the flowback quality standards in Marcellus shale, it may not be able to meet the requirements from other shale, both temporally and spatially, due to the variability of flowback quality. Thus complete analysis of flowback quality is necessary for future treatment implementation.

The flowback water contains both inorganic and organic compounds. The organic matters are mainly composed of volatile organic compounds including benzene, toluene and xylenes. The inorganic compounds can be divided into two parts as ions and cations. Major ions are calcium, iron, magnesium, sodium, and strontium and potassium etc. Additionally, the pH value of flowback water ranges from 5-8.¹²

The characteristics of flowback water is initially similar to fracturing fluids, but at greater flowback times, the composition of the water gradually comes to resemble the formation water. Thus through the whole returning process, flowback quality varies largely depending on how long it has contact with the shale formation. Table 2.4 lists the major parameters in flowback water, making it obvious that flowback water quality varies dramatically from one shale to another. For example, the average concentration of calcium (Ca) from Fayetteville shale is 256.3 mg/L. The concentration of Ca goes up to 2921mg/L in Marcellus shale. The flowback water from Barnett shale contains 2242 mg/L. The biggest differences is in the concentration of barium (Ba), which ranges from 0.8 to 347 mg/L (table 2.4).

Table 2.3. Comparison of average flowback quality for different shale plays¹³

		Fayetteville	Marcellus	Barnett
Na	(mg/L)	5362.6	24445.0	12453.0
Mg	(mg/L)	77.3	263.1	253.0
Ca	(mg/L)	256.3	2921.0	2242.0
Sr	(mg/L)	21.0	347.0	357.0
Ba	(mg/L)	0.8	679.0	42.0
Mn	(mg/L)	0.5	3.9	44.0
Fe	(mg/L)	27.6	25.5	33.0
SO ₄	(mg/L)	149.4	9.1	60.0
HCO ₃	(mg/L)	1281.4	261.4	289.0
Cl	(mg/L)	8042.3	43578.4	23797.5
TDS	(mg/L)	15,219	72,533	39,570
S.G.		1.010	1.050	1.030

Total Dissolved Solids

TDS is the total amount of matter dissolved in water, including metal, salts and minerals.

The sum of anions (negative charge) and cations (positive charge) is the total concentration of TDS. Usually, TDS is expressed in units of milligram per liter (mg/L) and parts per million (ppm).

The concentration of TDS increases as the water volume decreases with time for Marcellus shale (fig. 2.6). The reason for the increasing concentration of TDS maybe related to the water contact with shale formation. The longer the water contact with shale formation the more minerals will dissolve in water, which finally returns to the surface as wastewater.

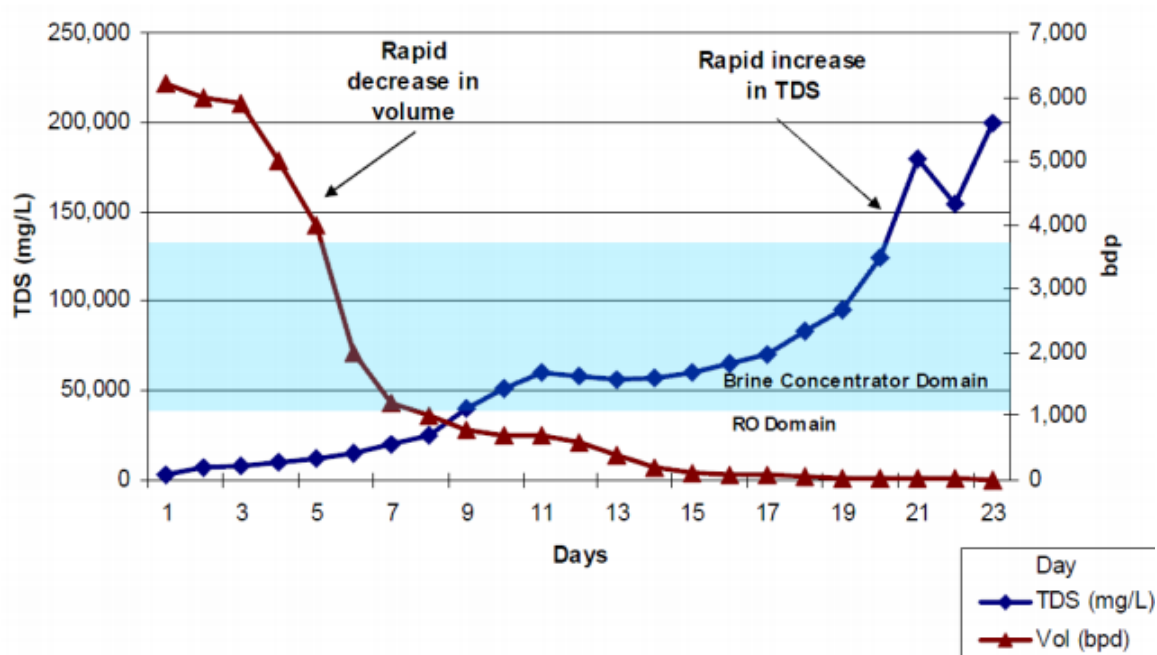


Figure 2.6. Concentration of TDS vs. water volume for Marcellus shale¹⁴

Alkalinity

The measure of water's capacity to neutralize acids is called alkalinity.¹⁵ Bicarbonate and carbonates, etc. all could combine with hydrogen ion (H^+). Without this capacity, if any acid were added to the water, the pH would change directly. Alkalinity in flowback water is influenced by underground rock type, the injected fracturing fluid components and the time the water was exposed to the underground formation. The longer the fluid has contact with the formation, the greater the potential capacity of neutralizing acids. Temperature is another parameter that may have an effect on alkalinity. When the sample's pH decrease to 4.2, all alkaline compounds are used up; thus this point can be used to measure the concentration of total alkalinity. The unit of total alkalinity is mg/l or ppm of calcium carbonate ($CaCO_3$).

Total concentration of alkalinity increases with time for horizontal wells #68 and #69 (fig. 2.7). Well #68 used PermStim fracturing fluid (injected pH 5.0) and well #69 was injected with SliverStim fracturing fluid (injected pH 10.2) for drilling.

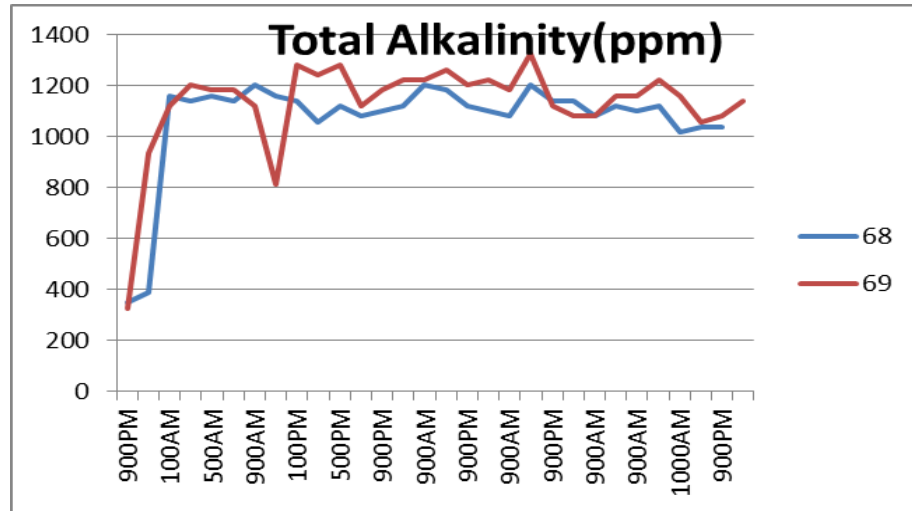


Figure 2.7. Total alkalinity vs. drilling time for well #68 and well #69 (2013)

2.2.1 Hydraulic Fracturing

Hydraulic fracturing is a process of injecting fracturing fluids that commonly contain water, sand and chemical additives under high pressure. The pressure must exceed the shale formation resistance and thus enlarge the cracks or fissures in the formation. The process significantly improves the recovery from shale gas and oil reservoirs by stimulating the oil and gas to flow back to the wellhead. The volume of water for hydraulic fracturing varies from rock formation to type of drilling wells. Typically, a vertical well requires 100,000 to 1,000,000 gallons of water, while fracturing process for a horizontal well needs 3-7 million gallons of water. Although drilling vertical wells cost less, horizontal wells are more productive.

Before the operators or service companies perform a hydraulic fracture treatment of a well (either vertical or horizontal), they conduct a series of tests to ensure that the well, wellhead equipment, and the fracturing equipment are in proper working order and will safely withstand the fracture treatment pressures and pump rates.¹⁶ Hydraulic fracturing for a horizontal well is divided

into several stages. The lateral length for a shale gas well ranges from 1,000 ft to more than 5,000 ft. Because the length of exposed wellbore, it is usually not possible to maintain a downhole pressure sufficient to stimulate the entire length of a lateral in a single stimulation event.¹⁷

Based on the characteristic of shale formation such as permeability, porosity, rock formation, TOC and thickness to name a few, the constituents of fracturing fluids vary from one shale play to another. Currently, three major types of shale gas hydraulic fracturing:

- Slick-water fracturing is probably the most common form of well drilling. The fluid is composed primarily of water and sand and a friction reducer (to reduce drag in tubing), biocides (to prevent microbial degradation), scale inhibitors (to reduce potential scaling forming), surfactants (to avoid water-wetting of formation) and propping agents (to keep formation permeability).¹⁸
- Gel fracturing always contains more chemical additives compared to slick-water fracturing. Usually, water-based liner gels and cross-linked gels are used for gel fracturing to raise viscosity of fluid so that it can contain more sand. Formation characteristics including pressure, temperature, permeability, porosity and zone thickness all contribute to gel selection.¹⁹
- Hybrid fracturing can be seen as the combination of slick-water fracturing and gel fracturing.

Typical fracturing fluid composes water, sand and chemical additives. The number and percent of chemical additives vary depending on the conditions of the well drilled. For example, the following well (fig. 2.3) is a typical fracture fluid for Marcellus shale play.

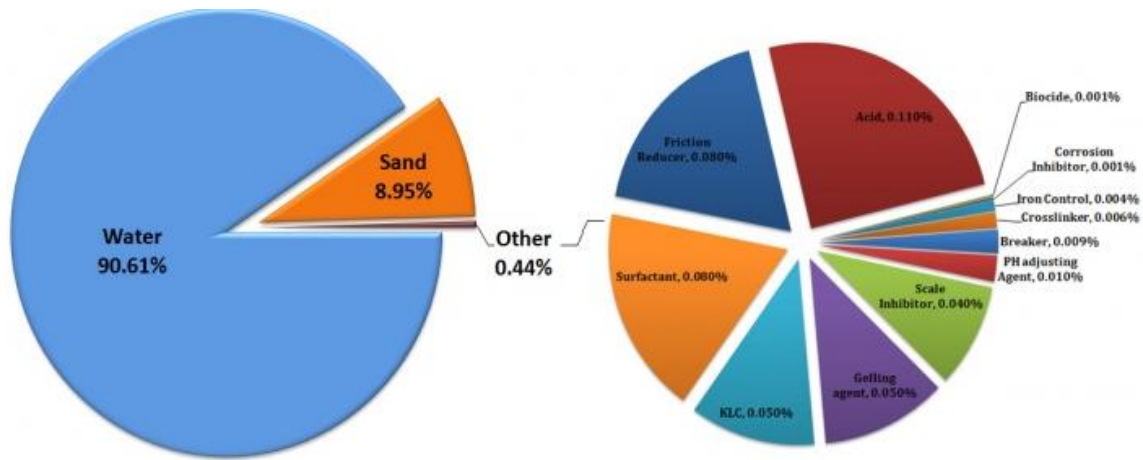


Figure 2.3. Volumetric composition of shale gas fracture fluid²⁰

There is no one-size fluid that fits needs for different shale gas explorations. Each component serves a specific, engineered purpose.²¹ The difference between fracture fluid is as small as a change in the concentration of chemical additives. Thus understanding the purpose of each chemical additive seems pretty valuable for picking a suitable fracturing system. Table 2.2 provides a summary of additives, their main compounds, the reason why they are used for fracturing and other common uses for these compounds.²²

Table 2.4. Fracturing fluid additives

Additive Type	Main Compound(s)	Purpose	Common Use of Main Compound
Diluted Acid (15%)	Hydrochloric acid or muriatic acid	Help dissolve minerals and initiate cracks in the rock	Swimming pool chemical and cleaner
Biocide	Glutaraldehyde	Eliminates bacteria in the water that produce corrosive byproducts	Disinfectant; sterilize medical and dental equipment
Breaker	Ammonium persulfate	Allows a delayed break down of the gel polymer chains	Bleaching agent in detergent and hair cosmetics, manufacture of household plastics
Corrosion Inhibitor	N,n-dimethyl formamide	Prevents the corrosion of the pipe	Used in pharmaceuticals, acrylic fibers, plastics
Crosslinker	Borate salts	Maintains fluid viscosity as temperature increases	Laundry detergents, hand soaps, and cosmetics
Friction Reducer	Polyacrylamide	Minimizes friction between the fluid and the pipe	Water treatment, soil conditioner
	Mineral oil		make-up remover, laxatives, and candy
Gel	Guar gum or hydroxyethyl cellulose	Thickens the water in order to suspend the sand	Cosmetics, toothpaste, sauces, baked goods, ice cream
Iron Control	Citric acid	Prevents precipitation of metal oxides	Food additive, flavoring in food and beverages; Lemon Juice ~7% Citric Acid
KCl	Potassium chloride	Creates a brine carrier fluid	Low sodium table salt substitute
Oxygen Scavenger	Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
pH Adjusting Agent	Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Washing soda, detergents, soap, water softener, glass and ceramics
Proppant	Silica, quartz sand	Allows the fractures to remain open so the gas can escape	Drinking water filtration, play sand, concrete, brick mortar
Scale Inhibitor	Ethylene glycol	Prevents scale deposits in the pipe	Automotive antifreeze, household cleansers, and deicing agent
Surfactant	Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, and hair color

2.3.2 Horizontal Drilling

Horizontal drilling is the process of drilling a well from the surface to a subsurface location just above the target oil or gas reservoir called the “kickoff point”. Then the well bore from the vertical plane is deviated around a curve to intersect the reservoir at the “entry point” with a near horizontal inclination, all the while remaining within the reservoir until the desired bottom hole location is reached.²³ The first recorded true horizontal well, drilled near Texon, Texas, was completed in 1929.²⁴ The successful horizontal drilling activity in Barnett shale increased the interest of the service companies and operators for development of the other shale plays in the United States.

Compared with vertical wells, drilling horizontal wells is a more costly investment, but the new drilling technique has overwhelming advantages. First and foremost, it can increase the recovery and production from shale formation. Secondly, the horizontal wells are effective for reaching narrow reservoirs formation. Finally, horizontal drilling has less environmental impact due to its smaller footprint. The comparison (fig. 2.4) between a horizontal well and a vertical well indicates that horizontal wells could reach more shale and oil reservoirs. Currently, horizontal wells are classified in three types: short-radius, medium-radius and long-radius. Short-radius wells typically have a curvature radius of 20-45 feet, being the 'sharpest turning' of the three types. Medium-radius wells typically have a curvature radius of 300-700 feet, with the horizontal portion of the well measuring up to 3,500 ft. Long-radius wells typically have a curvature radius of 1,000-4,500 feet, and can extend a great distance horizontally.²⁵

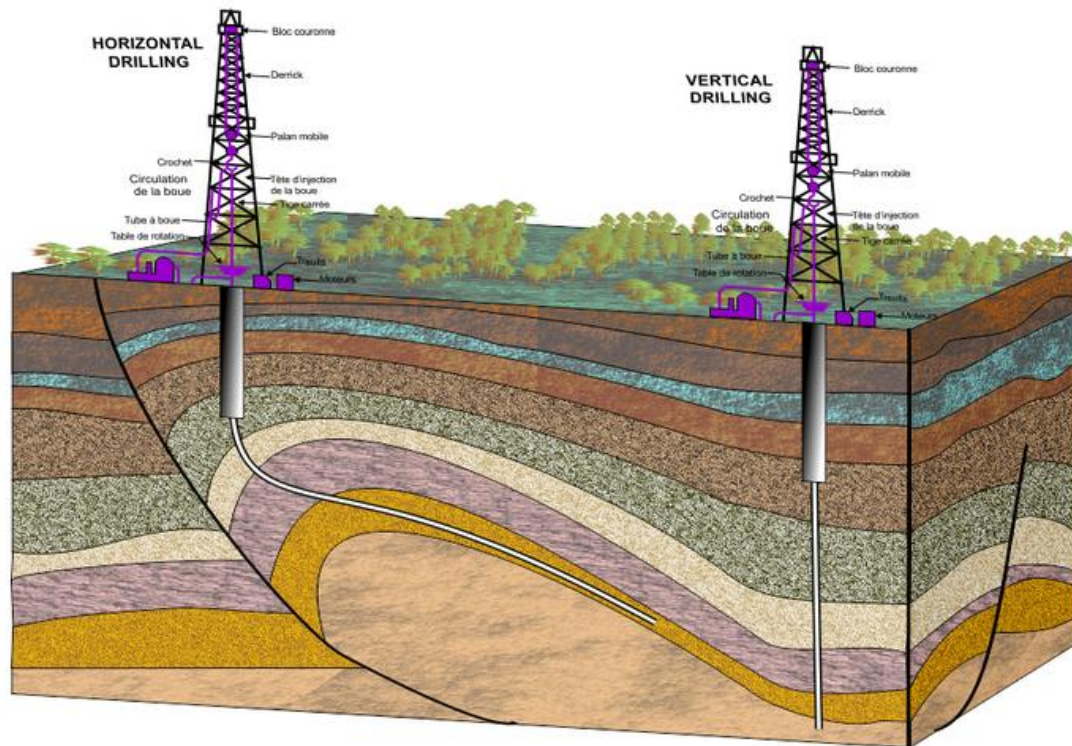


Figure 2.4. Comparison of horizontal well and vertical well²⁶

2.3 Flowback Quality

Flowback water becomes wastewater after the hydraulic fracturing process is complete. Until recently, there has not been an exact standard to distinguish flowback from produced water. Generally, flowback water—which occurs in the first two to three weeks after injection—has a murky appearance because of a high concentration of TSS. The amount of flowback recovered ranges from 20%-50% of fracturing fluid. The statistic (fig. 2.5) depicts the salinity of the flowback water from different U.S. shales expressed in concentration of TDS of 2011. The flowback quality varies from one shale play to another; often even if it is in the same shale play it still shows some differences. For example, the average TDS from Marcellus shale is 120,000 ppm, while the maximum TDS from the same shale is as high as 280,000 ppm—twice as large as the average concentration.

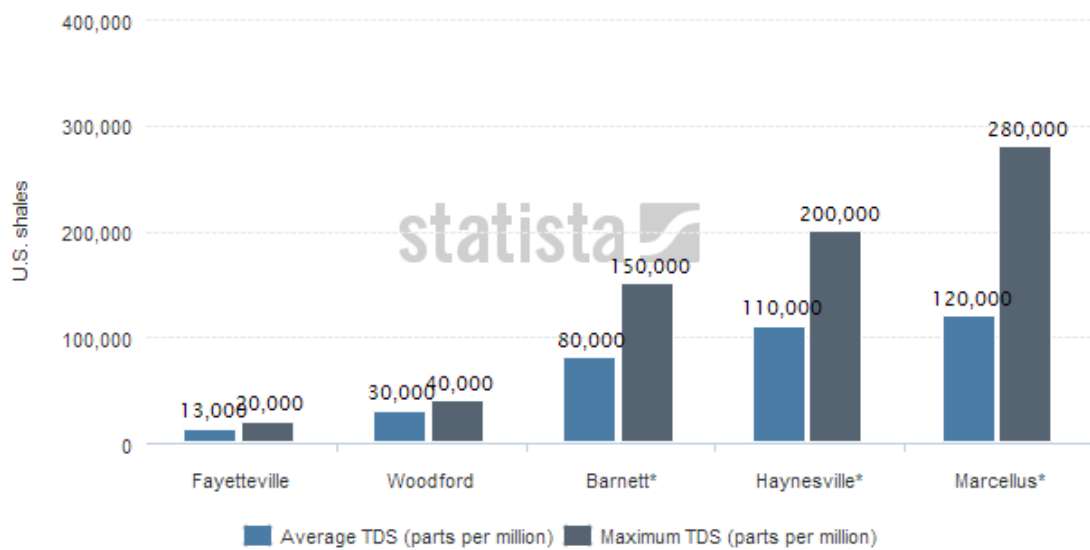


Figure 2.5. Salinity of the flowback from selected U.S. shales in 2011²⁷

Flowback water comes from the recovery of fracturing fluid but also contains the minerals, organics and inorganics sealed in the shale formation. Both the original fracturing fluid as well as the shale composition determines the flowback fluid quality (table 2.3). After the hydraulic fracturing in the Marcellus shale and some other gas-producing shales, the concentration of dissolved salts in flowback and production water increases dramatically with time.²⁸

Metals

Strontium (Sr), barium (Ba), calcium (Ca), magnesium (Mg), manganese (Mn) and iron (Fe) are the main metals that exist in flowback water, whether dissolved or as particles. Because of the high concentration of these metals, disposal is always a big problem whether the water is treated or reused. The high concentration of metals in flowback water may also cause the problem such as downhole scaling and plugging.

Salts

The high concentration of salinity is another concern in flowback water from oil/gas fracturing process. Dissolved solids contribute to the high concentration of salinity. Obviously, sodium (Na) and chloride (Cl) are primary matters that control the concentration of salinity from flowback water. This phenomenon is derived from the salts added in fracturing fluids as well as the solids in shale formation. The salinity concentration of natural seawater is up to 50,000 ppm, while flowback salinity is up to 80,000 ppm, which is much higher than the 25 ppm limitation (regulated by EPA) set for drinking water. Mg, Ca, potassium (K) and bicarbonate are other major ions that contribute to salinity. Barium and strontium (Sr) also exist in flowback water since the amount of sulfate is not high enough to precipitate Ba and Sr.

2.4 Environmental Concerns

The high drilling activities of shale gas bring the United States into a cleaner energy era, at least relative to coal. However, the hazardous chemicals, requirements of large volumes of fresh water, exposure of naturally occurring radioactive materials as well as busy transportation issues have already had an impact on environment and human health. The later part of this section will discuss the impact caused by a series of drilling activities in two aspects: water and land.

2.4.1 Water

Water Availability

The water resource for hydraulic fracturing comes from residential, commercial, and irrigation water, as well as underground water. As the development of shale gas becomes more and more attractive, more fresh water is needed to complete the drilling process. At the same time, the total volume of available fresh water is constant, the demand for water from operators and service companies is still increasing, and thus the available amount for local residents will decrease especially for arid areas such as Colorado.

Drilling a horizontal well usually consumes 3-7 million gallons of water. Considering an average of 4 million gallons, the volume is equal to 12 times the size of an Olympic swimming pool. The average drilling and fracturing needs for Haynesville shale is 90,000 barrels (3.78 million gallons) water and the average water needs for Fayetteville shale is 71,500 barrels (3 million gallons) water (table 2.5).

Table 2.5. Water average usage for multiple Shale plays²⁹

	Water used (average), bbls/well			Wells/year	Water MM bbls/year
	Drilling	Fracturing	Total		
Barnett	10,000	70,000	80,000	600	48
Fayetteville	1,500	70,000	71,500	250	18
Haynesville	25,000	65,000	90,000	200	18
Marcellus	2,000	90,000	92,000	600	55

Taking Marcellus shale as an example, in 2008 hydraulic fracturing used 650 million gallons water and accounted for 0.8% of annual water use in this area.³⁰ However, as the permit for horizontal wells is rising, a greater volume of water will be required in the next few decades.

