

DISSERTATION

MODELING OF WASTEWATER VOLUME FROM UNCONVENTIONAL OIL AND GAS  
FIELDS IN WATTENBERG FIELD, AND EVALUATION OF LOW SALINITY  
WATERFLOOD ENHANCED OIL RECOVERY ON SHALE WELLS

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## ABSTRACT

### MODELING OF WASTEWATER VOLUME FROM UNCONVENTIONAL OIL AND GAS FIELDS IN WATTENBERG FIELD, AND EVALUATION OF LOW SALINITY WATERFLOOD ENHANCED OIL RECOVERY ON SHALE WELLS

Reuse of wastewater from hydraulic fracturing (flowback and produced water) is a sustainable option for wastewater management practice in unconventional oil and gas fields. Reuse reduces fresh water demand but also lowers the environmental footprint by reducing the storage and transportation of both fresh and wastewater. A successful reuse practice requires a thorough understanding of both the quantity and quality of the wastewater, and more importantly, its potential impacts on well performance. In the first part of this study, wastewater production models were developed for horizontal shale wells in Wattenberg field .In addition, a solid characterization and distribution analysis on wells fractured with fresh and recycled water was performed to understand their impacts on wastewater quality. The second part of this study focuses on understanding the mechanisms of low salinity waterflood (LSF) in unconventional shale wells, and how oil recovery is impacted by the total dissolved solids (TDS) of the recycled brine. Results from the studies above are summarized in Chapter 4 through Chapter 7.

A framework for water production prediction was developed in Chapter 4. Water production models were developed with Arps equation for horizontal wells from five fields in Wattenberg field. For a better data fitting and modeling, three time periods were defined: Frac flowback, transition period and produced water. The frac flowback period is the first one month after production starts, followed with 5 months of the transition period and, thereafter, produced

water period. A correlation was found between water production volume and locations of wells,; thus, location is very important for estimating water production. Additionally, wells with low gas-oil-ratio (GOR) tend to have higher water recovery.

In Chapter 5, sources of variability in flowback and produced water volumes from horizontal oil and gas wells were identified from external factors (time, location, type of frac fluids, wellbore length, and water source).. Horizontal wells in the Denver-Julesburg basin operated by Noble Energy were studied and results show that water production varies with time, location and wellbore length.. Additionally, production volume variation with fracturing fluid type and water source (fresh versus recycled) was explored. Results indicate that both of these variables should also be considered when developing a general model for water production. A guar-based frac fluid resulted in greater water production when compared to a cellulose derivative-based fluid. Finally, wells fractured with a fresh water based fluid had significantly greater produced water volume than geospatially-paired wells with a 1/7-recycled/fresh blend based fluid.

Chapter 6 provides a qualitative and quantitative characterization of solids in frac flowback and produced water from five horizontal wells at two separate sites in the Wattenberg field of Northern Colorado. The difference in solids from wells fractured with fresh water and recycled water is compared, and their distribution and characterization are identified by particle size distribution measurement and X-ray photoelectron spectroscopy (XPS). Results show that particle were smaller and more uniform in produced water samples collected during the first week of production from the wells fractured with recycled water, suggesting that the recycled water was more compatible with the shale formation and wells fractured with recycled water tend to clean out faster.

Chapter 7 investigates two of the fundamental mechanisms of LSF, clay swelling and diffused double layer (DDL) expansion. Both mechanisms are impacted by the salinity/total dissolved solids (TDS) concentration of the injection water. To test these mechanisms, clay swelling tests and real-time contact angle measurements were performed in this study. Spontaneous imbibition was also conducted, with Niobrara shale core plugs from Denver-Julesburg Basin, to compare oil recovery from low salinity and high salinity brine. Results show an increase in oil recovery when the TDS of brine falls between 400 and 10,000 mg/L. These results also indicate that LSF improves oil recovery from unconventional shale formation, and therefore, an optimal TDS concentration exists for highest oil recovery.

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# 1. Introduction

With the expansion of unconventional oil and gas development in North America, water-related issues have been brought to concern for both well operators and service suppliers (IHS, 2012; Accenture, 2012). Since the invention of horizontal drilling, it has been widely adopted because of its higher production efficiency. A Large volume of fresh water is required for drilling and hydraulic fracturing of a horizontal well (King, 2013; Stephen, 2013). On the other hand, a significant amount of wastewater is generated along with the production of hydrocarbon (Sunshine, 2014; U.S. EPA, 2015). Historically the waste water was disposed into deep injection wells; however, new regulations from U.S. EPA have forced both operators and service suppliers to seek for alternatives for managing wastewater from shale oil and gas wells such as reusing the treated flowback and produced water.

In order to successfully reuse the frac flowback and produced water from oil and gas wells, several questions have to be answered: What is the quantity and quality of the frac flowback and produced water? What is the water quality required for reusing the wastewater? How the recycling/reusing affect oil and gas production? As a result, a lot of efforts are required to fully understand and address these questions.