Water Contamination

Hydraulic fracturing is the process of injecting large volumes of fresh water mixed with sands and chemical additives to create fissures and cracks for gas flow. Although the chemical additives only account for 0.5% of total volume, if 5 million gallons of water were injected into the ground that means that 25,000 gallons of chemicals were added to the fracture fluid and injected into the shale formation. There are hundreds of chemicals that can be added to fracture fluids, including high doses of carcinogens. A report stated that out of 2,500 hydraulic fracturing products, more than 650 of these products contained chemicals that are known human carcinogens or possible human carcinogens, regulated under the Safe Drinking Water Act (SDWA).³¹

At the completion of drilling activities, part of the injected fracture fluid will return to the surface as flowback and produced water. The returning fluid contains minerals, NORM and brine waters. However, due to the bad quality of this flowback wastewater, it is hard to find a proper sewage plant in some regions. Thus, improper handling of wastewater may pose a negative effect

to both environment and humans. In 2012, the Pennsylvania State University announced that water flowing back from gas wells after hydraulic fracturing contains high levels of radium.³²

Groundwater contamination is another concern for surface drilling activities. Accidental spills, leaking pits and improper disposal all may pollute potential groundwater resources. Additionally, groundwater methane contamination, derived from fracturing activities, is another problem. In 2006, over 7 million cubic feet (200,000 m³) of methane were released from a blown gas well in Clarks, Wyoming and shallow ground water was found contaminated.³³ The study conducted by the Colorado School of Public Health in 2011 also mentioned that methane contamination stemming from hydraulic fracturing was an issue.

2.4.2 Land

Earthquake

Hydraulic fracturing uses high pressure to create fissures and cracks in sealed shale formations to oil and gas flow back to surface. This means the permeability and original rock formation has already been destroyed before flowback even becomes an issue. According to British Columbia Oil and Gas Commission investigation, a series of 38 earthquakes occurring in the Horn River Basin area were caused by injection wells in 2009 and 2011.³⁴

Surface Disturbance

During the hydraulic fracturing and drilling process, the vast traffic that is needed to transport the drilling equipment and water makes a huge impact on communities. Such impacts include traffic congestion, damage to roads, dust and noise. States, local governments, and industry can work together in the initial planning phase of development to minimize these

problems.³⁵ However, no matter if it is vertical or horizontal well, drilling processes frequently destroy the original surface land. According to research, activities associated with gas development can affect wildlife and its habitat during the exploration, development, operation and abandonment phases.³⁶

2.5 Flowback Management

After the hydraulic fracturing and drilling is completed, the fracture water mixed with substances from the formation begins to return to the surface as flowback and produced water. It is important to meet the minimum requirements from EPA, SDWA and local government on how to properly handle and manage the wastewater. Another motive for learning to managing flowback water comes from the fresh water shortage in the United States. For example, the data from Natural Resources Conservation Service shows that the majority of Colorado is an arid place, which means the average yearly rainfall ranges from 5-10 inches. Combined with the higher development of fracturing activities and more population, the demand for water is rising dramatically.

Currently, the management of flowback can be divided into three categories: disposal, reuse and recycling. The following part of this study will focus on an explanation of each management approach for flowback water.

2.5.1 Flowback Disposal

The large amounts of fresh water transported to a drilling site and also the returning wastewater (flowback and produced water) need to be handled properly. The operators could build a large pond for collecting the flowback water, where wastewater will be evaporated naturally.

Another possible method is to transport these flowback waters to Public Owned Treatment Works (POTWs); however, in some regions, POTWs do not work well for wastewater from oil and gas wells. The final possible method includes dumping wastewater to the permitted wells (always Class II) which is regulated by EPA Underground Injection Control (UIC) program. The EPA website illustrates three types of wells that belong to Class II for disposal water from oil and gas wells. The most common one is an enhanced recovery well which can increase the recovery of oil and gas; another type is disposal wells, which can only be used for disposing fluid associated with oil and gas production; and the last type is called hydrocarbon storage well, which only allows hydrocarbon liquid to be injected.³⁷ The following figure (fig. 2.8) shows the enhanced recovery well used for injection wastewater.

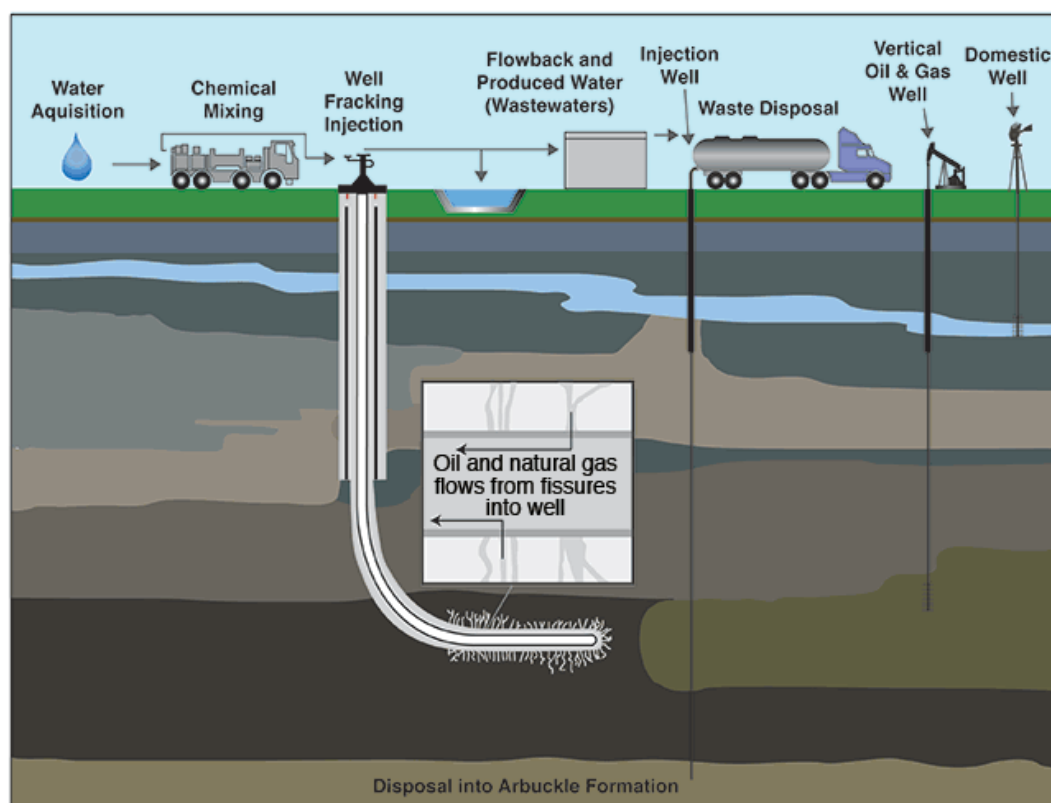


Figure 2.8. Hydraulic fracturing water for disposal³⁸

2.5.2 Flowback Reuse

In some cases, reusing fracturing fluid is a more practical method. For instance, the permitted wells used in the disposal method (see the previous section for details) are usually far away from the drilling site increasing the cost of wastewater transfer. In some states, including South Carolina and North Carolina, injected Class II wells are illegal or the cost for purchasing fresh water is too high. All these conditions make reusing fracturing fluid more appealing.

Reuse and recycling is attractive because it simply treats the water and then mixes it with fresh water to become usable fracturing fluid again. For one thing, reuse and recycling reduce the net demand for fresh water. For another, it lowers transportation costs in two ways: first, less fresh water needs to be transferred from a water source to the drilling site and second, less wastewater needs to be transported away from the drilling site. However, in order to reuse flowback as fracturing fluid, matter that can cause plugging during drilling have to be removed. For example, suspended solids, aluminum, barium, calcium, iron, magnesium and strontium etc required to be removed to a maximum total hardness of 2,500 mg/L as CaCO_3 .³⁹

In order to be reused as fracture fluid, either a portion or the total amount of flowback water can be used. Additionally, the reuse method requires that the mobile treatment be on-site in order to meet the specific qualifications. The distance between the drilling site and reuse water site is an important factor in deciding whether reuse, disposal or treatment is a more economic approach (fig. 2.9).

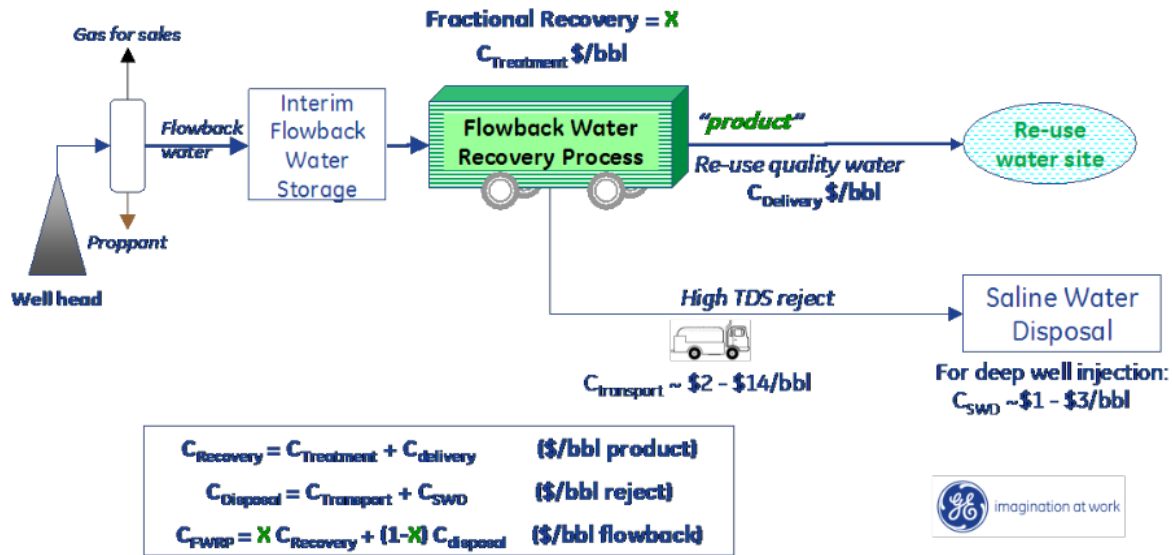


Figure 2.9. Flowback water recovery process for fracking reuse⁴⁰

2.5.3 Recycling

Recycling involves high-level treatment processes necessary to produce a quality of water that is close to fresh water. Recycling processes cost much more compared to both the disposal and the reuse methods. But recycling is needed when the reuse strategy is no longer useful and the disposal cost is too high or even abandoned in some places. Recycled water can be mixed with fresh water to produce low TDS fracture fluid or can be emptied into natural rivers and streams since the quality has already met the disposal regulations by EPA and SDWA.

2.5.4 Treatment

Although disposal is the easiest method of dealing with flowback water, the requirements are not always the same for every site—especially in areas where strict disposal regulations are published or in areas where disposal is banned. In Colorado, the total number of Class II injection

wells is only 874 (fig. 2.10)—far fewer than in Texas, Oklahoma, and others. Due to the low density of Class II injection wells and to the current water shortage, looking for other methods to handle flowback water is a major priority for operators in Colorado.

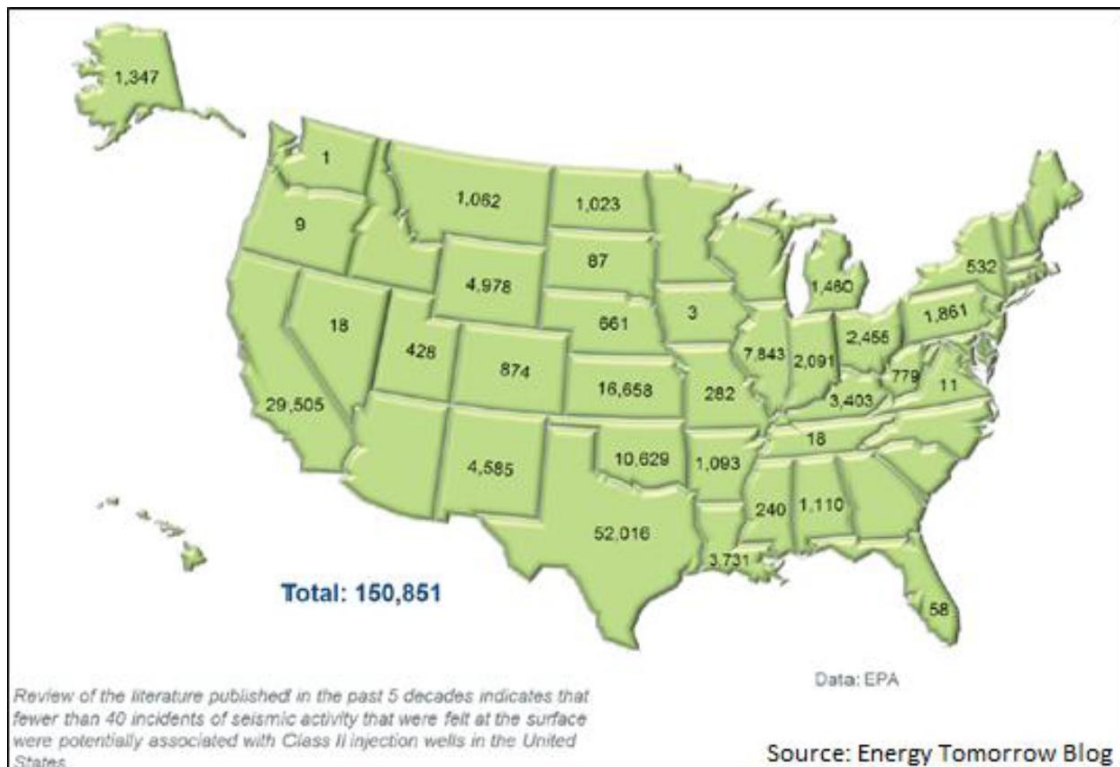


Figure 2.10. Class II injection wells across the United States

In general, flowback water contains a high concentration of chloride, Na and Ca. All these combined with Fe, K, Mg, Br, etc. contribute to high TDS for flowback water. Due to the complexity of chemical compositions and the huge variability of flowback water, POTWs are not equipped for flowback water treatment process. Therefore, on-site and off-site treatment facilities are necessary to reduce the potential impact on the environment.

Water treatment is based on end-use: whether it is reused in fracturing, discharged as surface water, used for agriculture or for human consumption.⁴¹ For instance, for reusing

flowback as fracture fluid, TDS concentration is not a big concern; for agricultural irrigation, standards require that TDS be less than 2,000 mg/L; for surface discharge, TDS is required to be less than 500 mg/L.

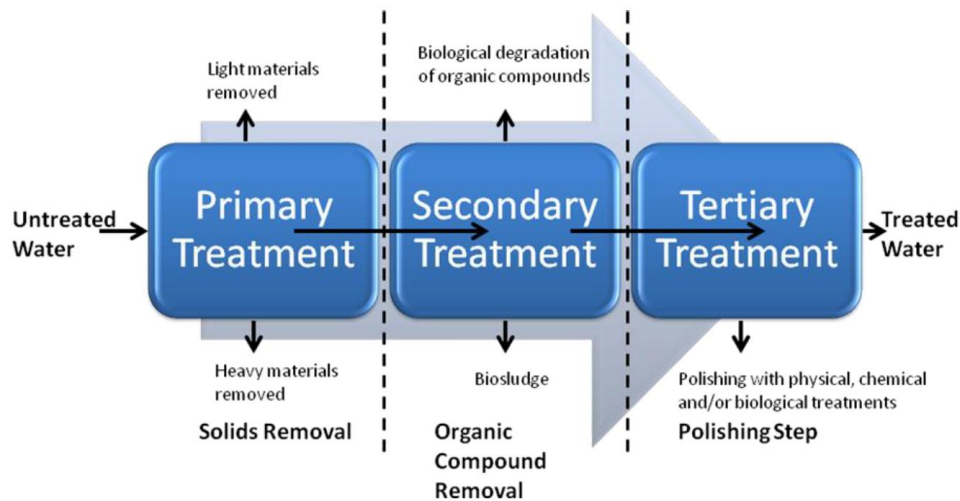


Figure 2.11. Water treatment stage⁴²

The whole water treatment process commonly contains three major phases to meet the target quality requirement. Primary treatment can be used for light material and heavy material removal. Secondary treatment always contains biological degradation of organic compounds. Final treatment, or tertiary treatment, is a polishing step including physical, chemical and biological treatment (fig. 2.11). The following table (table 2.6) lists current technology options for the removal of various contaminations in flowback water and the risk of implementing the equipment. Take TDS as an example: reverse osmosis and electrodialysis are all possible technology options. However, for determining treatment equipment, the potential risks, cost, flexibility and treatment arrangements are all considerations.

Table 2.6. Technology options for removal of various contaminations in flowback water⁴³

Technology	Brief description		TSS	TDS (monovalent)	Ca, Mg	Silica	Iron 2+	O&G	dissolved organics	Ba
Oil water separator	Coalescence of oil and removal through flotation	Performance Risks Cost risk Mobility	small particles							
Hydrocyclone	Utilized centrifugal force to separate solids and oils from water	Performance Risks Cost risk Mobility	small particles							
Lime softening	Addition of lime and soda ash to water to achieve hardness removal	Performance Risks Cost risk Mobility				dissolved Si				
Chemical Precipitation	Coagulant addition to develop floc, removing TSS, O&G and di-/trivalent ions	Performance Risks Cost risk Mobility				dissolved Si				via sulfate
Electrocoagulation	Uses electricity to dissolve an iron or aluminum electrode, and developing floc.	Performance Risks Cost risk Mobility			scale on electrode	dissolved Si			underlain removal	
Dissolved air flotation	Clarification of water by contact with minute bubbles, floating air/floc mass to surface	Performance Risks Cost risk Mobility	small particles							
Aeration and sedimentation	Aeration to oxidize reduced species to less soluble state.	Performance Risks Cost risk Mobility								
Biological Treatment	Process where microbes degrade organics.	Performance Risks Cost risk Mobility						high levels		
Sand or multi-media filtration	Vessel filled with sand or other granular media to remove TSS or colloids from water passed through it	Performance Risks Cost risk Mobility						smaller droplets		
Bag filters	A dead-end filter made of mesh material of specific micron size to remove TSS.	Performance Risks Cost risk Mobility	fast loading							
Ion exchange	The reversible exchange of ions between the liquid and a solid resin	Performance Risks Cost risk Mobility			fouling risk	or specific resin				
Walnut shell filter	Filter made from crushed walnut shells for O&G removal	Performance Risks Cost risk Mobility	small particles					not for high conc.		
activated carbon	A highly adsorbent form of carbon used to remove dissolved organic matter from water	Performance Risks Cost risk Mobility						too slow/inefficient		
Organoclay	Bentonite clay modified with quaternary amines, used as an adsorbent for O&G	Performance Risks Cost risk Mobility								
Fentons	Advanced oxidation using Fe and H ₂ O ₂ to produce hydroxyl radicals to degrade organics.	Performance Risks Cost risk Mobility						knives, chemicals		
Ozone	A strong oxidizing agent able to degrade organics.	Performance Risks Cost risk Mobility						knives, chemicals	fouling	
Chlorination	A strong oxidizing agent, although not as strong as ozone.	Performance Risks Cost risk Mobility								
Potassium permanganate	Used for oxidation of iron and manganese	Performance Risks Cost risk Mobility					dosing, inter-fouling			
Microfiltration	Low pressure membrane filtration process for removing TSS and colloids > ~0.1µm (cutoff varies by membrane)	Performance Risks Cost risk Mobility	small particles							
Ultrafiltration	Low pressure membrane filtration process for removing TSS and colloids > ~20nm (cutoff varies by membrane)	Performance Risks Cost risk Mobility								
Nanofiltration	Medium pressure membrane process for removing di- and tri-valent ions and species > ~1nm	Performance Risks Cost risk Mobility			fouling	fouling	fouling			fouling
Reverse Osmosis	Method for separating water from dissolved salts by passing feedwater through a semipermeable membrane at a pressure greater than the osmotic pressure.	Performance Risks Cost risk Mobility			fouling	fouling	fouling			fouling
Electrodialysis	Separation of ionic components using semipermeable ion-selective membranes operating in an electric field	Performance Risks Cost risk Mobility			fouling	fouling				

*Green = low risk; yellow = low to mid-level risk; red = substantial risk

Table 2.7. Treatment options for flowback water

Technology	Maximum Feed TDS (mg/L)	Energy Use (kWh/100 bbl)
Capacitive Deionization	5,000	20
Electrodialysis	40,000	-
Reverse osmosis	35,000	15-30
Evaporation	100,000	400
Membrane distillation	250,000	600-700
Crystallizer	300,000	1000-1300

* - data is not available

Five major treatment options used for removal of TDS in flowback water include: capacitive deionization, electrodialysis, reverse osmosis, evaporation, membrane distillation and crystallizer. Although TDS in flowback range from 5,000-300,000 mg/L and all can be treated by different processes, the cost will also increase with TDS. The flowback water from Barnett and Marcellus shale contain the highest concentration of TDS, about 100,000-300,000 mg/L, which indicates that only high-cost treatment maybe available for these sites (table 2.7).

2.6 Background Information of Wattenberg Field

Wattenberg Field was first discovered in 1970, located in the Denver-Julesburg (DJ) basin in northeastern Colorado (fig. 2.12). The area of Wattenberg Field is almost 1.9 million acres, which is similar to 81 townships.⁴⁴ The field has been active since 1970; the first oil band was discovered in DJ basin and has a depth of 8,000 ft.

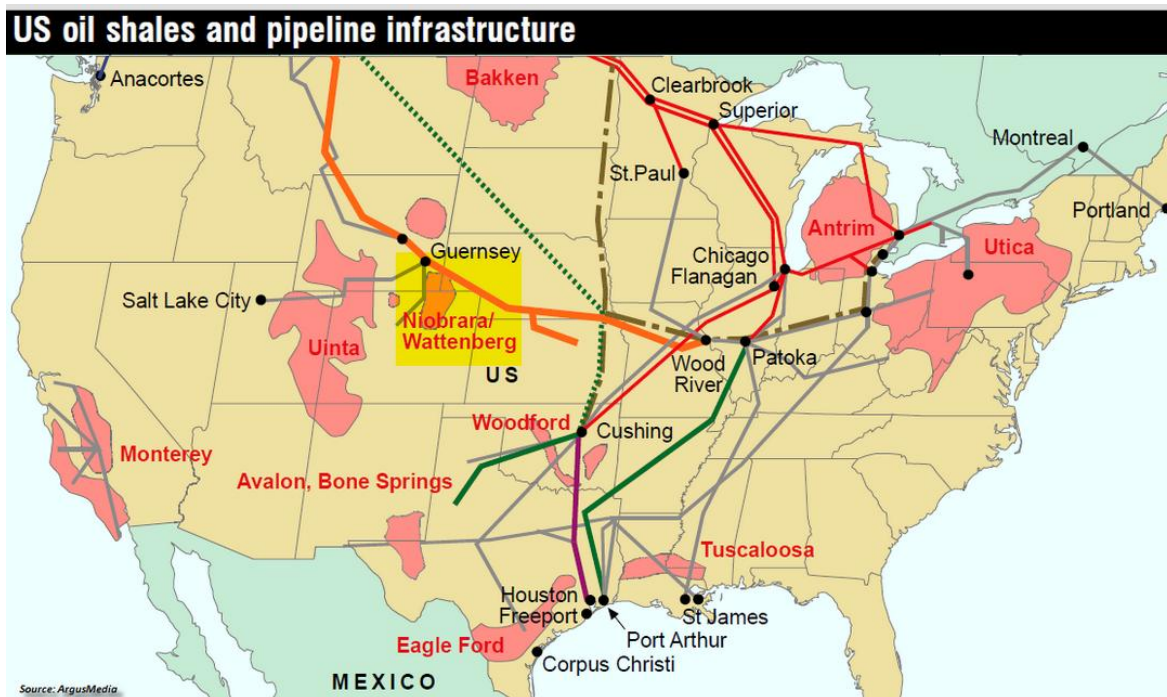


Figure 2.12. The Wattenberg Field location⁴⁵

The largest producer in Wattenberg Field is the DJ basin close to Denver area. The DJ basin now has 20,000 active wells and most of them are located in Wattenberg Field. The DJ basin drilling depth normally ranges from 5,500-7,500 ft and horizontal lateral is average 4,000-5,000 ft. This may be extending in future. Although the conventional gas reserve was decreased from 129 million cubic ft (MMcf) to 30 MMcf, the estimate of tight gas reserve has risen from 397 to 640 MMcf.⁴⁶ Since 2007, the advanced development in horizontal drilling and hydraulic fracturing improve the expansion of tight gas drilling in Wattenberg Field. Figure 2.13 shows that the cumulative production from Wattenberg Field reached its peak around 2006 and 2007. Currently, over 18,000 wells are drilling in Wattenberg field⁴⁷ and over 7,700 wells are operated by the Noble Energy Inc.

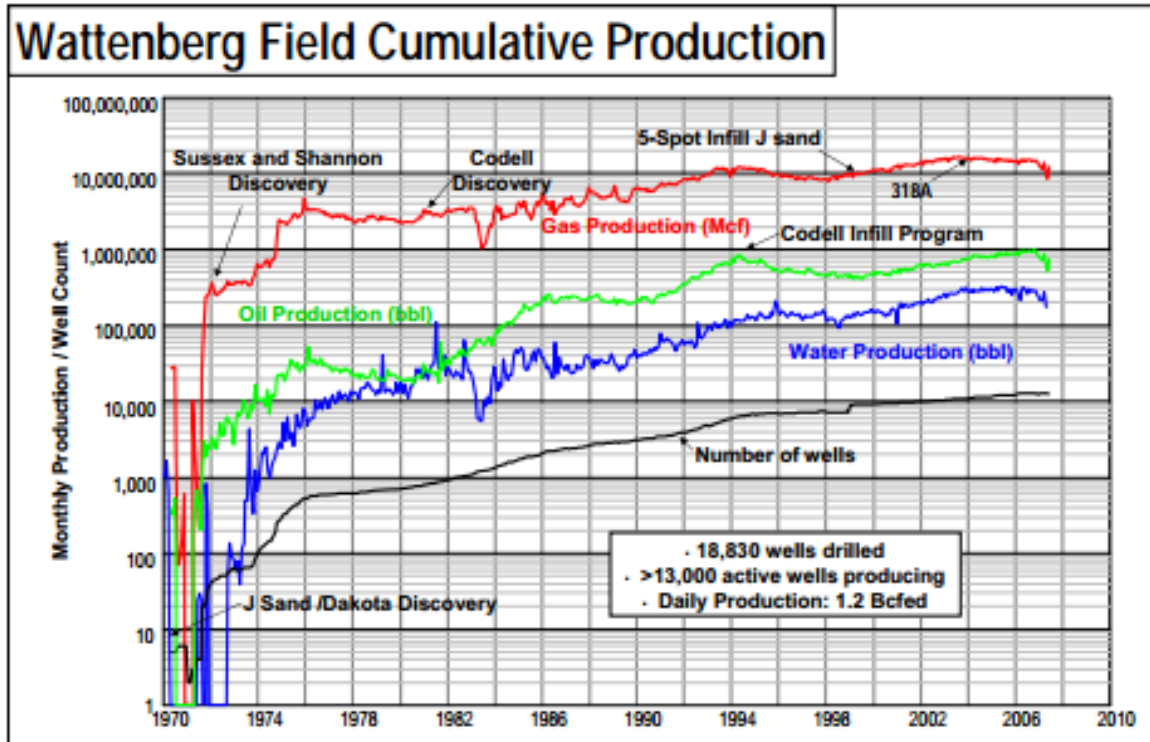


Figure 2.13. Wattenberg Field production of oil and gas until 2008⁴⁸

Since the Wattenberg Field is located in the DJ basin, both should have similar geological characteristics. Wattenberg Field is comprised of Sussex, Shannon, Niobrara, Codell, J Sandstone and Dakota layers (fig. 2.14). J Sandstone, Niobrara and Codell are the main zones for production of gas and oil. But in some place, all of the five zones are productive.

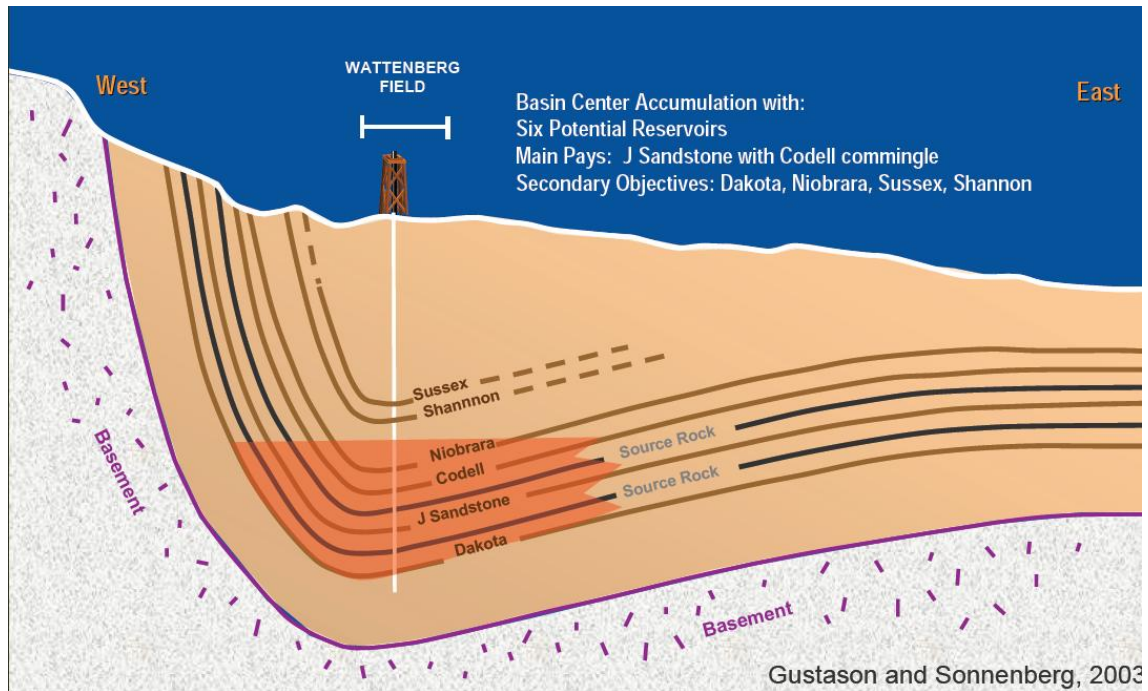


Figure 2.14. Diagrammatic cross-section Denver basin

Figure 2.15 illustrates current drilling activities happen in Wattenberg Field. All 5 types of shale formation have been displayed in Wattenberg Field including J sand distribute, the largest area in Wattenberg Field, which also contributes more than 30% of the oil and gas for Wattenberg Field. The deepest shale formation is Dakota, and it produces less than 10% of the whole Wattenberg Field. Codell and Niobrara are the medium deep formation, but the production is nearly 40%. Thus the medium shale formation contain both oil and gas reserves. In addition, drilling cost is lower there than in deeper formations such as Dakota and J Sandstone formation.

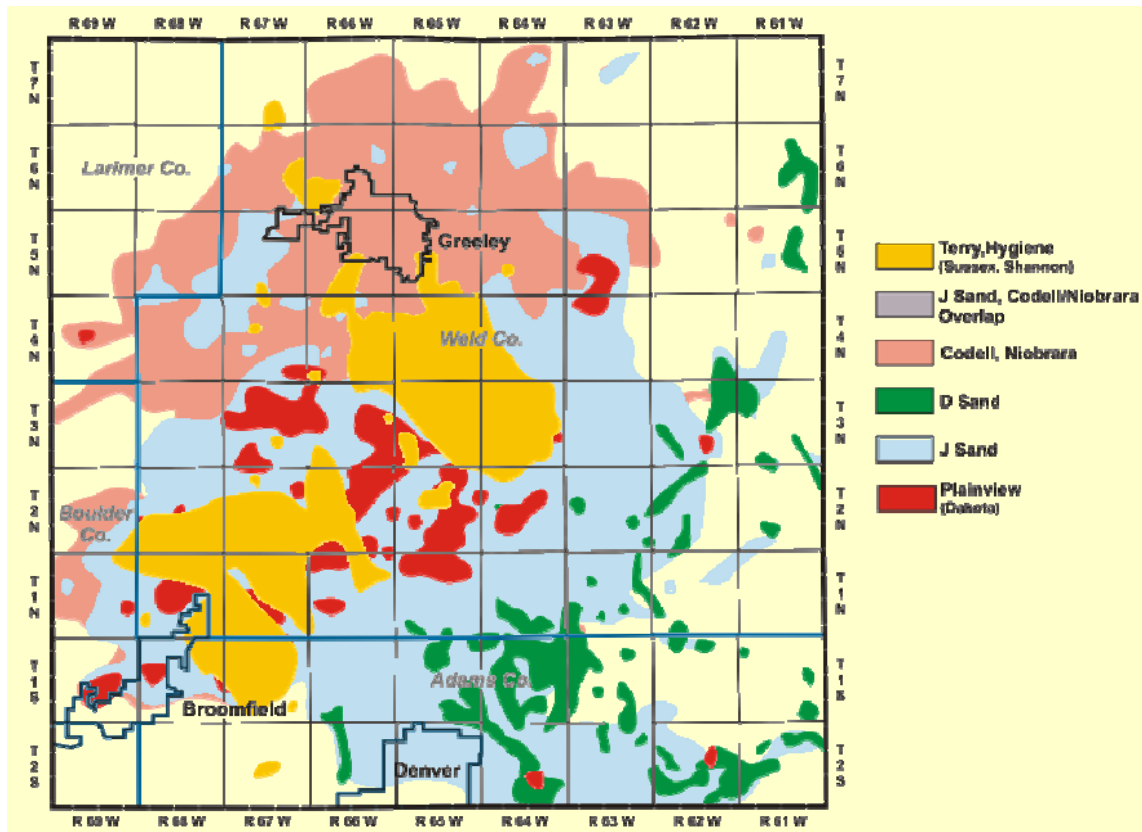


Figure 2.15. Current productive area in Wattenberg Field⁴⁹

2.7 Research Objective

. Due to the development of drilling activities, more and more wastewater is being produced. In addition, more strict environmental regulations have made simple disposal no longer accessible. Thus reusing and recycling flowback begins to appear more attractive for operators and service companies.

Reusing and recycling flowback water needs at least the basic water treatment, and sometimes also requires higher levels of treatment in order to obtain the required quality for reclaimed water. Treated water can be used as the new fracturing fluid by mixing it with fresh

water. Reusing it as a fracturing fluid can significantly reduced the required volume for fresh water and the cost of wastewater disposal (including reduce the transportation cost).

Reusing and recycling is an appealing process, but salinity, TDS, NORM and scaling, etc., make the treatment of flowback complex. Therefore, it is important to know the quality of flowback water because a treatment installation is based on the quality parameters of the flowback.

The goals of this paper are:

- i. Design a water collection plan in Wattenberg field
- ii. Collect water samples from wells #68 and #69 and analyze these water samples for quality
- iii. Determine temporal quality variability for wells #68 and #69
- iv. Assess correlations of ions

Chapter 3 Methods and Materials

The steps for measuring flowback water in Wattenberg Field are divided into three phases:

- 1) Field sampling and testing
- 2) Water sample measurement
- 3) Analysis of flowback quality data for two different fracturing fluids (PermStim and SliverStim)

3.1 Field Sampling and Test

3.1.1 Sampling site

Figure 3.1 shows the whole Wattenberg Field, which is divided into 90 townships. The township from south to north ranges from 2S to 8N, from west to east ranges from 62W to 70W. All the data comes from Colorado Oil and Gas Conservation Commission (COGCC). A more detailed view of the sampling site is shown in Figure 3.2; it is located in township 6N 63W, which is in northwestern of Wattenberg Field.



Figure 3.1. Wattenberg Field divided by townships⁵⁰

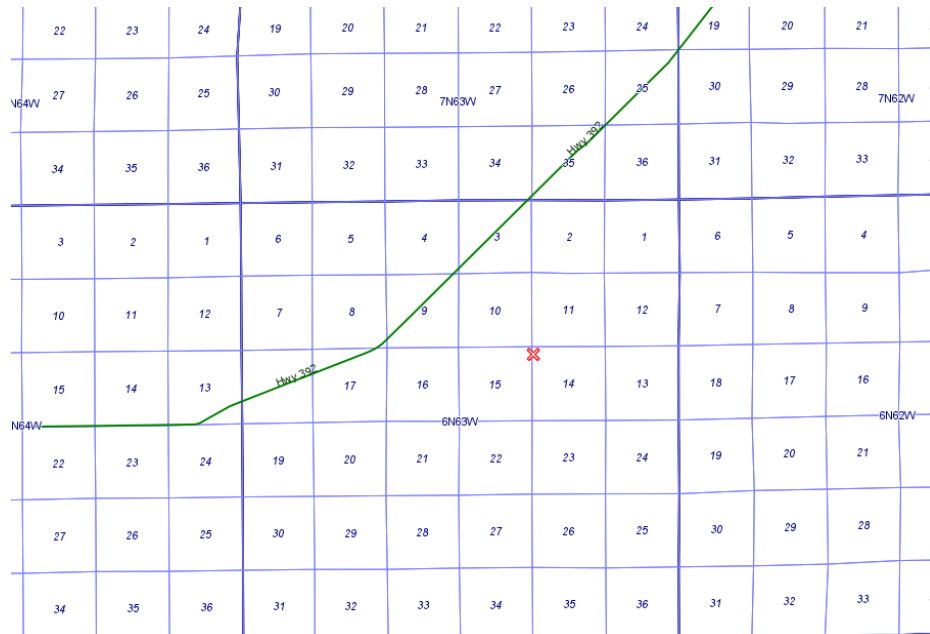


Figure 3.2. Sampling site in Wattenberg Field (Data Source : COGCC)

The red point in figure 3.2 is the exact point where we collected water samples in the study. Its latitude is 40.49239 and longitude is -104.4125 for well #69. The latitude for well #68 is 1049229 and longitude is -104.4125. The two wells are close to each other (100 yards) so in figure 3.1 it is shown as one point.

3.1.2 Field Sample Schedule

Water samples were collected from Wells Ranch State PC USX #AA16-69-1HNL and Wells Ranch State USX #AA16-68-1HNL. Both of them belong to Noble Energy Inc. and are located in the Wattenberg Field.

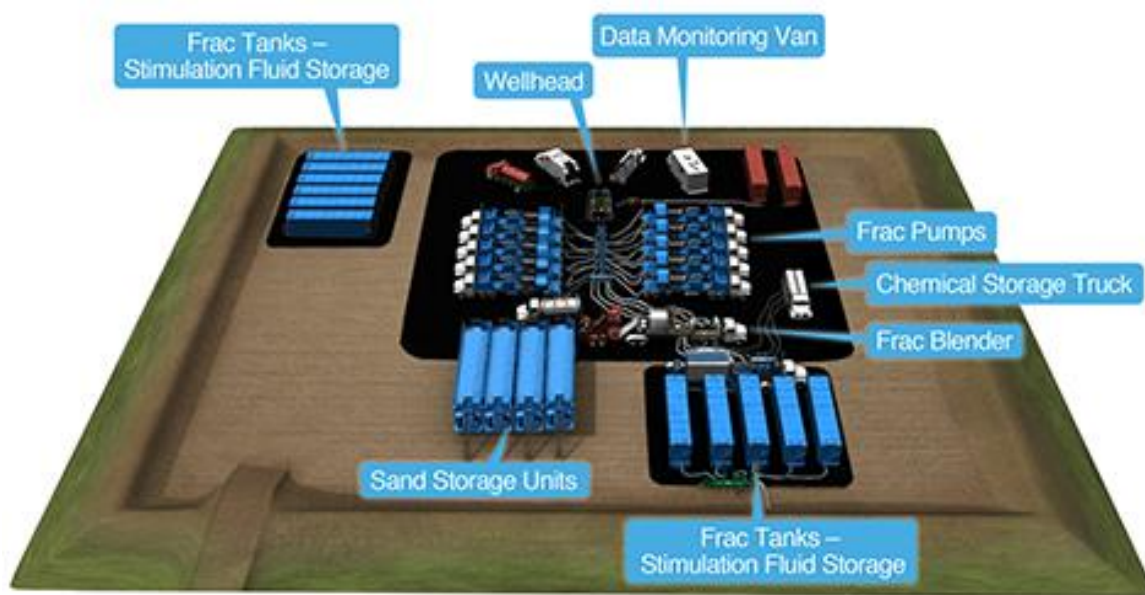


Figure 3.3. Common hydraulic fracturing equipment⁵¹

Although the fracturing process may take a short time to complete, the process requires a large amount of advanced technology and equipment (fig. 3.3). At the beginning, sand, water and chemical additives are mixed and pumped into a wellhead under high pressure (wells can be drilled vertically or may include horizontal sections). The fluids create fissures or cracks in the

underground rock formation and bring sand into cracks to hold them open. When the fracturing process is finished, the well's pressure is reduced, so that the fracturing fluid along with oil and gas can return to the surface. This fluid is known as flowback or produced water, and contains injected matter as well as the occurring materials such as brines, metals, radionuclides, and hydrocarbons.⁵² It always goes into the separator equipment first. Due to the density difference between oil and water, the water will always stay at the bottom of the equipment, while the oil flows on the surface of water. Since the pressure is reduced gas is no longer stable in water, and it turns into a gas phase and flows into the distribution pipeline.

The sampling timeframe was from March 21th to April 1st, 2013 (Appendix D). Due to the quick variability of flowback in both quantity and quality, the water samples were collected as Appendix B shows. From March 21th to 24th, water samples were collected from the wellhead (fig. 3.6). Then, starting on March 25th, we began to collect water samples from the wellhead (fig. 3.6), pre-separators (fig. 3.5) and post-separators (fig. 3.4) since the central separator tanks were already completed. Due to water run-out during scheduled sampling times, the total number of water samples collected was 73, including 8 water samples collected from post-separator and 6 water samples collected from pre-separator. All the raw data for water quality analysis is shown in Appendix B.

As shown in Appendix B, pH, dissolved carbon dioxide (CO₂), bicarbonate (HCO₃) and dissolved hydrogen sulfide (H₂S) were analyzed at the field trail. Noble Energy Inc. operators provided pressure data. The total volume of water samples needed for a field test was about 200ml. Appendix A shows that the measurement of the water quality parameters require at least 500 ml of water samples, Other parameters including metals (Ba, Fe, Al, Sr, Ca, Mg, B, K, Si, Na, Zr),

chloride, TDS, sulfate and bicarbonate were all tested in E-analytics Lab located in Loveland.

Before analysis, water samples were preserved as shown in Appendix A.



Figure 3.4. Separator equipment



Figure 3.5. Pre-separator sampling site

Two plastic bottles of 250 ml and one plastic bottle of 500 ml water samples were collected for wells #68 and #69 separately. One 250 ml plastic bottle was shipped to E-analytics Lab and another 250 ml sample was used for field test (Appendix D). The 500 ml water samples were tested in CSU Environmental Engineering Lab. All samples were refrigerated. Before analysis, the water samples needed to filter through a $0.45 - \mu\text{m}$ filter to remove grease and large oil particles.

During the whole sampling process, 59 samples were collected from the wellhead (fig. 3.6), 8 samples were from the post-separator (fig. 3.4) and 6 samples came from the pre-separator (fig. 3.5). To avoid the possible impact of samples from the pre-separator and post-separator on

analysis and to make the samples consistent, only the wellhead samples were analyzed. All the following results and discussion are based on the results of 59 samples from the wellhead.



Figure 3.6. Wellhead for hydraulic fracturing

3.2 Water Sample Analysis

3.2.1 The Importance of Quality Analysis

Flowback water is challenging to treat due to its high variability in both quantity and quality. For example, the flow rate of flowback water decreases with time; the quality parameters of flowback vary from one shale to another or even from one well to another and from day to day in a same well.

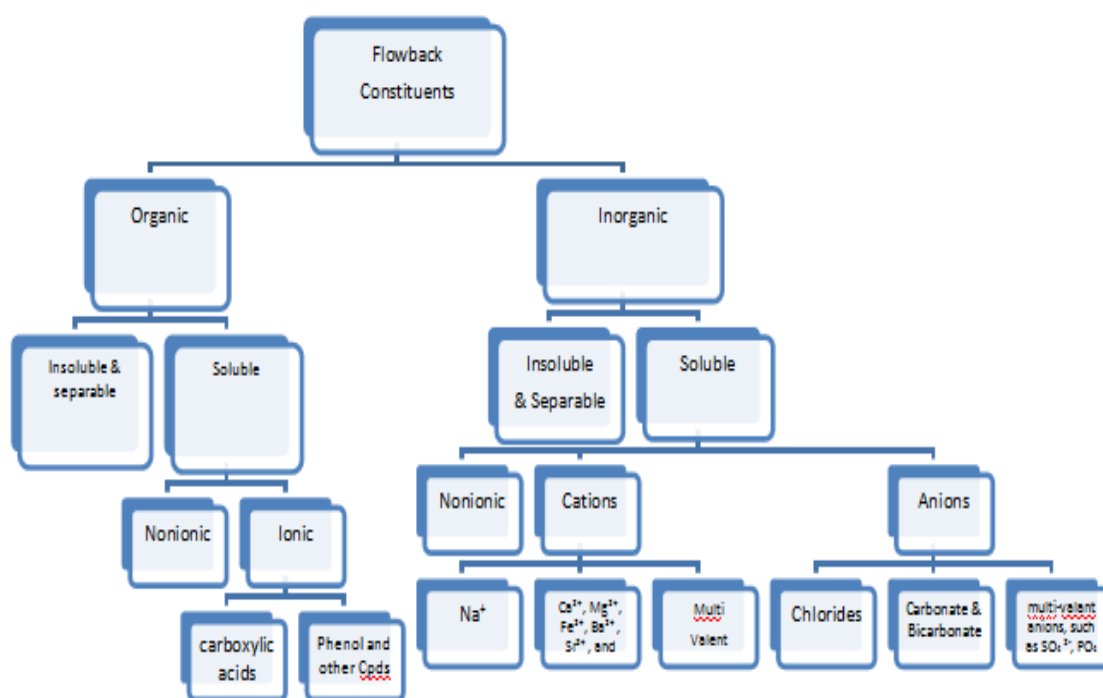


Figure 3.7. The components of flowback water (modified from A. W. Gaudlip)⁵³

From figure 3.7, flowback water components can be classified into organic and inorganic matter. Organic constituents are treated to become insoluble and soluble matter. And soluble components contain non-ionic and ionic (including carboxylic acid, phenol and compounds). Inorganic matter is comprised of particles and dissolved compounds or ions. The dissolved parts

can be divided into three parts: non-ionic, cations (including Na, K, Ca, Mg, Fe, Ba, Sr, etc.) and anions (chlorides, carbonate, bicarbonate and sulfate, etc.). In additionally, non-charged soluble inorganics are also present—silicate (H_4SiO_2) and borate (H_3BO_3).⁵⁴

Although flowback water composition is complex, reuse treatment currently focuses on chloride, total suspended solids (TSS), metals, sulfates, carbonates and bacteria. Table 3.1 illustrates the major parameters that exist in flowback water and their potential effects on the reuse process. However, the high concentration of TDS also needs to be removed since high TDS has a negative effect on treatment efficiency. The TDS of flowback water is pretty high from Marcellus shale, always around 200,000 mg/L.