In this document, a review of the literature with an emphasis on water management and impacts on oil and gas production from low salinity water flooding is provided in Chapter 2. An outline of the research objectives is presented in Chapter 3. Chapter 4 and 5 provide analysis of water production prediction from horizontal wells in Wattenberg Field and the variables in prediction. Chapter 6 illustrates an in-depth characterization of solids in flowback and produced water from horizontal wells fractured with fresh and recycled water. In Chapter 7, fundamental

mechanisms of low salinity waterflooding on shale cores have been studied to determine the optimal TDS concentrations for best oil recovery rate.

## 2. Literature Review

### 2.1 Introduction

By the end of 2012, the proved onshore shale oil and gas reserves in the United States were 7.34 billion barrels and 129.4 trillion cubic feet separately. More than 90% of the shale oil reserves came from five shale plays: Eagle Ford, Bakken, Barnett, Marcellus and Niobrara (U.S. EIA, 2014). According to the 2014 Annual Energy Outlook by U.S. EIA, 63% of energy use by the end of year 2012 was from oil and natural gas (Figure 2-1). With a projection from 2012 to 2040, an annual increase rate of 0.8%/year in natural gas consumption is predicted (Figure 2-1), which is driven by the increase in natural gas use for electricity generation and industrial use (U.S. EIA, 2014).

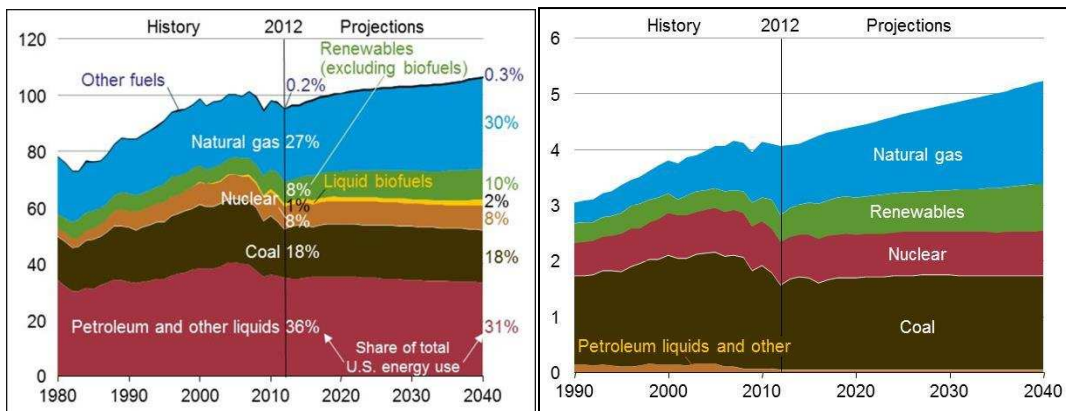


Figure 2-1. Primary energy use and electricity generation in the United States by fuel (U.S.EIA, 2014)

There are two main origins for natural hydrocarbon: Thermogenic and biogenic/microbial. Thermogenic hydrocarbon is derived from buried organic matter that is subjected to increased temperature and pressure with increased burial in the subsurface and is typically produced over 3,000 feet underground. Biogenic/microbial hydrocarbon is derived from the metabolic processes of organisms near the surface, and it is composed almost purely of methane and can be found in

sediment at depths of 10 to 300 feet underground. Organic rich shales are very common thermogenic resources, and hydrocarbons can inevitably migrate from these source rocks into porous conventional reservoirs (Gurule, 2013).

Figure 2-2 shows a sketch of the types of hydrocarbon deposits including both conventional and unconventional resources, which are defined based on the relative ease of development, cost, and recovery techniques. Conventional hydrocarbon resources generally consist of reservoir rocks with relatively high permeability, and can be targeted with vertical wells. Unconventional reservoirs typically have lower porosity and permeability, and hydrocarbons are usually distributed throughout pore spaces. As a result, specialized technology (such as hydraulic fracturing) is required to extract oil and gas from unconventional reservoir. Therefore, it is usually easier and cheaper to produce conventional hydrocarbons (Perry and Lee, 2007).

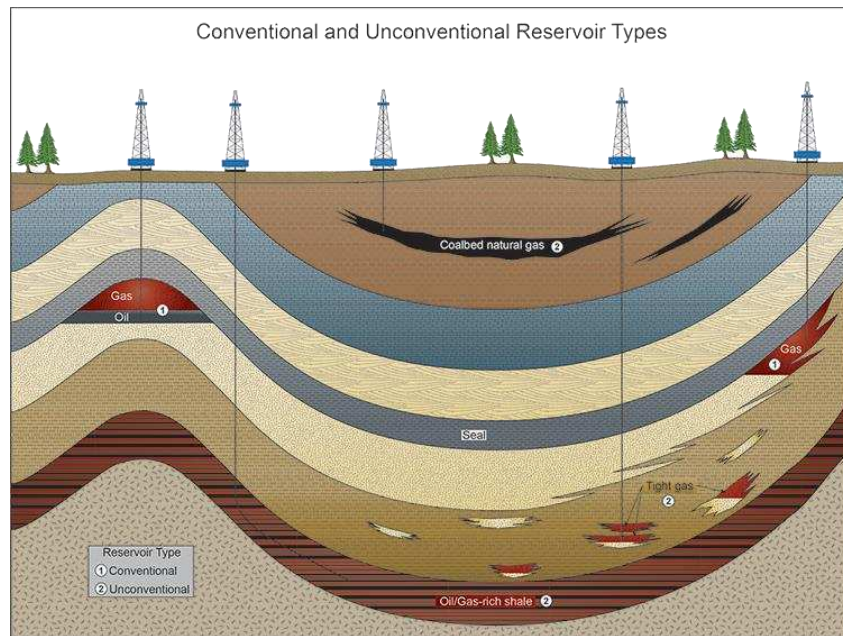


Figure 2-2. Types of conventional and unconventional hydrocarbon deposits (Wyoming State Geological Survey)

With the increase in energy demand, oil and gas companies have been putting more efforts into exploring and developing unconventional hydrocarbons. There are more than 20 shale plays in the lower 48 states of United States (Figure 2-3), and they are found through the Mountain West, the South and throughout the Northeast's Appalachian Basin (U.S. EIA, 2011). In order to extract oil and gas from deep shale plays, hydraulic fracturing was developed and widely used to create fractures in the rocks to allow hydrocarbons to flow out. Typically water and sand make up 98 to 99.5 percent of the hydraulic fracturing fluid, and the remaining 0.5 to 2 percent is comprised of chemical additives such as gel, crosslinkers, and breakers (Hubbert and Willis, 1972). Water use for hydraulic fracturing varies from basin to basin, and in the Greater Wattenberg field part of the Denver-Julesburg Basin, an average of 2.8 million gallons of water is used for a 20-stage horizontal well (Carlson, 2012; Goodwin and Douglas, 2012). As a result, a high wastewater volume is expected from the large amount of water used.

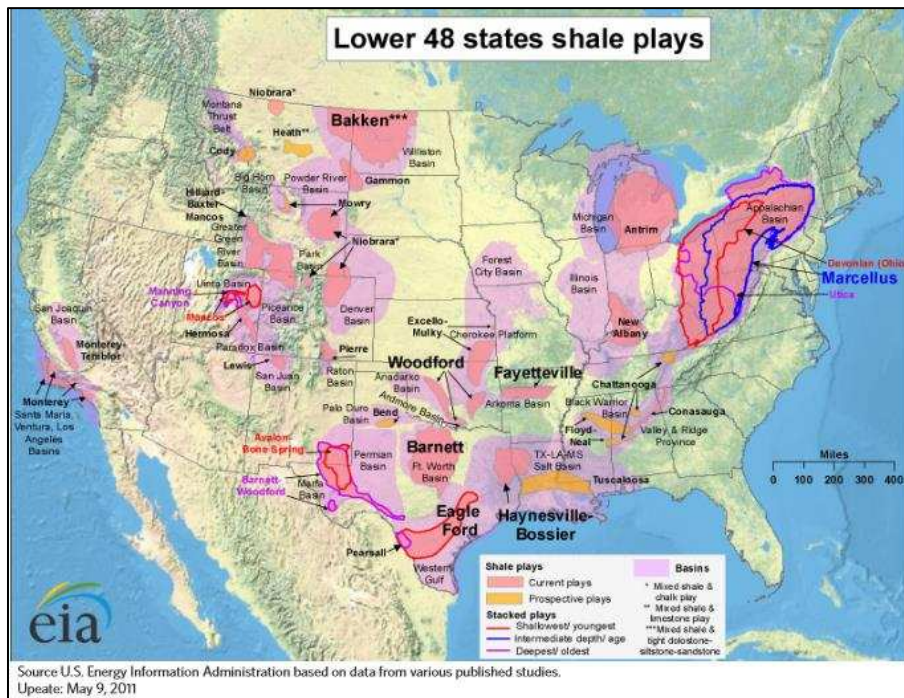


Figure 2-3. Map of U.S. shale gas and shale oil plays as of May 9, 2011. (U.S. EIA, 2011)

## **2.2 Water Production from Oil and Gas Wells**

Along with the extraction of oil and gas, water also comes to the surface as the largest waste stream (Neil, et al., 2004). It is estimated that 56 million barrels of produced water are generated every day from onshore oil and gas production in the United States (U.S. Government Accountability Office, 2012).

### **2.2.1 Sources and Mechanisms**

The sources of wastewater from oil and gas wells include hydraulic fracturing fluids, formation water, and aquifers. It is estimated that an average of 20-40% of injected hydraulic fracturing water is recovered, which made hydraulic fracturing water the major source of wastewater from shale gas wells (Schramm, 2011). Formation water is the water existing in the shale formation, and can be brought up to the surface with the production of oil and gas. Meanwhile, once a well is drilled through aquifers, it could also be a potential source of wastewater once the casing is failed.