Table 3.1. Major consideration for reusing flowback water⁵⁵

Concerns	Impact for reuse as fracturing fluid
Scaling (CaCO_3 , CaSO_4 , etc.)	Drilling equipment fouling and loss formation permeability
Total suspended solids (sands, silts, clays, scale particles)	Formation damage, loss of permeability
Metal (Fe)	Form plugging (iron oxides)
Friction Reducer effectiveness (Chloride, TDS)	React with metals and form precipitation
Bacteria	Growth in fracture fluid and cause plugging

A major problem for reusing flowback as a fracture fluid is that it contains a high concentration of scale-forming components. When two incompatible fluids mix with each other, precipitation will occur. This would rapidly block the fractures in gas bearing formations.⁵⁶ In another words, the potential production of gas and oil would decrease while financial costs would increase due to cleanup for the drilling wells.

Based on Leone and Scott's study, three major mechanisms can trigger the formation damage:⁵⁷

I. Hydrodynamic

- a. During fluid flow the pressure gradient happens, some fine particles move along the fluid flow to cause migration damage.

II. Physicochemical

- a. Swollen clay or fine particles occupies more of the pore space so the permeability declines.

III. Geochemical (the most important reason for scaling happens for re – using flowback)

- a. The injected fluid is not compatible with the natural formation fluid which results in none equilibrium system. For example, sulfate in fracturing fluid can react with calcium in formation to form solids in porous system.

Scaling and fine particles are the major concerns for the oil and gas industry when considering reuse. It mainly comes from the changes in physical and chemical properties (including pH, temperature, partial pressure of CO₂, etc.) or the incompatibility between injected fluids and formation water.⁵⁸ According to Moghadasi, etc.,⁵⁹ during various oil and gas activities , drilling, production, water flooding and stimulation are the four sections that may cause scaling formation.

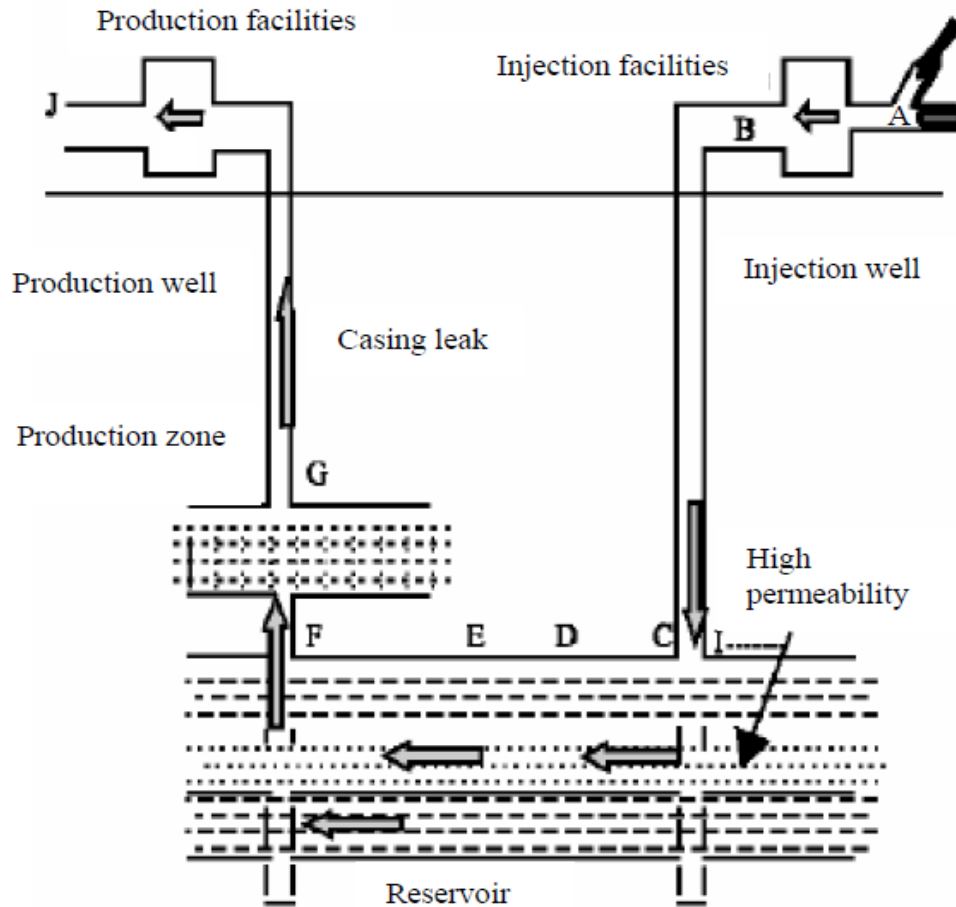


Figure 3.8. Diagram of oil/gas field in which location produce scale⁶⁰

Figure 3.8 illustrates the potential location in which scaling may occur. From A to B, high pressure is added in order to re-inject mixed brine fluid. From B to C, the pressure and temperature are all increasing and the solubility of ions and cations may change. From C to D, pressure declines as the temperature continues to rise, and solution composition may be adjusted by cation. From C to F, the process of exchange, mineral dissolution and other chemical reactions with rock formation are going on. From D to F and E to J (in the reservoir formation and wellhead) pressure and temperature decrease, the re-injected fluid begins to release carbon dioxide and the water begins to evaporate. At points G and F, the most active place for the mixing of re-injected

fluid and formation fluid occurs, which causes the chemical reaction and solids precipitation to happen.

Other concerns of reusing fracture fluid are particulates and TDS. Particulates are organic or inorganic matter (sand, silt and corrosion products) that precipitate in fluid. TDS indicates the total dissolved ions in fracture fluid usually come from initial injected fluid and geological formation. In theory, low density of particulates and TDS are not a big problem; however, according to research, the quantities of TDS kept at high concentration are amenable to treatment equipment—especially reverse osmosis. Although crystallization is an effective way to remove TDS, the high energy cost makes the process no longer valuable.

Therefore, a complete understanding of the components in flowback water and an analysis of the formation compositions are prerequisites to avoiding scaling formation and to increasing the effectiveness of treatment equipment. Based on the quality parameters and the possible chemical reactions between two different fluids, installing a proper treatment facility can largely reduce the risk of scale formation for both surface and underground equipment.

3.2.2 Water Sample Measurement

Dissolved carbon dioxide (CO_2), pH, temperature, bicarbonate (HCO_3) and dissolved hydrogen sulfide (H_2S) were analyzed at the field trial and data is shown in Appendix C. Temperature was measured by thermometer (fig. 3.9), and Fisher Scientific Accumet AB15 Basic and Bio-Basic pH/mV/ °C Meter measured pH. For analysis of total dissolved CO_2 concentration, 20 mL of the water samples were added to a clean 125 mL Erlenmeyer flask and then 5 drops of Phenolphthalein were added and swirled to mix well. The mixture was titrated with 0.045N sodium hydroxide, and we recorded how many mLs of titrant was used and then multiplied by

79.2 to get the ppm dissolved CO_2 . To determine dissolved bicarbonate (HCO_3^-), we added 20 mL water to a clean flask, added 5 drops of phenolphthalein and 5 drops of methyl purple, and titrated with 0.02N sulfuric acid until a purple color remained for 30 seconds. We recorded mLs titrant and multiplied mLs titrant by 61 to get ppm dissolved bicarbonate. Gas phase H_2S was determined by filling provided tube to 7.5 mL line; we added 5 drops indicator and 5 drops buffer (15% HCL). We then remembered the number of drops of sulfide reagent 2 until the water sample turned blue. If it required only one drop, we counted it as zero. Otherwise, the recorded ppm of H_2S was equal to the number of drops multiplied by 0.5. For calculation chlorides, just calibration was needed. To use distill water to make sure it read zero. Then we applied a few drops of water to be tested and read the refractive index and converted to ppm of chloride with chart. After all the process was finished, we cleaned the instruments and stored the pH tube in a pH 7 buffer.



Figure 3.9. Tools for measuring temperature

E-analytics Lab is responsible for testing metals (including Ba, Fe, Al, Sr, Ca, Mg, B, K, Na, Zr, Si), chloride, TDS, sulfate and bicarbonate.

Table 3.2. Total cost for one sample in E-analytics Lab.

Item	Quantity	Rate	Amount
Carbonate & Bicarbonate	1	12.00	12.00
Chloride	1	15.00	15.00
Sulfate	1	15.00	15.00
First Metal	1	25.00	25.00
Additional Metal (s)	10	10.00	100
		Total	167.00

*First metals includes Al, Ba, Fe, Al, Sr, Ca, Mg, B, K, Na, Si

*Additional metal is Zr

Table 3.2 demonstrates the capital cost charged by E-analytics Lab for testing metals, additional metal, sulfate, chloride, carbonate and bicarbonate.

Table 3.3. E-analytics analytical methods

Analyze Parameter	Methods	Method limit
Major cations: Dissolved sodium, calcium, magnesium, potassium, iron, zirconium, silicon, strontium	EPA Method 6010C	
Major anion: Chloride, sulfate	EPA Method 300	For Chloride: 10- 10,000mg/L
Dissolved metals: barium, boron, aluminum,	EPA Method 6010C	
Other anion: carbonate and biocarbonate	EPA Method 310	

Table 3.3 shows all the water quality parameters that were analyzed by E-analytics Laboratory and the standards used for measuring. All the method are suggested by EPA and have a testing limit so that if the samples are over or below testing limits, the data would be not available.

Chapter 4 Results and Discussion

Since the flowback water quality is crucial to choosing a treatment process, it is necessary to analyze flowback quality. The following parts will discuss flowback quality in three ways: statistical analysis, temporal analysis (focus on figuring out the differences between two different fracturing fluids) and correlation between different ions.

4.1 Statistical Analysis of Chemical and Physical Quality for Flowback Water

All water samples were collected from well #68 and well #69. The sampling time was within three weeks to make sure all the samples were in the flowback range. Physical and chemical characterization such as pressure, temperature, pH, dissolved CO₂ and HCO₃, H₂S and chloride were recorded once the samples were collected. The the water samples were sent to E-analytics Laboratory to measure other quality parameters (table 4.1).

Table 4.1. Measurement schedule

Flowback quality parameter	
Field test	pH, temperature, pressure, dissolved CO ₂ and HCO ₃ , H ₂ S, chloride
E – analytics Lab.	Ba, Fe, Al, Sr, Ca, Mg, B, K, Na, Zr, Si, chloride, sulfate and bicarbonate, TDS

Since chloride and bicarbonate were tested both in the field and E-analytics, comparing the accurate measured data is necessary to make sure that the following results are closer to its true changing trend.

A complete summary of flowback water quality for our study is shown in table 4.2 and table 4.3. The standard deviation means how much variation or dispersion exists from the average. A

low standard deviation shows that the data tend to be close to the average number of samples; otherwise, it indicates that the sample are dispersed widely. Standard error is an estimate of how close to the sample mean your sample is likely to be. Usually, standard error will increase with the bigger sampling number, while standard deviation will not be affected.

Table 4.2. Flowback water quality for well #69 in Wattenberg Field

Analyst	pH	TDS (mg/L)	Temperature (°F)			
Mean	7.28	10669.66	119.76			
Standard Deviation	0.26	2038.88	15.27			
Standard error	0.05	378.61	2.83			
Median	7.33	11000.00	122.50			
Min	6.76	1180.00	71.00			
Max	7.65	12800.00	136.00			
Range	0.89	11620.00	65.00			
Analyst	HCO ₃ (mg/L)	SO ₄ (mg/L)	Cl (mg/L)			
Mean (mg/L)	1129.48	94.48	6183.10			
Standard Deviation	185.55	133.59	1387.95			
Standard error	34.46	24.81	257.74			
Median	1179.00	70.00	6200.00			
Min (mg/L)	325.00	0.00	90.00			
Max (mg/L)	1322.00	650.00	7850.00			
Range	997.00	650.00	7760.00			
Analyst	Al	Ba	B	Ca	Fe	Mg
Mean (mg/L)	1.30	3.63	14.65	113.46	38.56	19.07
Standard Deviation	0.68	0.88	3.49	17.69	14.91	4.79
Standard error	0.13	0.16	0.65	3.28	2.77	0.89
Median	1.16	3.72	15.10	110.00	37.10	18.10
Min (mg/L)	0.78	0.10	2.82	95.70	10.30	15.30
Max (mg/L)	4.01	4.63	19.30	185.00	57.60	42.10
Range	3.23	4.53	16.48	89.30	47.30	26.80
Analyst	K	Na	Sr	Si	Zr	
Mean (mg/L)	119.11	4520.79	15.21	45.39	20.99	
Standard Deviation	43.35	1099.86	3.35	9.25	10.60	
Standard error	8.19	204.24	0.62	2.07	2.37	
Median	103.00	4616.00	15.40	47.40	20.70	
Min (mg/L)	27.70	179.00	1.94	10.60	0.43	
Max (mg/L)	190.00	6458.00	20.90	53.70	53.10	
Range	162.30	6279.00	18.96	43.10	52.67	

Table 4.3. Flowback water quality for well #68 in Wattenberg Field

Analyst	pH	TDS (mg/L)	Temperature (°F)			
Average	7.33	9107.24	117.50			
Standard Error	0.05	442.16	2.69			
Median	7.27	9840.00	119.50			
Standard Deviation	0.26	2381.09	14.49			
Min	6.99	1140.00	73.00			
Max	7.94	12300.00	132.00			
Range	0.95	11160.00	59.00			
Analyst	HCO₃ (mg/L)	SO₄ (mg/L)	Cl (mg/L)			
Average (mg/L)	1067.21	201.03	5328.46			
Standard Error	37.16	17.15	353.99			
Median	1118.00	210.00	5460.00			
Standard Deviation	200.10	92.36	1839.40			
Min (mg/L)	346.00	30.00	80.50			
Max (mg/L)	1200.00	460.00	8880.00			
Range	854.00	430.00	8799.50			
Analyst	Al	Ba	B	Ca	Fe	Mg
Average (mg/L)	2.88	2.56	11.63	126.33	34.19	17.84
Standard Error	0.22	0.16	0.72	4.22	2.74	1.14
Median	2.90	2.77	12.20	118.00	31.30	15.60
Standard Deviation	1.12	0.80	3.72	21.91	14.23	5.91
Min (mg/L)	0.77	0.18	1.22	97.00	5.35	13.70
Max (mg/L)	4.52	3.52	17.40	178.00	71.50	39.20
Range	3.75	3.34	16.18	81.00	66.15	25.50
Analyst	K	Na	Sr	Si	Zr	
Average (mg/L)	47.81	3658.37	13.08	41.76	38.24	
Standard Error	6.20	225.64	0.83	2.29	5.13	
Median	35.70	3654.00	13.10	44.05	35.55	
Standard Deviation	32.21	1172.45	4.29	9.73	21.78	
Min (mg/L)	13.90	167.00	1.78	15.20	0.28	
Max (mg/L)	192.00	5599.00	21.40	48.30	66.80	
Range	178.10	5432.00	19.62	33.10	66.52	

* Brackish TDS: 5,000 – 35,000 ppm; Saline TDS: 35,000-50,000 ppm; Brine TDS: 50,000-150,000+ ppm

All samples were collected from horizontal wells #68 and #69 located in Wattenberg Field and water quality parameters varied significantly during the flowback period. Take well #68 as an example: the minimum and maximum content of TDS was 1,140 mg/L and 12,300 mg/L respectively; chloride ranged from 80.5 mg/L to 8,880 mg/L during sampling time; the range of

sodium was from 167 mg/L to 5,599 mg/L; the minimum concentration of calcium was 97 mg/L and maximum was 178 mg/L. In another direction, for well #69, the minimum and maximum of TDS was 1,180 mg/L and 12,800 mg/L, respectively; chloride ranged from 90 mg/L to 7,850 mg/L during sampling time; the range of sodium was from 179 mg/L to 6,458 mg/L; the minimum concentration of calcium was 95.7 mg/L and maximum was 185 mg/L. For both wells, flowback water was dominated by $\text{Cl} - \text{Na} - \text{HCO}_3^-$.

4.2 Temporal analysis

All water samples in the study were collected from the wellhead, so the water samples just contained the fluid from a single well. Although the total number of samples from the wellhead was 59, one sample was missing; finally, 58 samples were analyzed in our study.

In the following sections, “time” is defined as “drilling time”, which indicates to the length of one well’s sampling time from the first we collected water samples (March 21st, 9:00 p.m.). For example, the sample was collected on March 22st 1:00 a.m., its drilling time was 4 hours which equaled to the sampling time minus the first sampling time.

$$\text{Drilling time} = \text{sampling time} - 1^{\text{st}} \text{ sampling time (March 21}^{\text{st}} \text{ 9 pm)}$$

Wells #68 and #69 were located in the same place so the geological formation should be the same for both wells. However, the fracturing fluids were different for each well. PermStim fracturing fluid was applied to well #68 with initial pH 5.0; well #69 was injected with SliverStim fracturing fluid with initial pH 10.2. Therefore, we computed the analysis data from wells #68 and #69 to draw in the same figure and tried to figure out the trend and differences between two wells based on the fracturing fluid variability. All raw data used for analysis are shown in Appendix B.

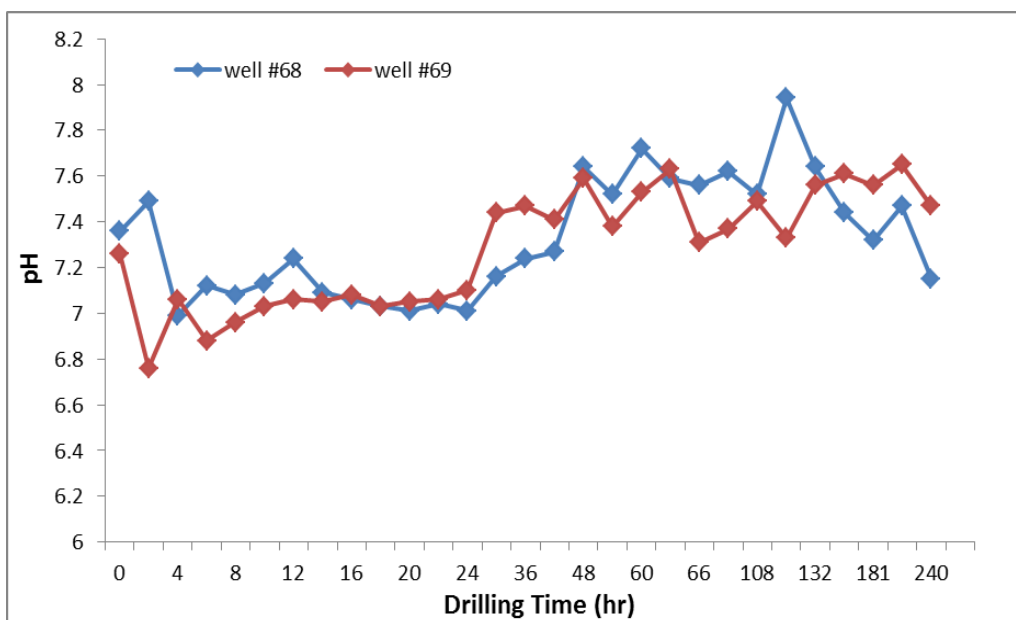


Figure 4.1. Plot of pH vs. drilling time for well #68 and well #69

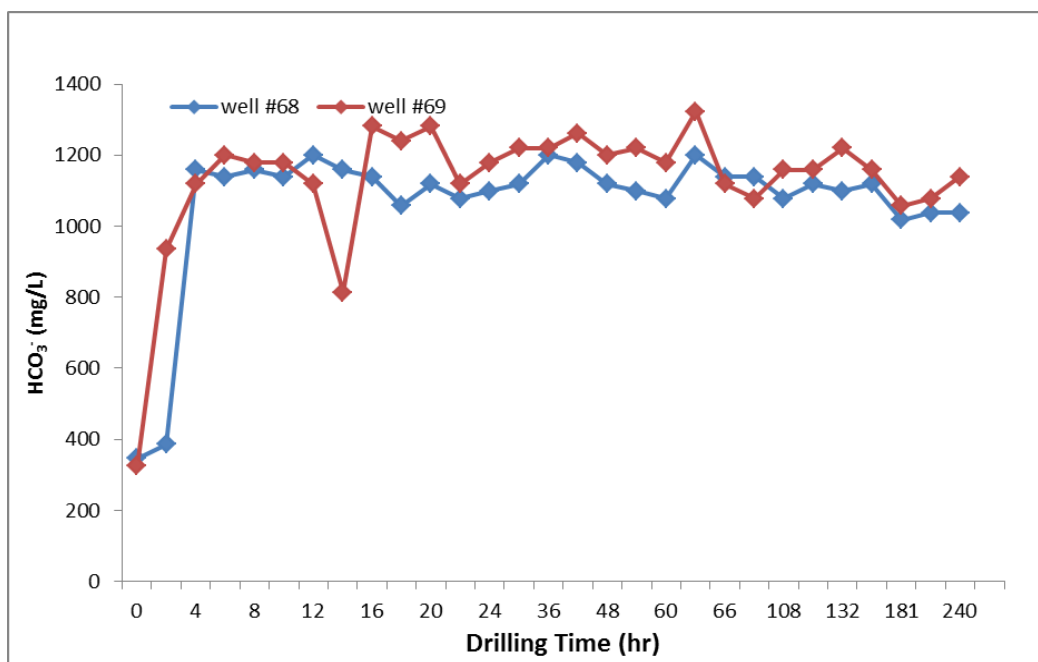


Figure 4.2. Plot of HCO₃⁻ vs. drilling time for well #68 and well #69

Although the injected fluid pH varied from well #68 to well #69, the output pH for both wells ranged from 6.7 to 7.9. From figure 4.1, the variability of pH was low between well #68 and

#69. The pH ranged from 6.5 to 8; bicarbonate is the dominant carbon ion dissolved in fluid.

Therefore, the concentration of bicarbonate also showed a similar trend for both wells as pH.