### **2.2.2 Characteristics of Wastewater from Oil and Gas Wells**

Wastewater from oil and gas wells can be characterized as frac flowback water and produced water. Frac flowback water refers to the water returned during the early stage of production (usually 7-10 days after hydraulic fracturing), and it contains chemicals, metals, and other components that are used for hydraulic fracturing. Frac flowback water usually has high salinity and total dissolved solids (TDS) concentrations, as well as organics and metals from the fracturing fluids (Schramm, 2011). A comparison of water quality between feed water (water for hydraulic fracturing) and frac flowback water is shown in Table 2-1. A significant increase of TDS is observed from frac flowback water, as well as organic compounds like methanol and total organic carbon (TOC).

Table 2-1. Comparison of water quality between feed water and frac flowback (mg/L)

Parameter	Feed Water	Frac Flowback
<b>pH</b>	8.5	4.5 to 6.5
<b>Calcium</b>	22	22,200
<b>Magnesium</b>	6	1,940
<b>Sodium</b>	57	23,300
<b>Iron</b>	4	539
<b>Barium</b>	0.22	228
<b>Strontium</b>	0.45	4,030
<b>Manganese</b>	1	4
<b>Sulfate</b>	5	32
<b>Chloride</b>	20	121,000
<b>Methanol</b>	-	2,280
<b>TOC</b>	-	5,690

Produced water is defined as any water that is produced after frac flowback. It can be either formation water or hydraulic fracturing water left in the formation. Typically produced water flows throughout the entire lifecycle of a well along with the oil and gas generation. It is not clearly understood when frac flowback switches to produced water, and it can vary from a few days to a couple of weeks. This (produced) water is very saline with high TDS, and has similar water quality to formation water. Highly dependent on the location and formation, the produced water quality can vary significantly (Schramm, 2011). It is also believed that produced water has higher TOC concentrations due to the grease and oil in the water. Average produced water TDS concentration from six shale plays in the United States is shown in Table 2-2.

Table 2-2. Produced water TDS concentrations in different shale plays (Alleman, 2011)

Shale Play	Range of TDS (mg/L)
<b>Barnett</b>	500 to 200,000
<b>Fayetteville</b>	3,000 to 80,000
<b>Haynesville</b>	500 to 250,000
<b>Marcellus</b>	10,000 to 300,000
<b>Woodford</b>	500 to 40,000
<b>Niobrara</b>	1,000 to 200,000

### 2.2.3 Water Production Modeling

In order to better understand the water production from shale oil and gas wells, a water production model was developed based on Noble Energy, Inc. (Noble) wells in Wattenberg field, Northern Colorado. Frac flowback and produced water were modeled with Arps Equation, which was commonly used for oil production from shale reservoirs (Bai, 2013). In Bai's study, frac flowback period was defined as the first 30 days after hydraulic fracturing, followed by produced water period. Figure 2-4 shows the modeled production rate for both horizontal and vertical wells in Wattenberg field, Northern Colorado. It is clearly observed that horizontal wells have much higher water production than vertical wells, and the same trend was shown in oil and gas production too.

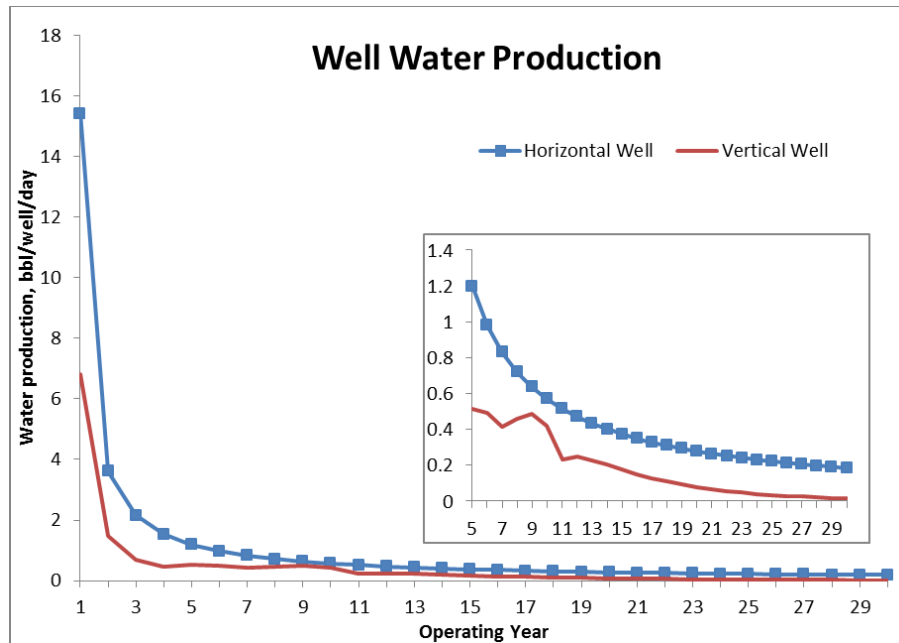


Figure 2-4. Modeled horizontal and vertical well water production in Wattenberg field

Water quantity can be used for defining frac flowback and produced water; however, the more accurate model can be developed when water quality is considered as well. Due to the



difficulty in obtaining wastewater quality data from shale oil and gas wells, there is no reported study on modeling frac flowback and produced water from the perspective of water quality.