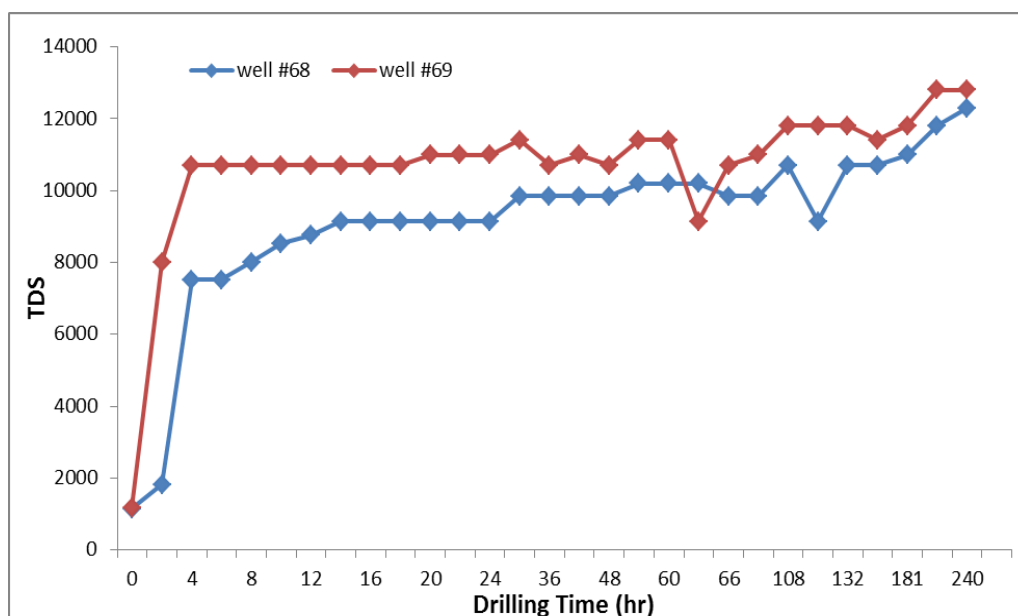


Figure 4.3. Plot of TDS vs. drilling time for well #68 and well #69

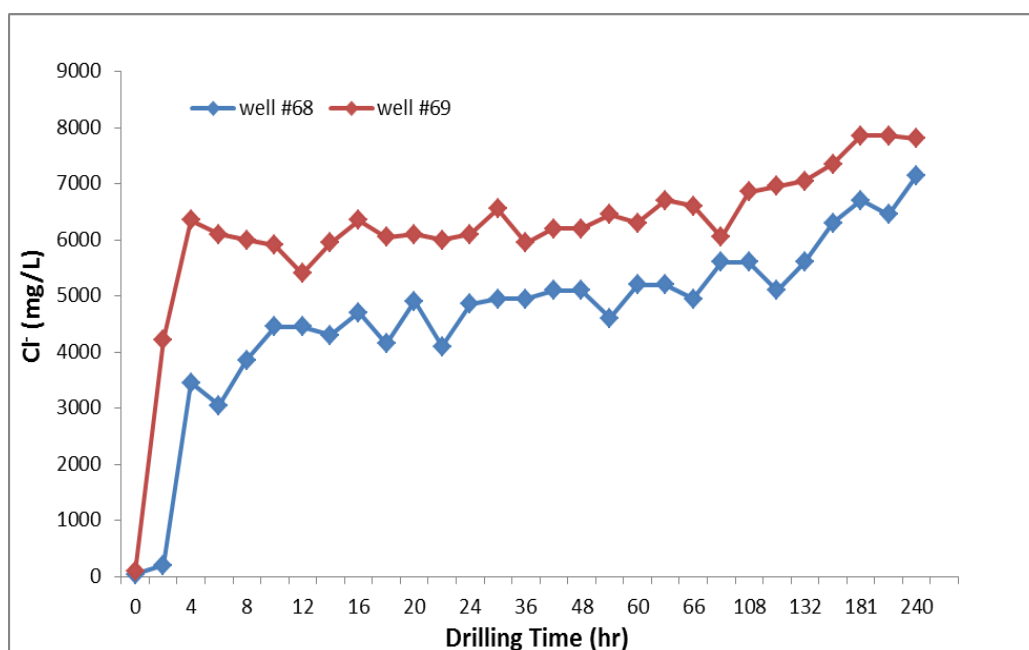


Figure 4.4. Plot of Cl⁻ vs. drilling time for well #68 and well #69

TDS indicates the total amount of organic and inorganic compounds that dissolved in water.

Figure 4.3 illustrates the rising trend of TDS as the drilling time increased. The TDS from well #69 contained a relatively higher concentration than well #68. In flowback water, chloride was the main contributor to TDS, thus the chloride from well #69 also showed a higher concentration than well #68 (fig. 4.4).

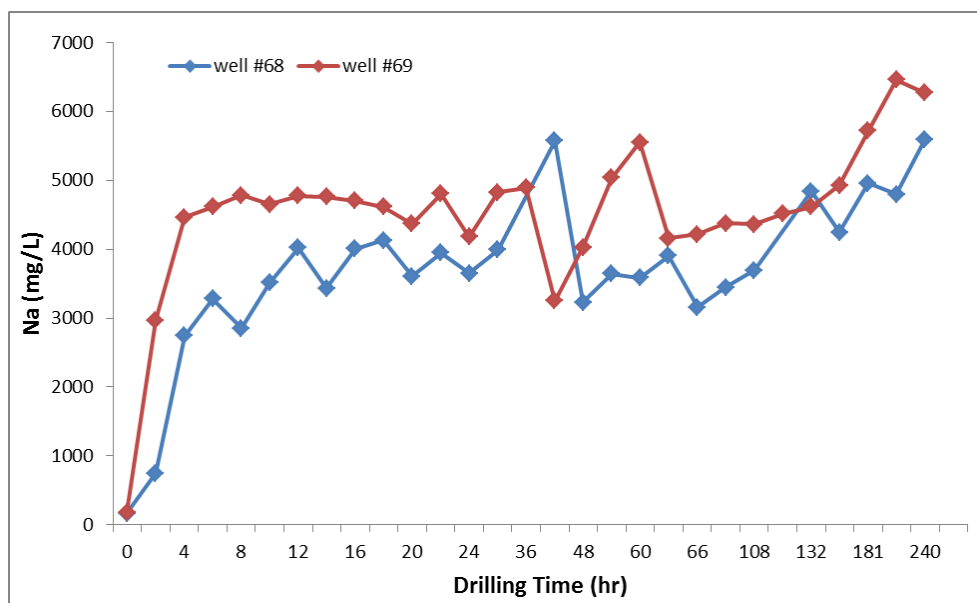


Figure 4.5. Plot of Na⁺ vs. drilling time for well #68 and well #69

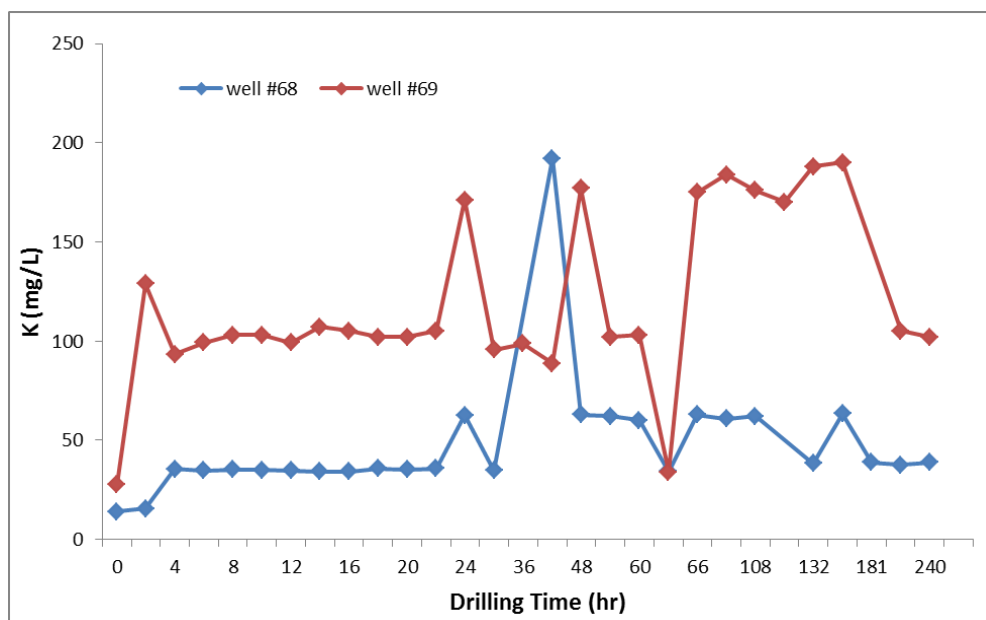


Figure 4.6. Plot of K^+ vs. drilling time for well #68 and well #69

Both Na and K exist in fracturing fluid and geological formation water. In our study, the concentration of Na and K was higher in well #69.

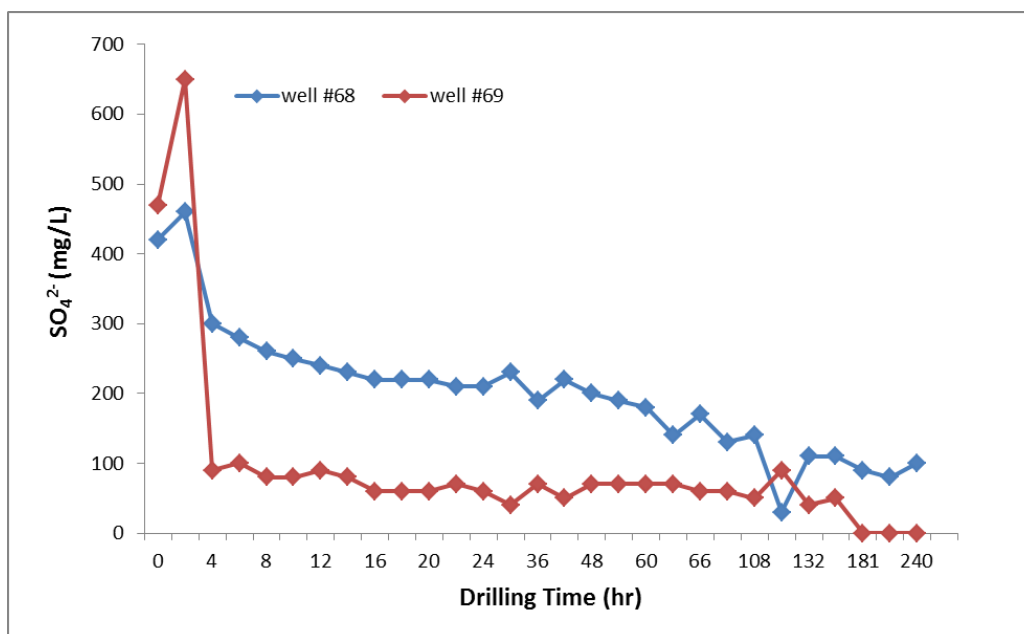


Figure 4.7. Plot of SO_4^{2-} vs. drilling time for well #68 and well #69

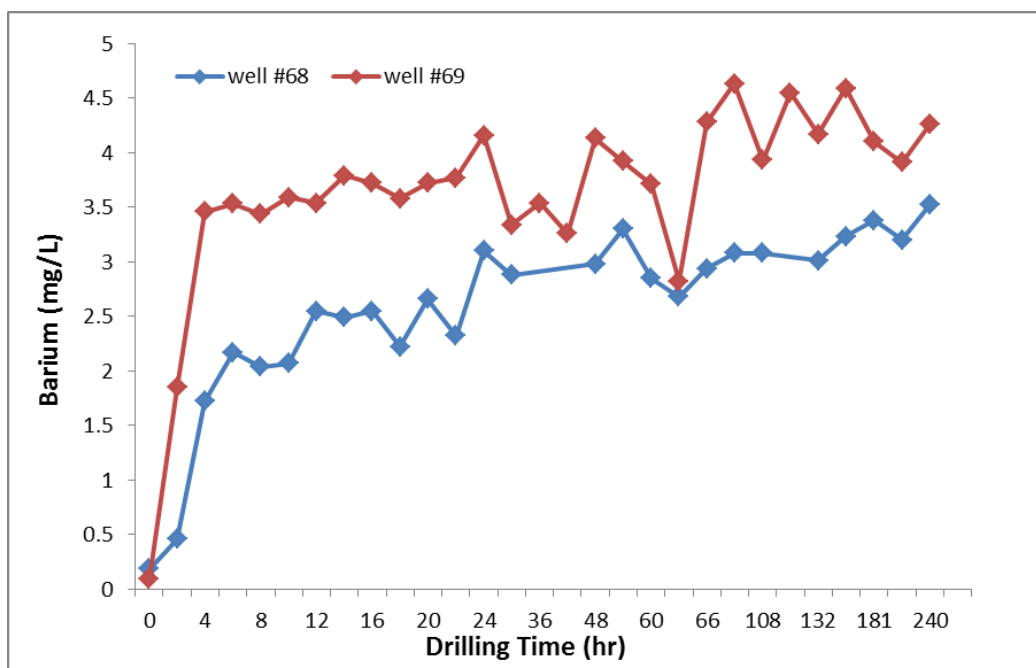


Figure 4.8. Plot of Ba^{2+} vs. drilling time for well #68 and well #69

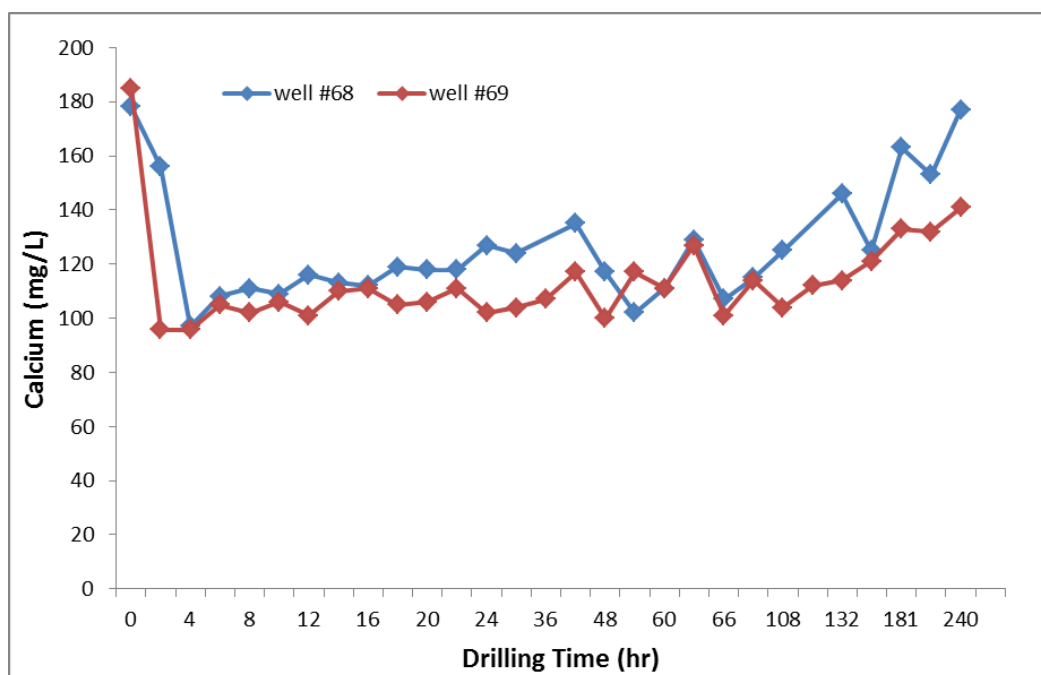


Figure 4.9. Plot of Ca^{2+} vs. drilling time for well #68 and well #69

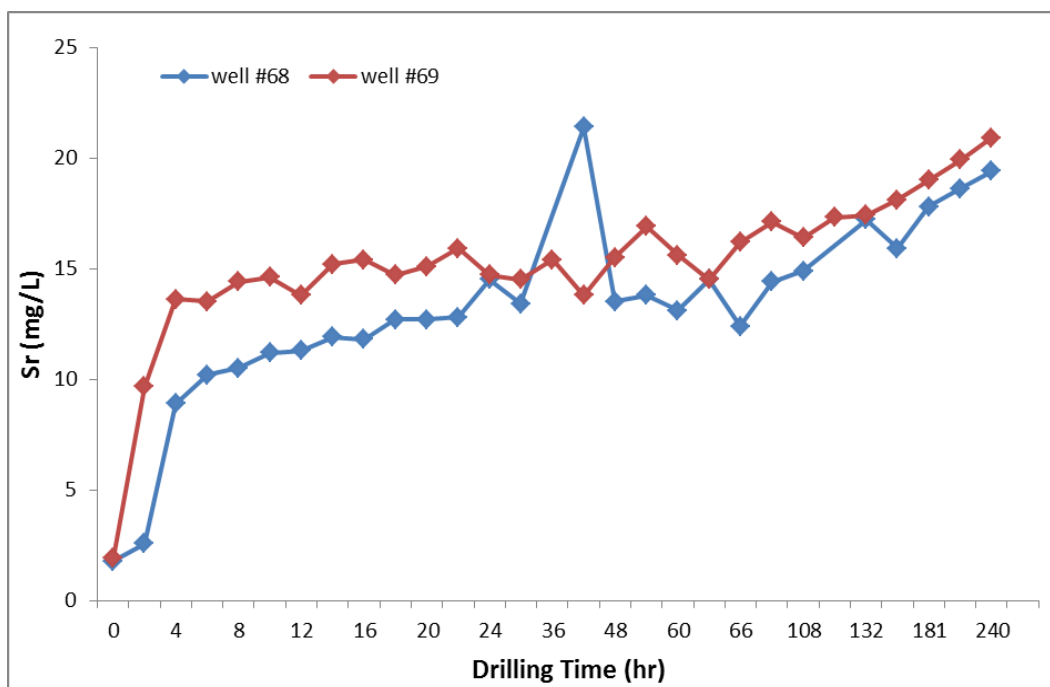


Figure 4.10. Plot of Sr^{2+} vs. drilling time for well #68 and well #69

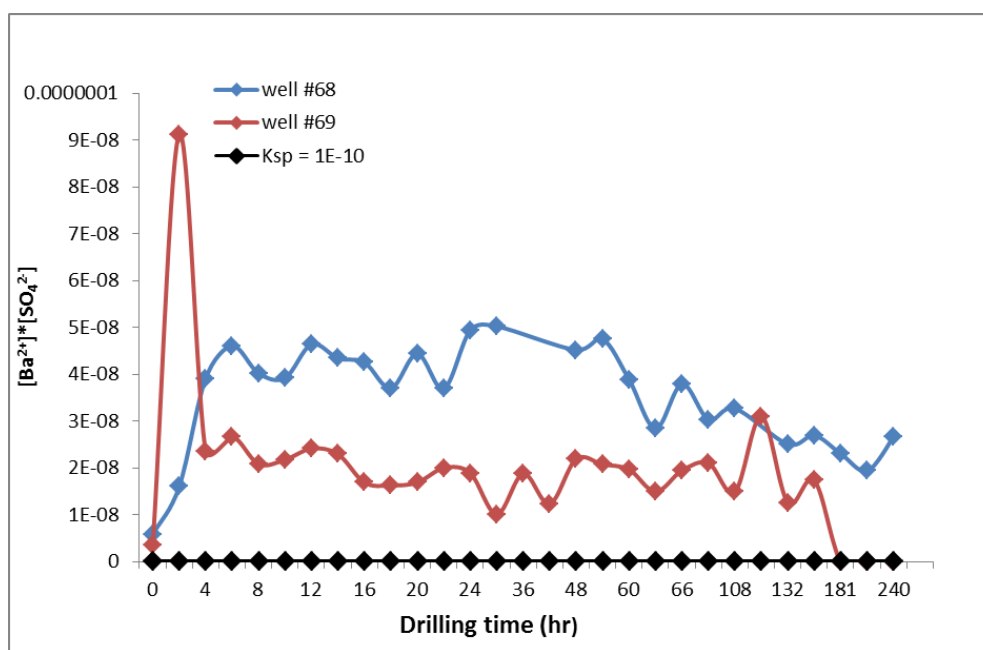


Figure 4.11. Plot of $K_{sp}(\text{BaSO}_4)$ and $Q(\text{BaSO}_4)$ vs. drilling time for well #68 and well #69

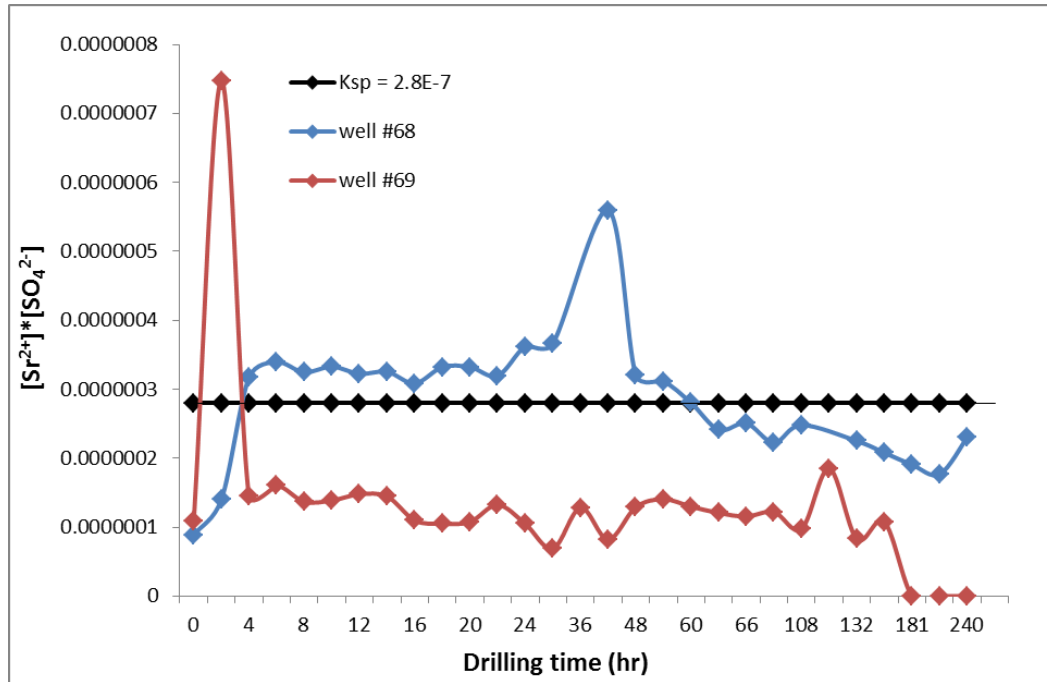


Figure 4.12. Plot of $K_{sp}(\text{SrSO}_4)$ and $Q(\text{SrSO}_4)$ vs. drilling time for well #68 and well #69

Ba, Ca and Sr can react with sulfate ion to form BaSO_4 , CaSO_4 and SrSO_4 , which are insoluble or have minor solubility in water. $K_{sp}(\text{BaSO}_4) = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1 \times 10^{-10}$ is constant and $Q(\text{BaSO}_4) = [\text{Ba}^{2+}]_{\text{actual}}[\text{SO}_4^{2-}]_{\text{actual}}$ is determined by actual concentration of Ba^{2+} and SO_4^{2-} . When $Q > K_{sp}$, precipitation is produced, otherwise, solubility of precipitation happens. Therefore, for well #69, BaSO_4 was the primary precipitation, while for well #68, both SrSO_4 and BaSO_4 were significantly.

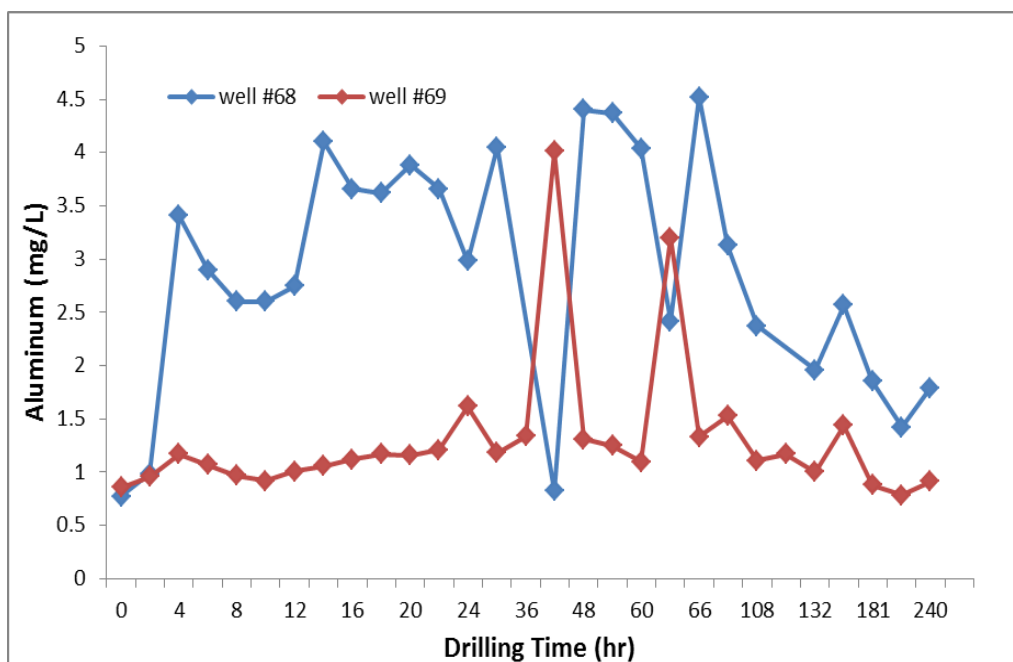


Figure 4.13. Plot of aluminum vs. drilling time for well #68 and well #69

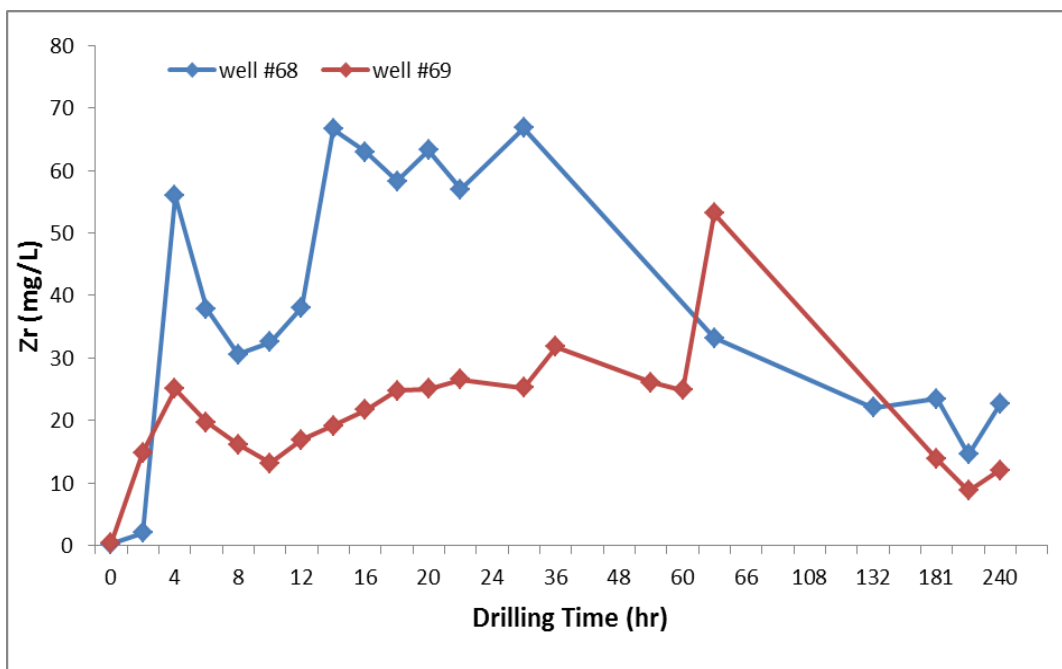


Figure 4.14. Plot of zirconium vs. drilling time for well #68 and well #69

Al^{3+} is soluble in acid solution; however, if Al^{3+} meets with OH^- , $\text{Al}(\text{OH})_3$ will form. This is precipitation in water. Since the injected fluid in well #69 had a higher pH of about 10.2, it indicated the amount of OH^- was also much higher in well #69 than well #68. This may explain why the concentration of Al^{3+} in well #68 was higher since seldom did OH^- exist in well #68 fracturing fluid. The trend of zirconium in figure 4.12 made it obvious that zirconium ion was more stable in acid fluid.

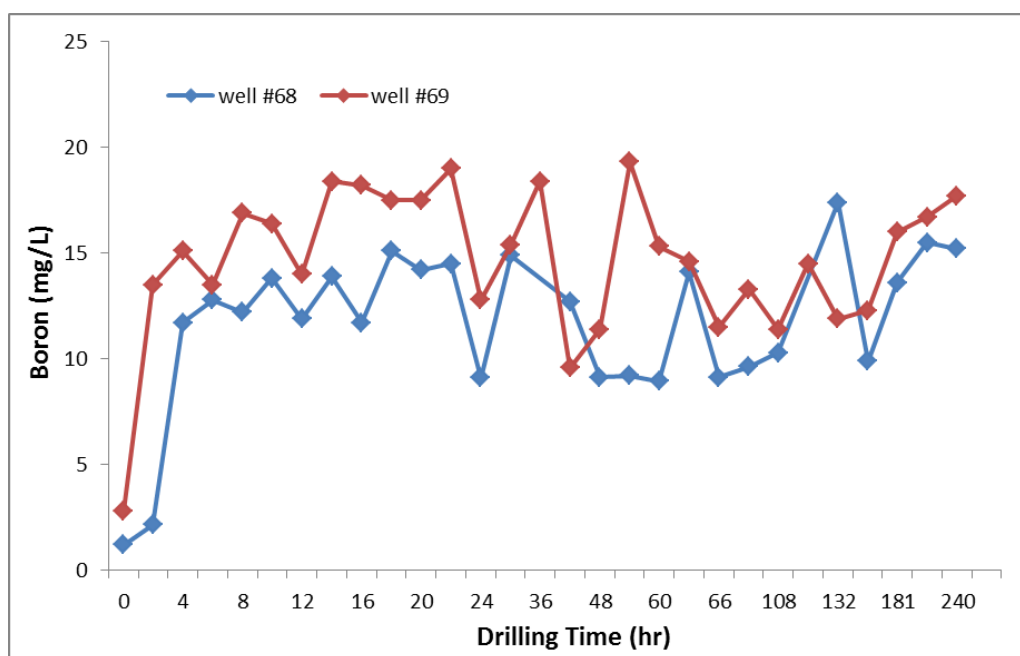


Figure 4.15. Plot of boron vs. drilling time for well #68 and well #69

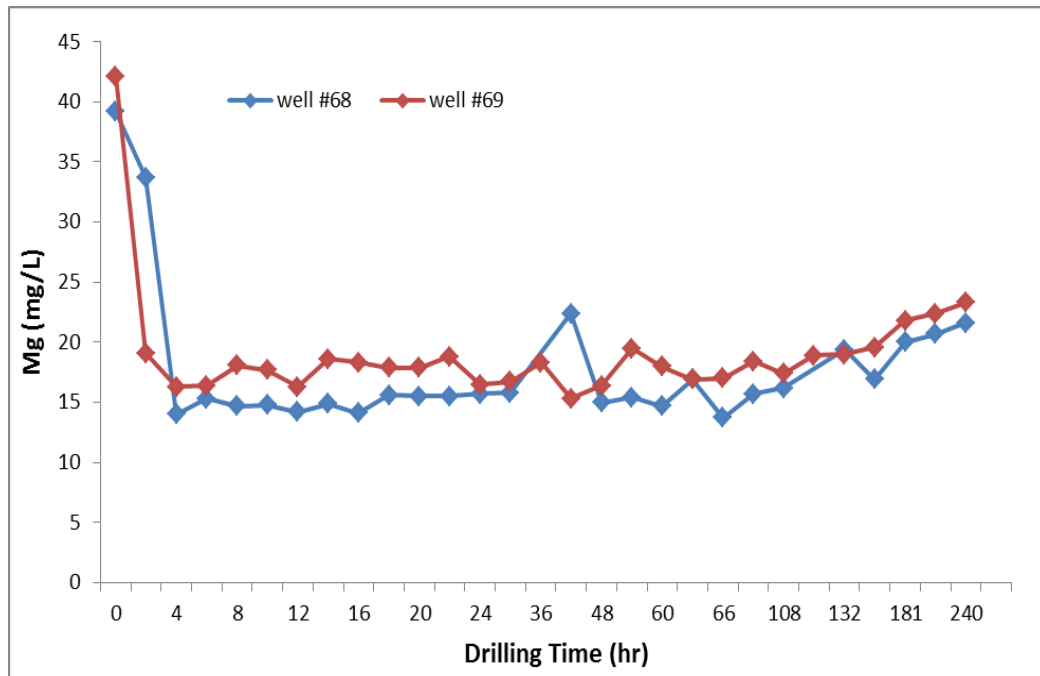


Figure 4.16. Plot of magnesium vs. drilling time for well #68 and well #69

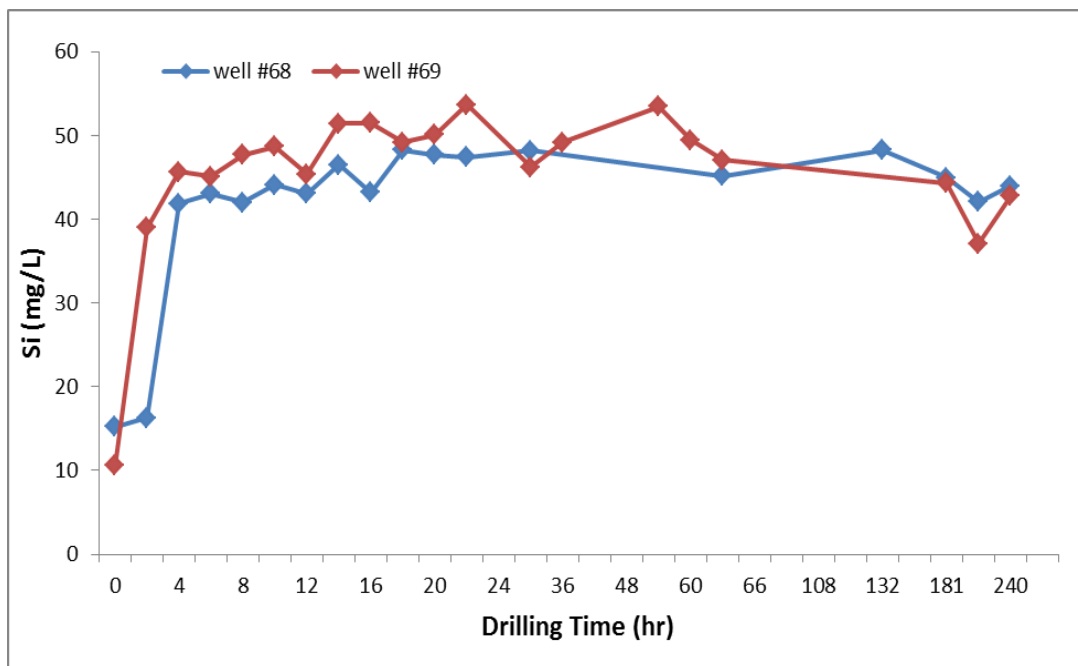


Figure 4.17. Plot of strontium vs. drilling time for well #68 and well #69

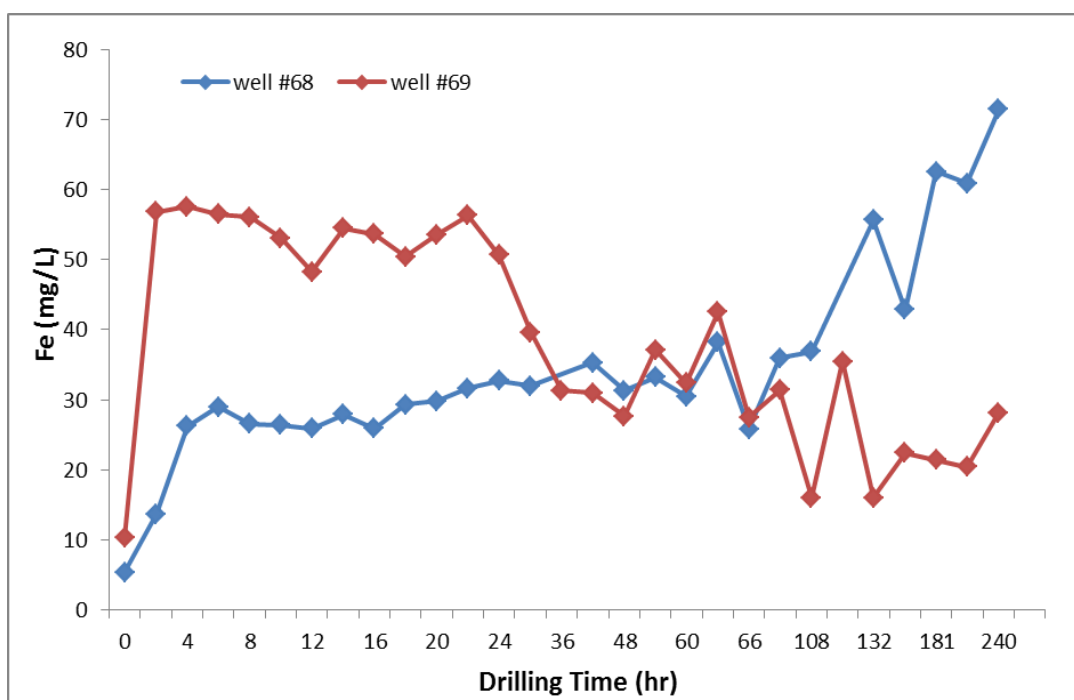


Figure 4.18. Plot of iron vs. drilling time for well #68 and well #69

Based on the data analysis, B, Fe, Sr and Si were all higher in well #69. However, when drilling time reached 66 hours, the concentration of Fe in well #68 had increased dramatically and was much higher than well #69.

Table 4.3. Statistics comparison between well #68 and well #69

	#68	#69	#68	#69	#68	#69	#68	#69
Analyst	pH		TDS (mg/L)		Temperature (°F)		SO ₄ ²⁻ (mg/L)	
Mean	7.33	7.28	9107.24	10669.66	117.5	119.76	201.03	94.48
Median	7.27	7.33	9840	11000	119.5	122.5	210	70
Min	6.99	6.76	1140	1180	73	71	30	0
Max	7.94	7.65	12300	12800	132	136	460	650
Analyst	Al		Ba		Ca		Fe	
Mean (mg/L)	2.88	1.30	2.56	3.63	126.33	113.46	34.19	38.56
Median	2.90	1.16	2.77	3.72	118	110	31.3	37.1
Min (mg/L)	0.77	0.78	0.18	0.1	97	95.7	5.35	10.3
Max (mg/L)	4.52	4.01	3.52	4.63	178	185	71.5	57.6
Analyst	Na		Sr		Si		Zr	
Mean (mg/L)	3658.37	4520.79	13.08	15.21	41.76	45.39	38.24	20.99
Median	3654	4616	13.1	15.4	44.05	47.4	35.55	20.7
Min (mg/L)	167	179	1.78	1.94	15.2	10.6	0.28	0.43

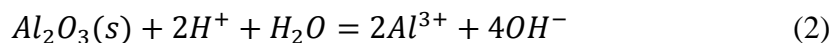
Max (mg/L)	5599	6458	21.4	20.9	48.3	53.7	66.8	53.1
Analyst	HCO ₃ ⁻		Cl ⁻		Mg		K	
Mean (mg/L)	1067.21	1129.48	5328.46	6183.1	17.84	19.07	47.81	119.11
Median	1118	1179	5460	6200	15.6	18.1	35.7	103
Min (mg/L)	346	325	80.5	90	13.7	15.3	13.9	27.7
Max (mg/L)	1200	1322	8880	7850	39.2	42.1	192	190

Table 4.4. Comparison between PermStim (well #68) and SilverStim (well #69)

	PermStim (#68)		SilverStim (#69)	
Purpose	Trade Name	Ingredients	Trade Name	Ingredients
Gelling Agent	WG-39	polysaccharide ethanol heavy	WG-18	guar
Non-ionic Surfactant	OilPerm A	aromatic petroleum naphtha	GasPerm 1100	ethanol
Buffer	BA-20 Buffering Agent	acetic acid	BA-40L Buffering Agent	potassium carbonate
Crosslinker	CL-41	inorganic salt sodium	CL-37 crosslinker	glycerine
Breaker	Optiflo-III Delayed Release Breaker	persulfate ammonium acetate	Vicon NF Breaker	chlorous acid sodium salt
pH	5.0		10.2	

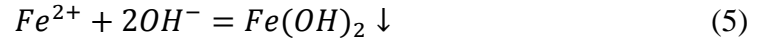
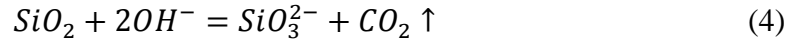
Conclusions and analysis from the above figures and tables are as follows:

1. Acetic acid and potassium carbonate existed in well #68 and well #69, which caused the initial pH to be 5.0 and 10.2 respectively (table 4.4). However, through a series of chemical reactions, output pH for both wells were close to neutral.



CaCO₃ and Al₂O₃ are abundant in the formation rock. For well #68, equations (1) and (2) combined to increase pH (fig. 4.1).





SiO₂ is also common in rock formation. For well #69, equations (3), (4) and (5) explained the reduced pH (fig 4.1).

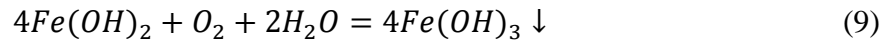
2. Although well #68 and well #69 were located in the same place and drilled in same vertical length, well #69 contained more potassium, chloride and sodium than well #68 (fig. 4.4 to fig. 4.6). This was caused by injecting different fracturing fluids which were comprised by different matters (table 4.4).
3. Barium and strontium could react with sulfate that resulted in precipitation. Therefore, the sulfate was higher indicated the lower constituents of barium and strontium for well #68, while well #69 was in an opposite direction (fig. 4.7, 4.8, 4.10).



BaSO₄ was the primary precipitation in well #69, while for well #68, both SrSO₄ and BaSO₄ were produced (fig. 4.11 to fig. 4.12).

4. Both CaCO₃ and MgCO₃ are prolific in formation rock. Although CaCO₃ and MgCO₃ can only be dissolved in acid fluid, figures 4.9, and 4.14 and table 4.3 express similar content, with a trend of calcium and magnesium for well #68 and well #69. This similarity illustrates that calcium and magnesium mainly came from formation water rather than rock formation.

5. Although SiO₂ does not dissolve in acid water except for hydrofluoric acid, strontium content for both wells showed the same trend. Therefore, the underground formation water might be a main source of dissolved strontium in flowback water.
6. In the rock formation, iron could be something like hematite on quartz grains. Quartz becomes quite soluble at high pH (equation 4), so dissolution of quartz might be helping Fe in solution. However, iron is not stable under high alkaline condition which will result in precipitations.



4.3 Correlation between different ions

Ions vs. TDS

TDS indicate the total amount of organic and inorganic ions that are dissolved in fluid. TDS in flowback water commonly comes from cations (Na⁺, K⁺, Fe³⁺, Ca²⁺, Si⁴⁺ and Sr²⁺) and anions (Cl⁻ and SO₄²⁻). The total ions (including cations and anions) are closely to TDS. The following figures showed the relationship between TDS and different ions.