#### **2.2.4 Current Water Management**

Currently most of the frac flowback and produced water is injected into deep disposal wells, and there are more than 30,000 injection wells around the nation for wastewater disposal from oil and gas wells (U.S.EPA, 2014). Although deep well injection has been widely adopted for wastewater management in oil and gas industry, it is considered unsafe because of the potential contamination of water aquifers and other related issues. All the operators are enforced to follow the disposal regulations in each state, and generally, these disposal wells were inspected at least once a year to ensure no contamination has occurred. Induced seismicity is another major concern of deep well injection, and earthquakes related to injection wells have been reported in Texas, Ohio, and Colorado. A 4.8 magnitude earthquake happened in South Texas where a lot of oil and gas wells are located, and seismologists explained that the injection of wastewater from oil and gas field was the cause (Bernier, 2011). The most recent earthquake reported in Greeley, CO was also believed to be due to deep well injection of wastewater from oil and gas fields (Dunn, 2014). Because of all the potential impacts from deep well injection, no new disposal well is permitted by EPA and oil companies have to find alternatives for handling wastewater (Vidic, 2010).

Other possible wastewater management practices are evaporation ponds; disposal to publicly owned treatment works (POTWs); and treatment for reuse or surface discharge. However, all these options are limited by the high salinity and TDS concentrations in the frac flowback and produced water.. Figure 2-5 shows an example of the treatment process for produced water, and it can vary significantly depending on the end use of treated water. For

instance, a TDS removal process (Reverse Osmosis) is required for surface discharge and agricultural use, and for hydraulic fracturing water, TDS removal becomes not critical (Kimball, 2010).

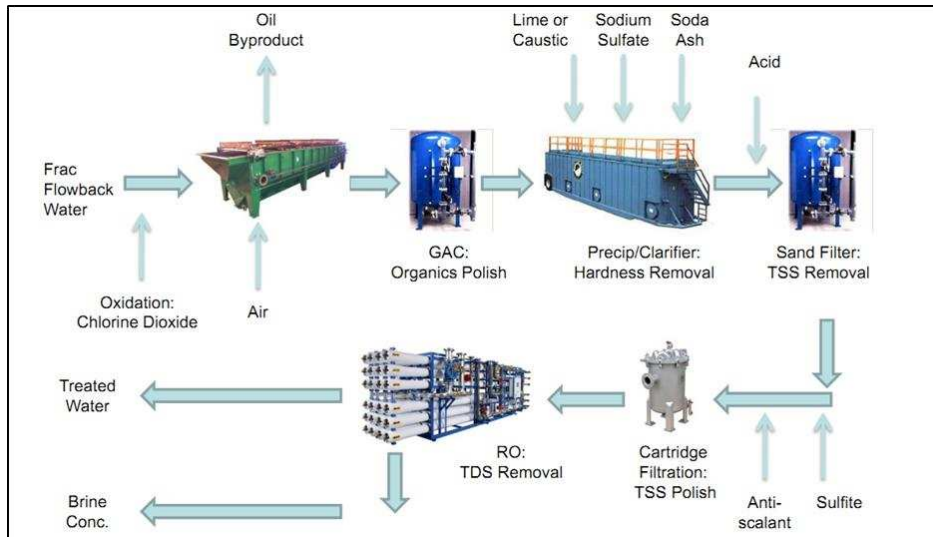


Figure 2-5. An example of produced water treatment process

In order to improve the water-energy sufficiency and eliminate environmental impacts from disposing of wastewater, oil and gas companies have started reusing wastewater for hydraulic fracturing. By recycling wastewater on site, both the fresh water demand for hydraulic fracturing and the number of truck trips for water delivery are decreased. In the Wattenberg Field, an average of 2.8 million gallons of water is used to drill and hydraulic fracturing one 20 stage horizontal well (Goodwin, 2012), and 30% of that water is recovered during the first 30 days of production. However, due to the complexity of the chemical composition of the wastewater, there are still concerns regarding the scaling of the well caused by using recycled water. Further studies are required to identify the essential compounds that need to be removed for recycling (Pickett, 2009).

## **2.3 Oil Recovery from Conventional and Unconventional Natural Gas Fields**

In the United States, the average oil recovery rate from a conventional oil well is between 5 – 15% after the primary recovery stage, and it could reach 35 – 45% after the secondary recovery stage (Tzimas, 2005). The primary recovery stage refers to the production period that was driven naturally by reservoir pressure, and the pressure will fall over the lifetime of the well. When the pressure is insufficient to force the oil to come up to the surface, secondary recovery methods are applied to increase the reservoir pressure by water injection, natural gas injection and gas lift (Tzimas, 2005; Nilsen, 2015).

For unconventional wells, the average recovery factors for shale gas generally ranged from 20 to 30 percent, with values as low as 15 and as high as 35 (U.S. EIA, 2013). However, the recovery rate can vary significantly from different shale plays; even in the same basin, there can be significant variations in depth, porosity, carbon content, pore pressure, clay content, thermal maturity, and water content that could lead to different oil recovery rates (U.S. EIA, 2011).

### **2.3.1 Enhanced Oil Recovery (EOR) in Conventional Reservoirs**

In conventional oil and gas operations, low-salinity waterflooding (LSF) has been widely used to improve oil recovery. When Tang and Morrow (1997) reported a limited improve in crude oil recovery by LSF, the idea gained so many attentions that researchers and organizations tried to identify, reproduce and explain the theory behind it. A series of studies had been done and showed increases in oil recovery through the injection of diluted brine (Tang and Morrow, 1999; Patil, et al, 2008; Boussour, et al, 2009; Cissokho, et al, 2009; Robertson, 2010; Rivett, et al, 2010). An average of 5-15% incremental in oil recovery was observed with LSF (Henthorne, et al, 2013). Morrow and Tang (1998) identified that wettability of the clay and the composition

of the brine was two critical factors on LSF effects. Hughes, et al (2010) summarized the suggested LSF mechanisms in Table 2-3.

Table 2-3. Overview of suggested low salinity flooding mechanisms (Hughes, et al, 2012)

Effect type	Mechanism	Explanation	Reference	Indications
Pressure/ permeability	Osmosis	Distributed clays separating brine with different salinities create an additional (osmotic) pressure that enhances the water drive.	Buckley, 2009	Low salinity water flooding does not seem to work for mineral oil (River, 2009)
Pressure/ permeability	Clay particle (fine) movement	Due to the expansion of the electric double layer (and maybe also ion exchange) clay particles and other mixed-wet fines are removed from the rock surface at low salinity conditions leaving a water wet spot. The migrating fines might block narrow pore throats and cause microscopic diversion of the injected water.	Tang, 1999	Fines migration has sometimes been observed in low salinity core flooding but BP claims never to have seen this (Lager, 2006). Also refuted by (Rivett, 2009)
IFT reduction	Alkaline flooding behavior	pH rises during low salinity flood high enough to saponify certain components of the oil. Thereby lowering the interfacial tension between water and oil (in a similar way to alkaline flooding)	Buckley, 2009	pH increase is not seen in all experiments and is usually not as high as in alkaline flooding. (Buckley, 2009; Zhang, 2006)
IFT reduction	“Salt-in” effect	The charged oil components on the surfaces of the clays are easier to desorb and dissolve in the water phase; “salt-in” effect. The loosened particles lower the interfacial tension between water and oil like surfactant flooding.	Austad, 2008	This potential mechanism has not been widely discussed. Austad suggested experiments to check the theory which led to the pH-induced ion exchange theory (Austad, 2010)
Wettability change	Multicomponent Ion Exchange (MIE)	Due to expansion of the electric double layer and cation exchange capacity of the clay complex, bound charged organic components of the oil and substituted by $Ca^{2+}$ leading to an increase in water wetness	Lager, 2006-8; Ligthelm, 2009	Low salinity brines without $Ca^{2+}$ and $Mg^{2+}$ ions have been seen to increase recovery (Tang, 1999; Austad, 2010)
Wettability change	pH driven	The cation exchange capacity of the clays is triggered by near surface pH changes brought about by protons substituting $Ca^{2+}$ on the clay surfaces in low salinity water flooding.	Austad, 2010	No contraindications published yet, as the theory was first presented in April 2010.

### 2.3.3 Previous Studies on Factors Affecting EOR

#### *Wettability and Spontaneous Imbibition*

With the success of LSF in conventional oil and gas reservoir, more attentions had been gained on the suitability of LSF in unconventional shale reservoir. According to a 10-year study of reusing frac fluids for hydraulic fracturing in Canada, gas production from wells that were fractured with recycled water was statistically higher than wells fractured with fresh water (Monroe, et al, 2013). No other similar reports have been published since the reuse of frac flowback and produced water is still on its early stage. However, many laboratory tests have been done to measure the wettability of shale rocks to verify the impact on oil production from saline water. Amott-Harvey index is usually used to describe the wettability of a rock in drainage processes (oil wet or water wet), with the definition of  $AI = I_w - I_o$ ,  $I_w$  is the water wet index and  $I_o$  is the oil wet index of rock, and they both can be obtained from core analysis (Amott, 1959; Dake, 1977). Spontaneous (or capillary) imbibition is one of the most commonly used methods to evaluate the impact. Imbibition of frac fluids into the rock matrix has been identified as one of the mechanisms for fluid loss and reservoir damage (Paktinat, et al, 2006; Bahrami, et al, 2012). Shale core samples from different fields were also tested in several spontaneous imbibition studies.