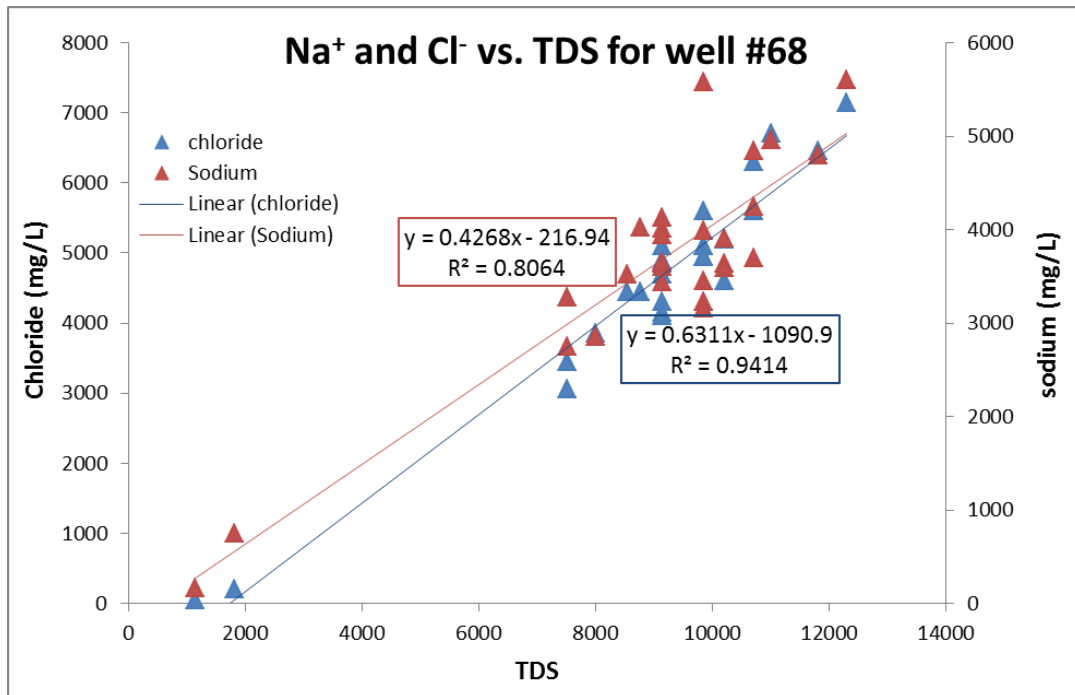


Figure 4.19. Plot of Na⁺ and Cl⁻ vs. TDS

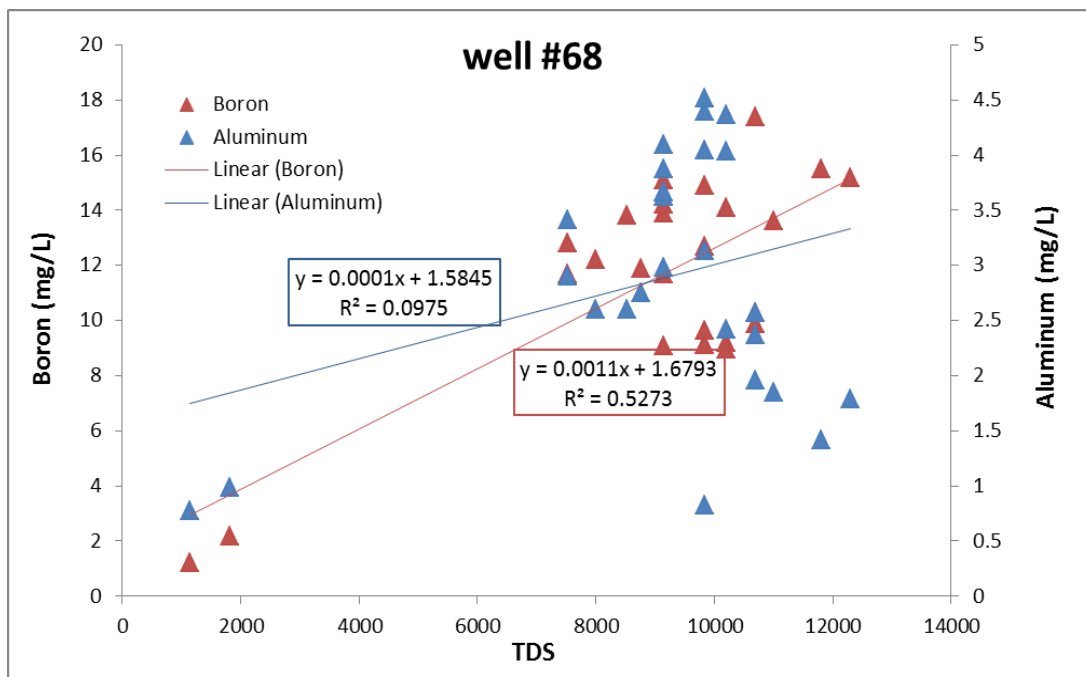


Figure 4.20. Plot of boron and aluminum vs. TDS

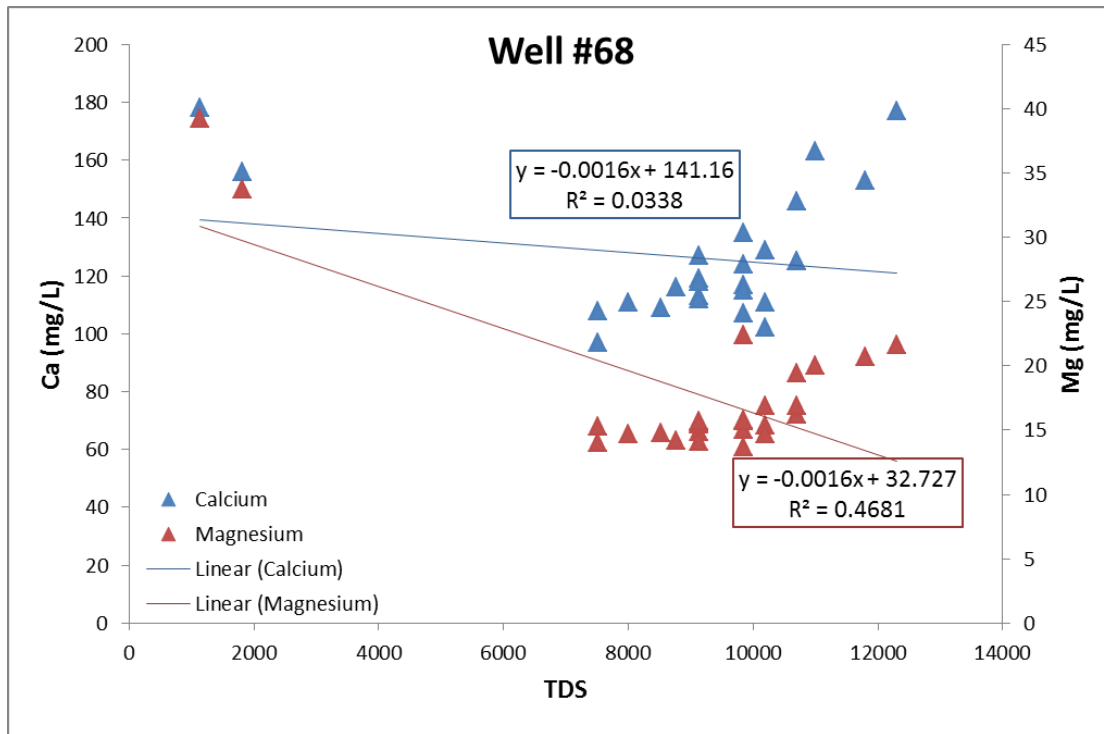


Figure 4.21. Plot of calcium and magnesium vs. TDS

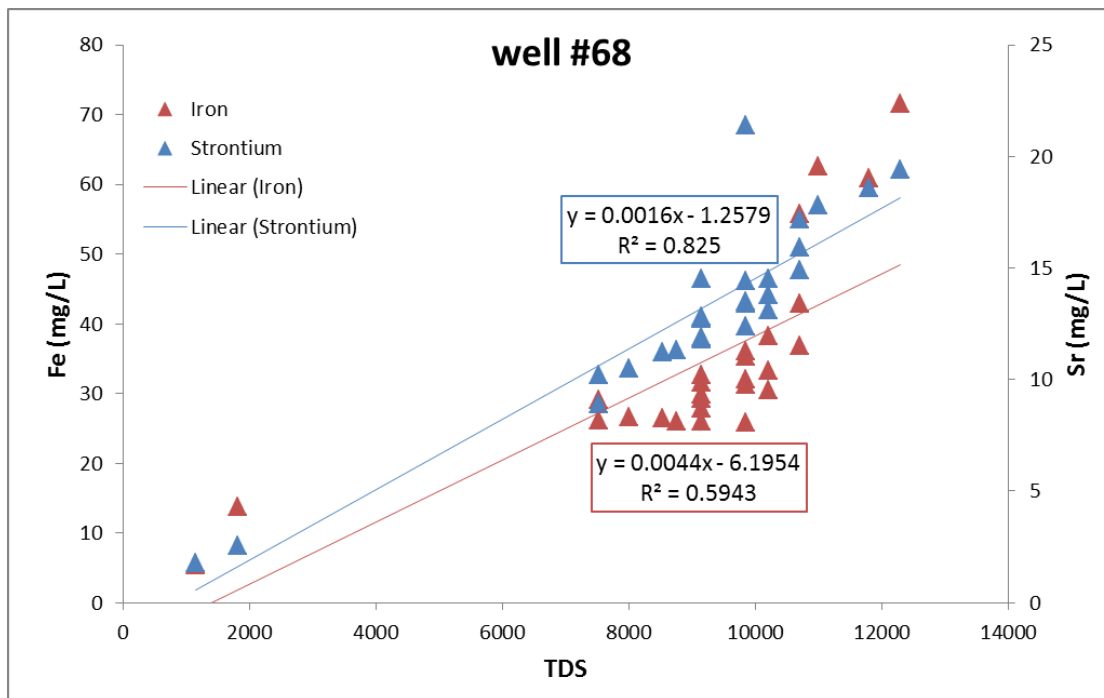


Figure 4.22. Plot of iron and strontium vs. TDS

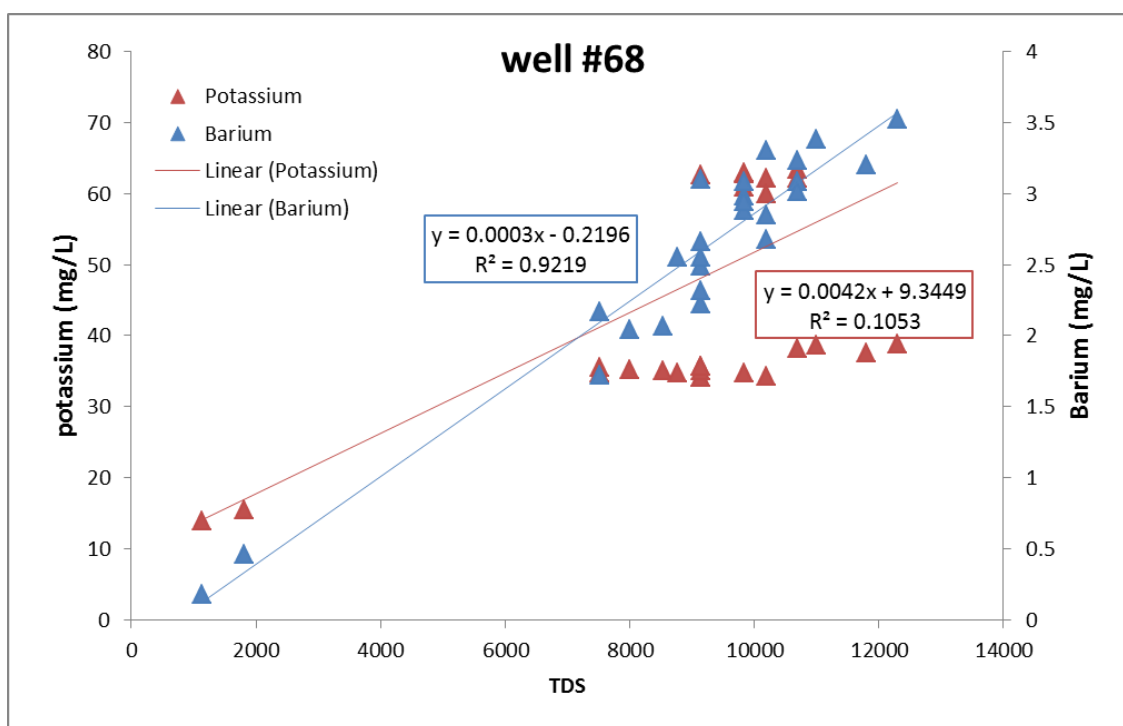


Figure 4.23. Plot of barium and potassium vs. TDS

For well #68, chloride and barium had the closest correlations to TDS with R^2 of linear fitting of both parameters greater than 0.92, followed by strontium and sodium with R^2 larger than 0.80, which also showed a good linear relationship. Iron, boron and magnesium had medium linear correlations with TDS, R^2 was near to 0.50. Aluminum and calcium were the lowest linear correlations with TDS since the R^2 were smaller than 0.10 (fig. 4.17-fig. 4.21).

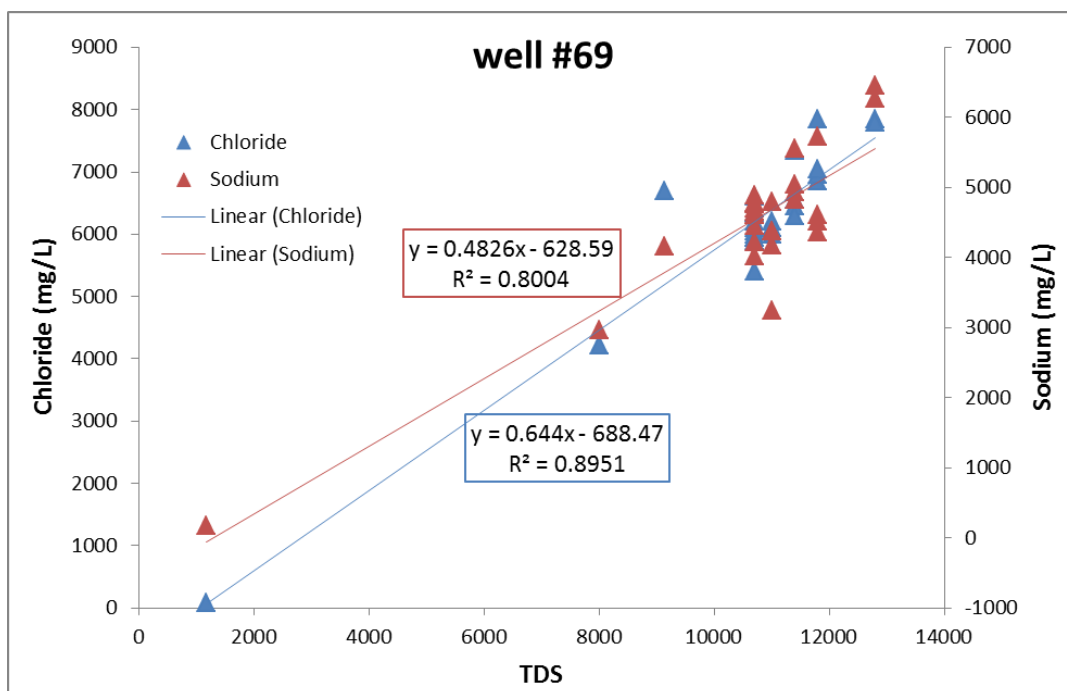


Figure 4.24. Plot of Na^+ and Cl^- vs. TDS

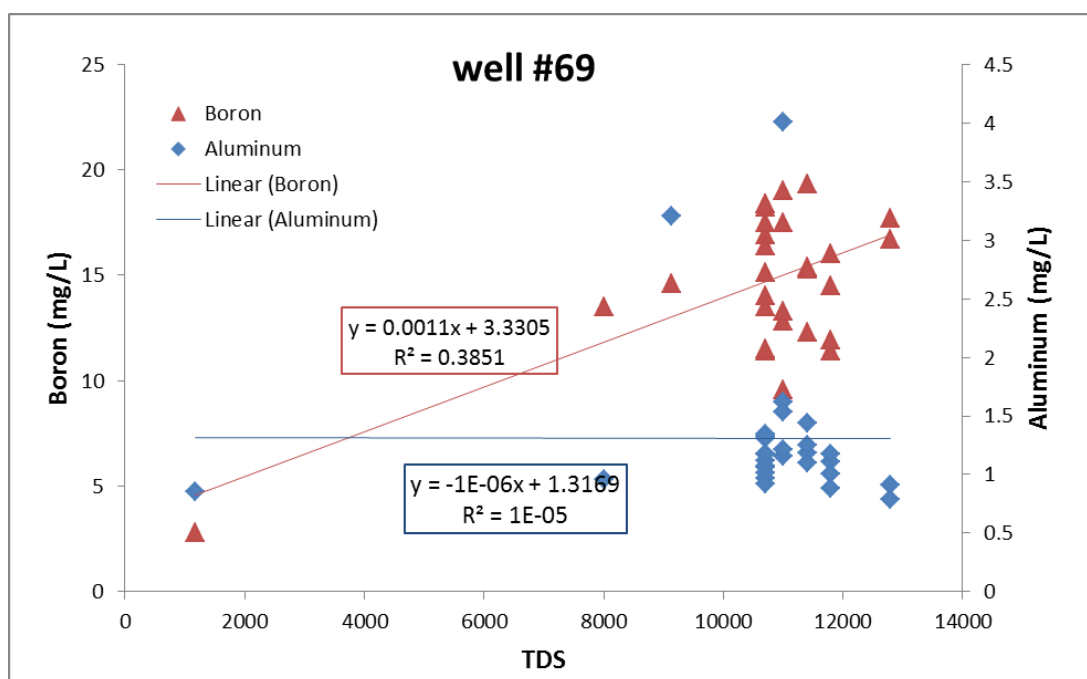


Figure 4.25. Plot of boron and aluminum vs. TDS

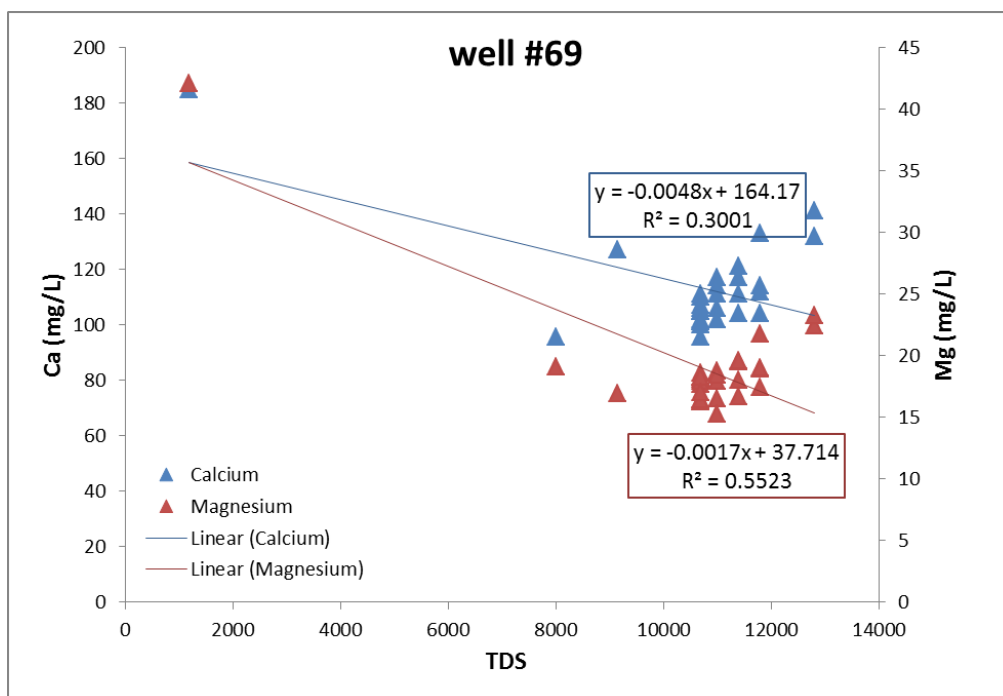


Figure 4.26. Plot of calcium and magnesium vs. TDS

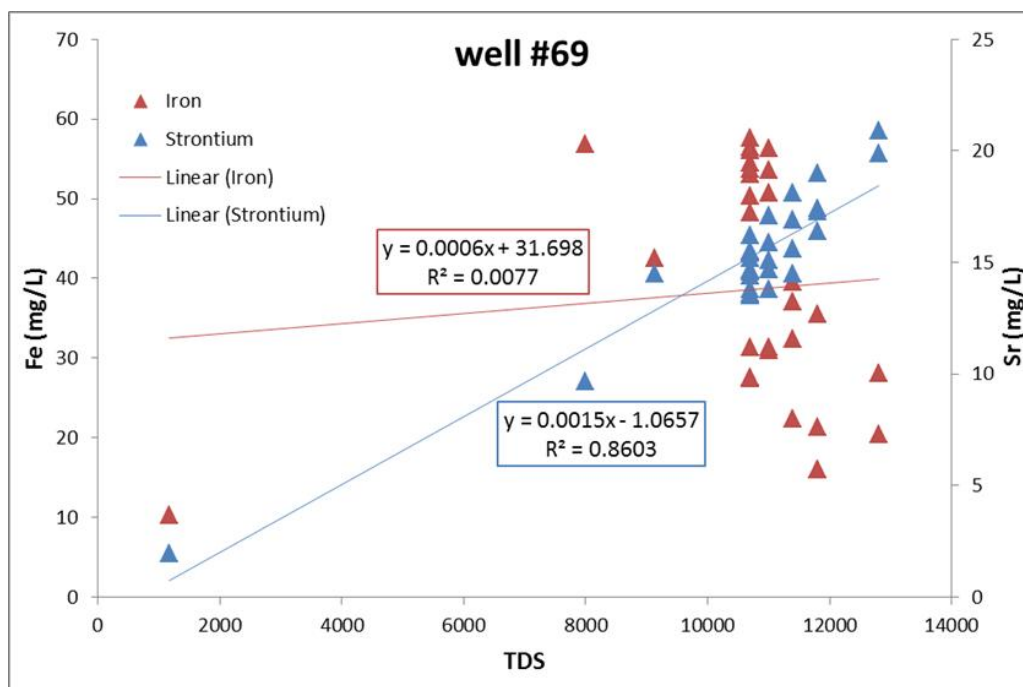


Figure 4.27. Plot of iron and strontium vs. TDS

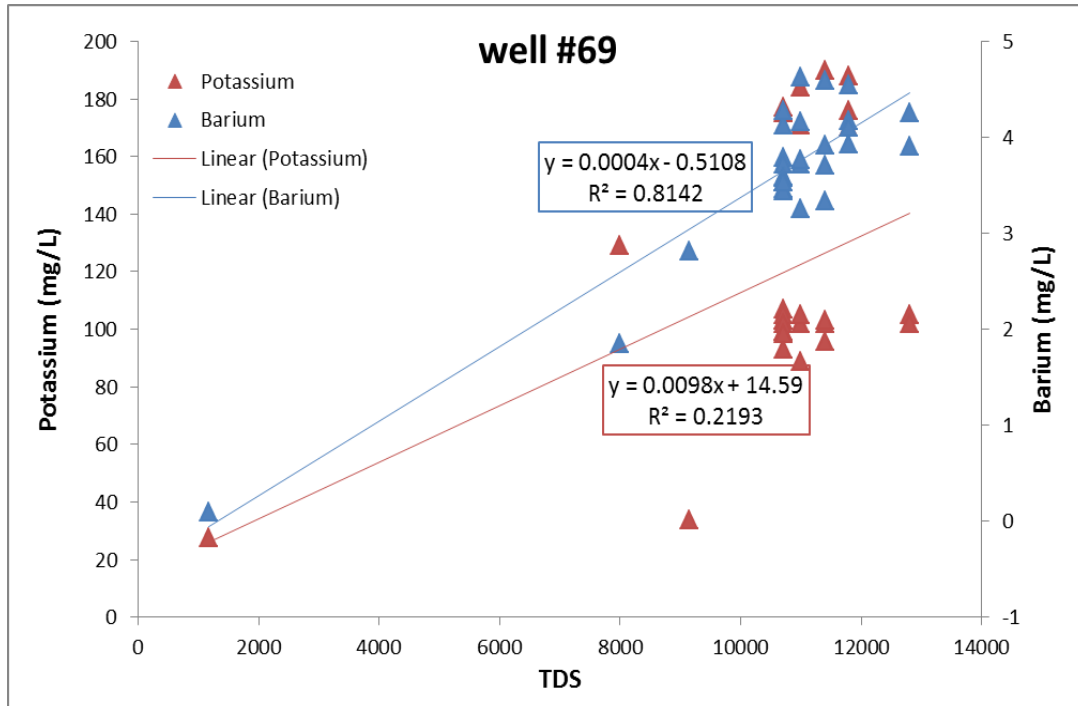


Figure 4.28. Plot of barium and potassium vs. TDS

For well #69, chloride had the closest correlation to TDS with R^2 of linear fitting of parameter larger than 0.89, then followed by strontium, barium and sodium with $R^2 > 0.80$, which also indicated a good linear relationship with TDS. Iron and aluminum were the lowest linear correlations with TDS, $R^2 < 0.01$ (fig. 4.22-fig. 4.26).

From figure 4.17 to figure 4.26, conclusions were collected as follows:

1. R^2 of linear fitting for aluminum with TDS was low for both well #68 and well #69. Especially for well #69, aluminum with $R^2 < 0.0001$, which indicates that the relationship between aluminum and TDS was negligible.
2. For well #68, iron with linear fitting of $R^2 = 0.59$ while R^2 was less than 0.01 for well #69. The lower correlation to iron with TDS may be caused by the higher concentration of OH^- in well #69. Iron would be reacting with OH^- to produce $\text{Fe}(\text{OH})_3$ precipitation.

3. Sodium correlated to TDS with R^2 of linear fitting and the parameter was larger than 0.80 for well #68 and well #69. The correlation of sodium to TDS was pretty close for both wells which indicated injected pH had not effect on sodium amount.

Ions vs. sulfate

The concentration of sulfate decreased during the flowback period while metals such as barium, calcium and strontium rose. This is due to production of scale forming coming from consuming sulfate ion.