Dehghanpour, et al (2013) measured spontaneous imbibition on shale samples from Horn River basin in Canada. Freshwater and KCl brine (2, 4, and 6 wt %) were used as imbibition fluids. Their results showed a noticeable imbibition rate enhancement during the first 20 hours of imbibition from KCl brine than fresh water, however, no significant difference in oil recovery rate was observed at different KCl concentrations. The results indicated that brine can

spontaneously induce microfractures in organic shale, and the presence of KCl does not consistently influence the imbibition rate.

In another study, Onyenwere (2012) tested the impacts on spontaneous imbibition rates from the addition of HCl, NaCl, and KCl. Results indicated that oil recovery rate decreased from 59% to 4% with the increase of NaCl concentration from 5 wt % to 30 wt %. The same trend was also observed from KCl brine when the concentration increased from 5 wt % to 10 wt %. Meanwhile, the addition of HCl could generally increase the porosity of core samples; however, it's highly dependable on the basin.

Similar studies have been done by Chen (2011) and Morsy (2014). In Chen's study, oil recovery rate increased significantly when surfactants were added to the brine. Surfactants can alter the wettability of rock from oil wet to water wet, and lower the interfacial tensions between the fractures and the matrix. Also, the shale core properties such as core dimension, permeability, and heterogeneity of porous medium can all affect the rate of spontaneous imbibition. In Morsy's study with shale cores from Eagle Ford shale, oil recovery rate was enhanced by alkaline flooding, which showed same results as Chen's that shale wettability was altered to strongly water-wet by using low alkaline concentrations. Morse's study also showed an enhancement in oil recovery from the Eagle Ford shale by mineral dissolution using low pH and high pH solutions.

Morsy and Sheng (2014) tested the imbibition characteristics of the Barnett shale and Marcellus shale formation. Results showed an increase in oil recovery from Barnett shale formation with different pH or alkaline solutions; however no similar observation was noticed in Marcellus shale formation. The comparison suggested that different amounts of clay content in

two formations could lead to various reactions. Also, their study indicated that clay swelling was the theory to explain the change in oil recovery.

Nasralla, et al. (2015) investigated the potential of low salinity waterflood to improve oil recovery in carbonate reservoirs by qualitative core flood, and their results suggested that the composition and salinity of brine have impacts on oil recovery in carbonate reservoirs: With low salinity brines, the rock wettability was altered towards less oil-wetness and the oil recovery was improved compared to seawater injection (high salinity brine).

A Halliburton study (Nguyen, et al. 2015) also demonstrated how low-salinity brine enhanced oil production in liquids-rich shale formations. Through a series of tests (including interfacial tension measurement, oil recovery test, emulsion tendency measurement, etc.), results all indicated that brine salinities have a significant impact on oil recovery for liquids-rich shale plays. Low salinity brines appeared to be more effective than high salinity brines, and the addition of surfactant yielded higher recovery at all salinities. However, in this study, the lowest brine salinity was 11,149 mg/L, which is still considered high salinity for a hydraulic fracturing process. Similar studies could be necessary at a lower salinity range (0 – 10,000 mg/L) for further understanding of the low salinity waterflood in unconventional shale.

### ***Contact Angle/Surface Tension Measurement***

Although spontaneous imbibition is commonly used to measure wettability and oil recovery rate in different brines, it has many limitations such as complex preparation processes, long experimental time and lower observation resolution. Mahani, et al (2014) introduced a new protocol to measure the basic kinetics of low-salinity waterflooding effect by measuring real-time contact angle between oil droplets and shale surface under different saline water. Oil was dropped onto the surface of shale patches which was submerged in high salinity (HS) brine and

the shape of droplets was constantly captured by camera until they became stable. The solution was then replaced with lower salinity (LS) brine, and the change of droplets' shapes was captured by high-resolution camera. The results showed in brine with a lower salinity, oil drops tended to detach the shale surface by increasing the contact angle and reducing the contact area (Figure 2-6). This study provided insights into a more fundamental understanding of oil/clay interaction. It demonstrated a rapid and accurate measurement on the change of wettability of shale; however, it cannot represent the real field condition since this measurement only focused on shale surface.