Table 4.4. Scale forming salts

salt	saturation concentration (mg/L)
calcium sulfate (CaSO_4)	680
strontium sulfate (SrSO_4)	146
barium sulfate (BaSO_4)	3

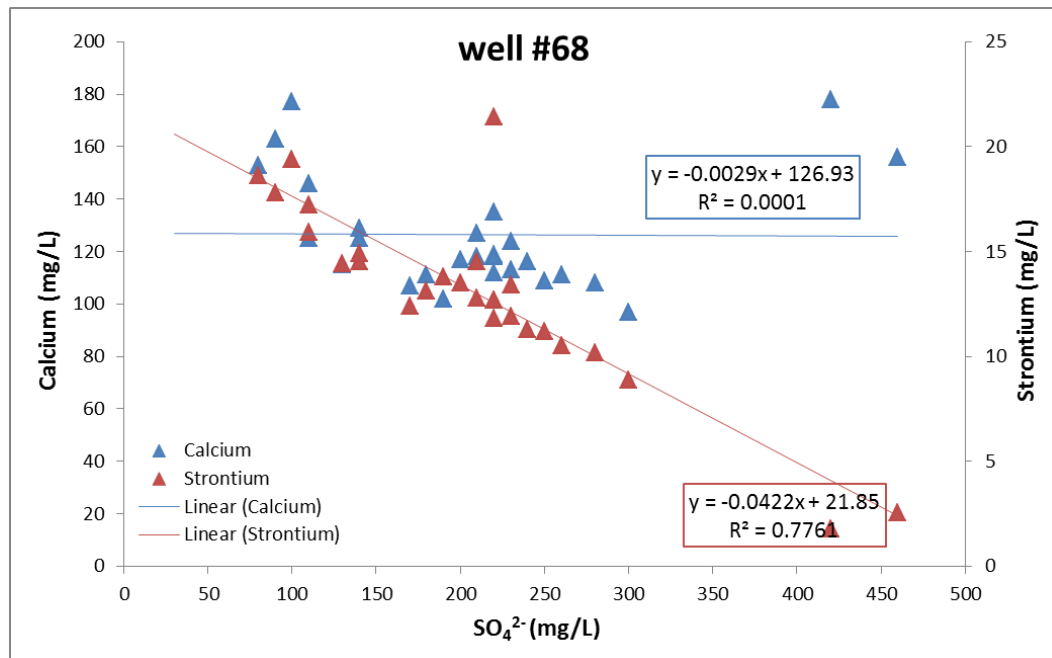


Figure 4.29. Plot of calcium and strontium vs. sulfate

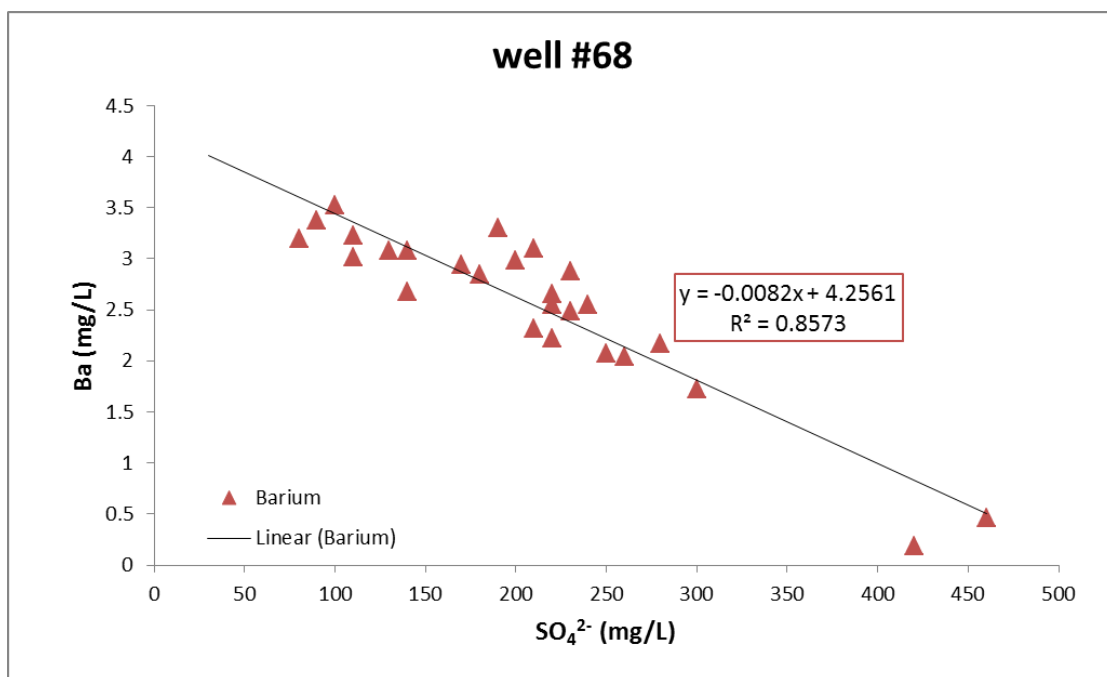


Figure 4.30. Plot of barium vs. sulfate

From figure 4.27 to figure 4.28, barium had the closet linear correlation with sulfate ($R^2 > 0.85$), followed by strontium with $R^2 > 0.77$, while the linear relation of calcium and sulfate was non-existent due to low $R^2 = 0.0001$.

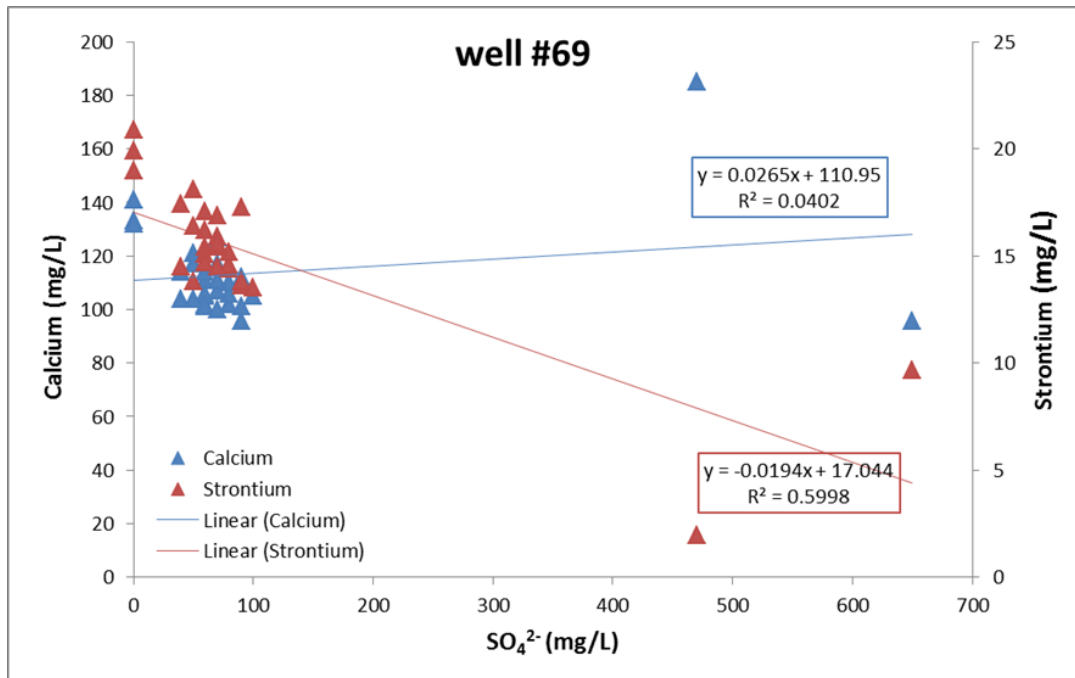


Figure 4.31. Plot of calcium and strontium vs. sulfate

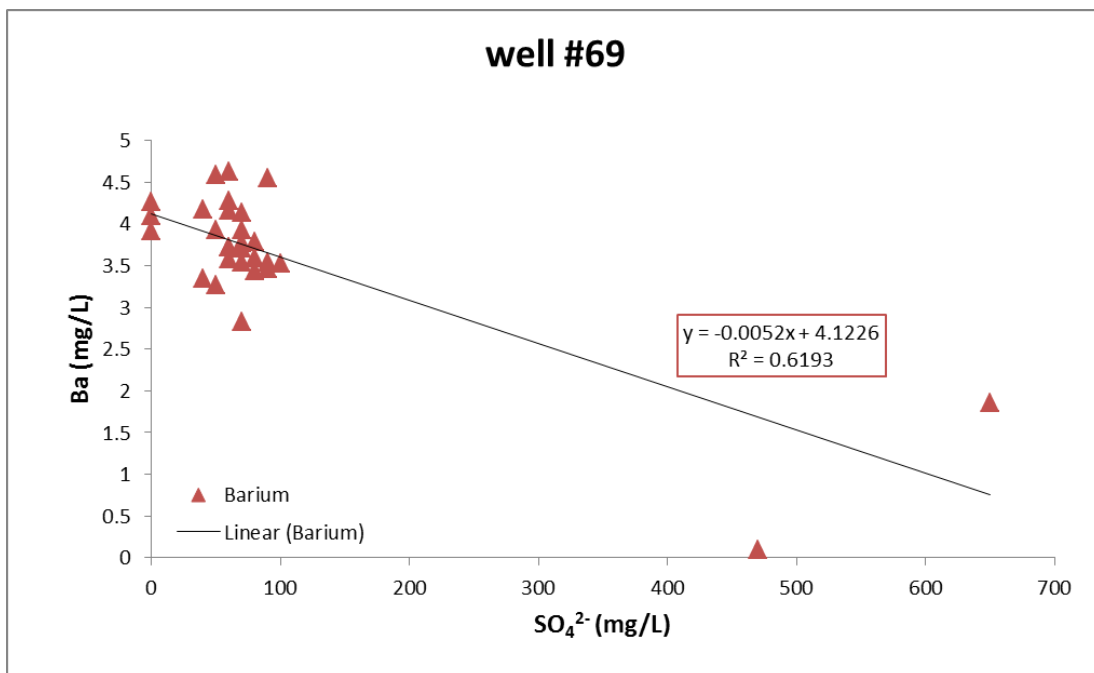


Figure 4.32. Plot of barium vs. sulfate

Figures 4.29 to 4.30 show the linear relationship of barium, strontium and calcium with sulfate. Among these cations, barium was the closest cation with linear correlation of $R^2 > 0.61$ to sulfate, then followed by strontium with $R^2 > 0.59$. However, the R^2 of calcium was 0.04, which indicates that the linear correlation is negligible.

Saturation concentration of BaSO_4 , SrSO_4 and CaSO_4 was 3 mg/L, 146 mg/L and 680 mg/L, respectively (table 4.4), which means BaSO_4 was the first to be precipitated. The sulfate concentration decreased with drilling time mainly due to the concentration of barium in flowback water. For both wells, barium showed the higher linear correlation with sulfate, while the linear correlation between calcium and sulfate was negligible due to its high saturation concentration.

Chapter 5 Conclusion

Flowback water is wastewater coming back from oil/gas wells after the hydraulic fracturing and usually is completed within 3 weeks. The flowback water quality depends on hydraulic fracturing water, geological formation and the time of water contact with underground formation.

In our study, the physical and chemical components parameters were analyzed and compared between well #68 and well #69, which were located in the same underground formation and injected with different fracturing fluid. Although the injected fluid for well #68 was PermStim (pH = 5.0) and well #69 was SilverStim (pH = 10.2), the output pH for both wells revealed nearly neutralized water. This phenomenon is illustrated during hydraulic fracturing processes as different chemical reactions happened in well #68 and #69.

For well #68, calcium and magnesium dissolved and consumed H^+ in fracture fluid, the procedure increased pH. For well #69, the dissolution of SiO_2 and precipitation of aluminum were the main reasons that caused pH decreases. The majority of calcium, magnesium and silicon depended on formation water. The concentration of aluminum was determined by injected pH and formation water. Potassium and boron mainly came from fracture fluid. Chloride, sodium and strontium might be affected by fracture fluid, formation water and formation rock. For both well #68 and well #69, the well linear fitting of R^2 for chloride with TDS and barium would be valuable for future prediction of flowback water quality in Wattenberg field.

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Appendix A

Sample Containers, preservation and holding time requirements

Parameter	Volume (mL)	Container	Preservation	Holding time
pH	25	G, P	None	Immed. & on-site
Cations	250	P	Field rinse, HNO ₃ pH<3	180 days
Anions	250	P	Field rinse	
Chloride	100-200	G, P	Cool 4 °C	28 days
Sulfate	50-100	G, P	Cool 4 °C	28 days
Alkalinity (CaCO ₃)	200	G, P	Cool 4 °C	14 days
BOD-5 day	500- 1000	G, P	Cool 4 °C	48 hrs
BOD- long term	500	G, P	Cool 4 °C	24 hrs
COD	50-250	G, P	H ₂ SO ₄ pH<2	28 days
Total & total volatile	100	G, P	Cool 4 °C	7 days
Turbidity	100-250	G, P	Cool 4 °C Store in dark	48 hrs
VOC	2 to 4 40 ml vials	G vials/TLS	HCl pH<2 No headspace Cool 4 °C ≤6 °C	14 days
Total organic carbon (TOC)	125	G	Store in dark HCl or H ₂ SO ₄ to pH<2	28 days
Total dissolved solids (TDS)			Cool 4 °C±2 °C	7 days
Oil and Grease	1000	G only wide mouth	H ₂ SO ₄ pH<2	28 days

Appendix B

Table B.1, Raw data for well #68

Well #	Sample #	Date	Time	Drilling hours	pH	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	TDS	SO ₄ ²⁻ (mg/L)	Aluminum (mg/L)	Barium (mg/L)	Boron (mg/L)	Calcium (mg/L)	Iron (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Strontium (mg/L)	Silicon (mg/L)	Zirconium (mg/L)
68	2	21-Mar	900PM	0	7.36	346	40	1140	420	0.772	0.183	1.22	178	5.35	39.2	13.9	167	1.78	15.2	0.278
68	4	21-Mar	1100PM	2	7.49	386	200	1820	460	0.987	0.46	2.16	156	13.7	33.7	15.6	749	2.56	16.3	2.1
68	6	22-Mar	100AM	4	6.99	1159	3450	7520	300	3.41	1.72	11.7	97	26.2	14	35.6	2745	8.89	41.9	55.9
68	8	22-Mar	300AM	6	7.12	1139	3050	7520	280	2.9	2.17	12.8	108	29	15.3	34.7	3279	10.2	43.1	37.9
68	10	22-Mar	500AM	8	7.08	1159	3850	8000	260	2.6	2.04	12.2	111	26.6	14.7	35.3	2851	10.5	42	30.6
68	12	22-Mar	700AM	10	7.13	1139	4450	8530	250	2.6	2.07	13.8	109	26.4	14.8	35	3516	11.2	44.1	32.6
68	14	22-Mar	900AM	12	7.24	1200	4450	8760	240	2.75	2.55	11.9	116	25.9	14.2	34.7	4023	11.3	43.1	38.1
68	16	22-Mar	1100AM	14	7.09	1159	4300	9140	230	4.1	2.49	13.9	113	27.9	14.9	34.2	3435	11.9	46.5	66.6
68	18	22-Mar	100PM	16	7.06	1139	4700	9140	220	3.66	2.55	11.7	112	25.9	14.1	34.1	4007	11.8	43.2	63
68	20	22-Mar	300PM	18	7.03	1057	4150	9140	220	3.62	2.22	15.1	119	29.3	15.6	35.7	4130	12.7	48.3	58.3
68	22	22-Mar	500PM	20	7.01	1118	4900	9140	220	3.88	2.66	14.2	118	29.8	15.5	35.1	3608	12.7	47.7	63.2
68	24	22-Mar	700PM	22	7.04	1078	4100	9140	210	3.66	2.32	14.5	118	31.6	15.5	35.7	3947	12.8	47.4	57
68	26	22-Mar	900PM	24	7.01	1098	4850	9140	210	2.98	3.1	9.1	127	32.7	15.7	62.6	3654	14.5	NG	NG
68	28	23-Mar	300AM	30	7.16	1118	4950	9840	230	4.05	2.88	14.9	124	32	15.8	34.8	3992	13.4	48.2	66.8
68	30	23-Mar	900AM	36	7.24	1200	4950	9840	190	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG
68	31	23-Mar	300PM	42	7.27	1179	5100	9840	220	0.821	NG	12.7	135	35.3	22.4	192	5576	21.4	NG	NG
68	34	23-Mar	900PM	48	7.64	1118	5100	9840	200	4.4	2.98	9.12	117	31.3	15	62.8	3230	13.5	NG	NG
68	36	24-Mar	300AM	54	7.52	1098	4600	10200	190	4.37	3.3	9.21	102	33.2	15.4	62.2	3641	13.8	NG	NG
68	38	24-Mar	900AM	60	7.72	1078	5200	10200	180	4.04	2.85	8.95	111	30.5	14.7	60	3589	13.1	NG	NG
68	39	24-Mar	300PM	66	7.59	1200	5200	10200	140	2.42	2.68	14.1	129	38.2	16.9	34.3	3905	14.5	45.2	33.2
68	42	24-Mar	900PM	72	7.56	1139	4950	9840	170	4.52	2.94	9.12	107	25.8	13.7	62.9	3158	12.4	NG	NG
68	45	25-Mar	900PM	96	7.62	1139	5600	9840	130	3.13	3.08	9.64	115	36	15.7	60.8	3445	14.4	NG	NG
68	48	26-Mar	900AM	108	7.52	1078	5600	10700	140	2.37	3.08	10.3	125	36.9	16.2	62.1	3692	14.9	NG	NG
68	51	26-Mar	900PM	120	7.94	1118	5100	9140	30	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG	NG
68	54	27-Mar	900AM	132	7.64	1098	5600	10700	110	1.96	3.01	17.4	146	55.7	19.4	38.2	4839	17.2	48.3	22.1
68	57	28-Mar	900AM	156	7.44	1118	6300	10700	110	2.57	3.23	9.9	125	42.9	16.9	63.3	4244	15.9	NG	16.9
68	63	30-Mar	1000AM	181	7.32	1017	6700	11000	90	1.85	3.38	13.6	163	62.6	20	38.7	4958	17.8	45	23.5
68	67	31-Mar	900AM	204	7.47	1037	6450	11800	80	1.42	3.2	15.5	153	60.9	20.7	37.6	4797	18.6	42.1	14.6
68	72	1-Apr	900PM	240	7.15	1037	7150	12300	100	1.79	3.52	15.2	177	71.5	21.6	38.9	5599	19.4	44	22.6

*NG means the data is not available

Table B.2, Raw data for well #69

Well #	Sample #	Date	Time	Drilling Hour	pH	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	TDS	SO ₄ ²⁻ (mg/L)	Aluminum (mg/L)	Barium (mg/L)	Boron (mg/L)	Calcium (mg/L)	Iron (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Strontium (mg/L)	Silicon (mg/L)	Zirconium (mg/L)
69	1	21-Mar	900PM	0	7.26	325	90	1180	470	0.858	0.097	2.82	185	10.3	42.1	27.7	179	1.94	10.6	0.433
69	3	21-Mar	1100PM	2	6.76	935	4220	8000	650	0.96	1.85	13.5	95.7	56.8	19.1	129	2971	9.67	39	14.9
69	5	22-Mar	100AM	4	7.06	1118	6350	10700	90	1.17	3.46	15.1	95.7	57.6	16.3	93.2	4463	13.6	45.7	25.1
69	7	22-Mar	300AM	6	6.88	1200	6100	10700	100	1.07	3.53	13.5	105	56.5	16.4	99.1	4615	13.5	45.1	19.7
69	9	22-Mar	500AM	8	6.96	1179	6000	10700	80	0.97	3.44	16.9	102	56.1	18.1	103	4787	14.4	47.7	16.2
69	11	22-Mar	700AM	10	7.03	1179	5900	10700	80	0.917	3.59	16.4	106	53.1	17.7	103	4652	14.6	48.7	13.2
69	13	22-Mar	900AM	12	7.06	1118	5400	10700	90	1.01	3.54	14	101	48.3	16.3	99.1	4774	13.8	45.4	16.9
69	15	22-Mar	1100AM	14	7.05	813	5950	10700	80	1.06	3.79	18.4	110	54.5	18.6	107	4762	15.2	51.4	19.2
69	17	22-Mar	100PM	16	7.08	1281	6350	10700	60	1.12	3.72	18.2	111	53.7	18.3	105	4706	15.4	51.5	21.7
69	19	22-Mar	300PM	18	7.03	1240	6050	10700	60	1.17	3.58	17.5	105	50.4	17.9	102	4616	14.7	49.2	24.8
69	21	22-Mar	500PM	20	7.05	1281	6100	11000	60	1.16	3.72	17.5	106	53.6	17.9	102	4371	15.1	50.1	25.1
69	23	22-Mar	700PM	22	7.06	1118	6000	11000	70	1.21	3.77	19	111	56.3	18.8	105	4804	15.9	53.7	26.6
69	25	22-Mar	900PM	24	7.1	1179	6100	11000	60	1.62	4.16	12.8	102	50.7	16.5	171	4183	14.7	NG	NG
69	27	23-Mar	300AM	30	7.44	1220	6550	11400	40	1.18	3.34	15.4	104	39.6	16.7	95.6	4831	14.5	46.2	25.3
69	29	23-Mar	900AM	36	7.47	1220	5950	10700	70	1.34	3.54	18.4	107	31.3	18.3	98.6	4896	15.4	49.2	31.8
69	32	23-Mar	300PM	42	7.41	1261	6200	11000	50	4.01	3.26	9.58	117	31	15.3	88.8	3253	13.8	NG	NG
69	33	23-Mar	900PM	48	7.59	1200	6200	10700	70	1.31	4.13	11.4	100	27.6	16.4	177	4026	15.5	NG	NG
69	35	24-Mar	300AM	54	7.38	1220	6450	11400	70	1.25	3.92	19.3	117	37.1	19.5	102	5039	16.9	53.5	26.1
69	37	24-Mar	900AM	60	7.53	1179	6300	11400	70	1.1	3.71	15.3	111	32.4	18	103	5554	15.6	49.5	24.9
69	40	24-Mar	900PM	72	7.63	1322	6700	9140	70	3.2	2.82	14.6	127	42.5	16.9	34	4158	14.5	47.1	53.1
69	41	24-Mar	300PM	66	7.31	1118	6600	10700	60	1.33	4.28	11.5	101	27.5	17	175	4216	16.2	NG	NG
69	46	25-Mar	900PM	96	7.37	1078	6050	11000	60	1.53	4.63	13.3	114	31.4	18.4	184	4377	17.1	NG	NG
69	49	26-Mar	900AM	108	7.49	1159	6850	11800	50	1.11	3.93	11.4	104	16	17.4	176	4360	16.4	NG	NG
69	52	26-Mar	900PM	120	7.33	1159	6950	11800	90	1.17	4.55	14.5	112	35.5	18.9	170	4513	17.3	NG	NG
69	55	27-Mar	900AM	132	7.56	1220	7050	11800	40	1	4.17	11.9	114	16	19	188	4616	17.4	NG	NG
69	58	28-Mar	900AM	156	7.61	1159	7350	11400	50	1.44	4.59	12.3	121	22.4	19.6	190	4929	18.1	NG	NG
69	62	30-Mar	1000AM	181	7.56	1057	7850	11800	0	0.881	4.1	16	133	21.4	21.8	NG	5721	19	44.3	13.8
69	68	31-Mar	900AM	204	7.65	1078	7850	12800	0	0.783	3.91	16.7	132	20.4	22.4	105	6458	19.9	37.1	8.77
69	73	1-Apr	900PM	240	7.47	1139	7800	12800	0	0.911	4.26	17.7	141	28.1	23.3	102	6273	20.9	42.8	12.1

*NG means the data is not available

Appendix C

On- site water sampling sheet

multi - chem	Analytical Tests - All samples must have # written on them		
Energy Company	Noble Energy	Sample Date	
Completele Well Name		Sample time	
		Sample #	
Water Complete			
Initial Temp.	°F	pH	
Final Temp.	°F	CO ₂ mg/L (dissolved)	
Initial Pressure	psig	Bicarbonate (HCO ₃)	
BBLS water flowed back		H2S ppm (Gas phase)	
BBLS oil flowed back		H2S mg/L (Dissolved)	
Gas flowed back (MCFD)		Chlorides	
Gas production (MCFD)		TDS (in ppt)	
Oil Production (BPD)		Conductivity (tds/.07)	
Water Production (BPD)			
Lab notes:			

Appendix D

Scheduled sampling time

Sampling Date	Sample Time	Time from Drilling (hr)
Thursday, March 21, 2013	09:00PM	0
Thursday, March 21, 2013	11:00PM	2
Friday, March 22, 2013	01:00AM	4
Friday, March 22, 2013	03:00AM	6
Friday, March 22, 2013	05:00AM	8
Friday, March 22, 2013	07:00AM	10
Friday, March 22, 2013	09:00AM	12
Friday, March 22, 2013	11:00AM	14
Friday, March 22, 2013	01:00PM	16
Friday, March 22, 2013	03:00PM	18
Friday, March 22, 2013	05:00PM	20
Friday, March 22, 2013	07:00PM	22
Friday, March 22, 2013	09:00PM	24
Saturday, March 23, 2013	03:00AM	30
Saturday, March 23, 2013	09:00AM	36
Saturday, March 23, 2013	03:00PM	42
Saturday, March 23, 2013	09:00PM	48
Sunday, March 24, 2013	03:00AM	54
Sunday, March 24, 2013	09:00AM	60

Sunday, March 24, 2013	09:00PM	72
Sunday, March 24, 2013	03:00PM	66
Monday, March 25, 2013	09:00PM	96
Tuesday, March 26, 2013	09:00AM	108
Tuesday, March 26, 2013	09:00PM	120
Wednesday, March 27, 2013	09:00AM	132
Thursday, March 28, 2013	09:00AM	156
Saturday, March 30, 2013	10:00AM	181
Sunday, March 31, 2013	09:00AM	204
Monday, April 01, 2013	09:00PM	240