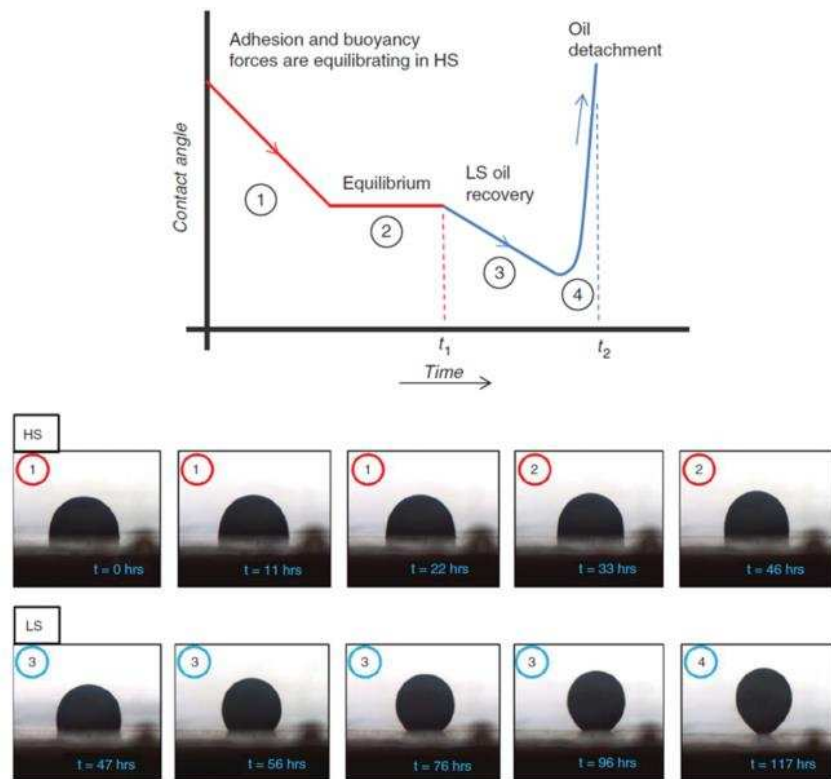


Figure 2-6. Oil droplet under HS brine and LS brine. The number on the pictures designate the events described in the figure above (Mahani, et al. 2014).



## Clay Swelling

Another interaction between the clay and fluid is clay swelling, which has been a major concern during the production of oil and gas. It was believed that the swelling of the clay could lead to a decrease in the porosity and permeability of the source rock, and eventually a decrease in hydrocarbon production. Typical swelling clays can absorb 200% or more of their mass in water, and increase their volume by more than 20 times (Mooney et al., 1952; Norrish and Quirk, 1954). As a member of the smectite group, montmorillonite is the most commonly used clay for swelling tests. Clay swelling happens when water molecules squeeze into the chemical structures of the clay minerals, and this causes an expansion of the clay volume. Figure 2-7 illustrates the mechanism of clay swelling.

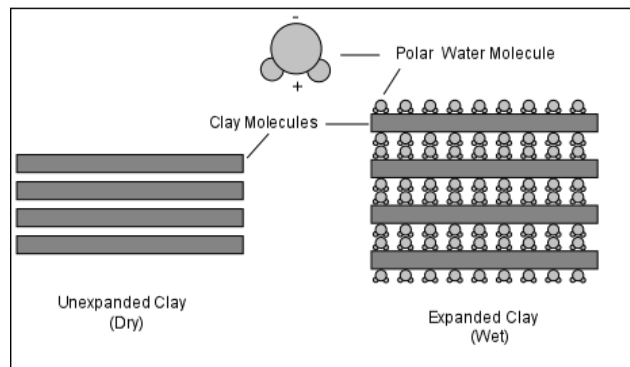


Figure 2-7. Mechanism of clay swelling (Expansive soil diagram, Tulane University).

In unconventional shale formation, clay swelling has also been observed in several studies (Chenevert, 1973; Osisanya, 1991; Chenevert and Osisanya, 1992). Although almost every study showed the occurrence of swelling in lab experiment, there is not any study performed on downhole conditions. Therefore, it is still not clear if clay swelling affects the hydraulic fracturing process and the production of hydrocarbons from unconventional shale formation. However, clay stabilizers are commonly added to fracturing fluids to prevent clay

swelling in all of the hydraulic fracturing jobs. Potassium chloride (KCl) is the most commonly used clay stabilizer, and the concentration of KCl in fracturing fluid could vary from 1 to 10%, based on the clay content in the shale. Gdanski (2000) introduced the “7% KCl” rule indicating that the operator may simply assume the worst case and choose to mix 7% of KCl water as base fracturing fluid. However, an average of 1.5 to 2% of KCl is adapted by most of the operators.

This study will focus on combining these two mechanisms (wettability alteration and clay swelling) and evaluating the applicability of LSF in unconventional oil and gas field in the Wattenberg field in Northern Colorado.

### 3. Research Objectives

Reuse of frac flowback and produced water for drilling and hydraulic fracturing of new wells has led to the following research questions: How much wastewater is expected? What treatment is required for beneficially reusing the wastewater? What could be the potential impact on well performance by using recycled water? Due to limited data collection and proprietary requirements from oil and gas operators, there are just limited published findings to answer these questions.

To gain a better understanding of these questions, this study proposes following research objectives:

- 1. Spatial analysis of wastewater (frac flowback and produced water) production from horizontal wells in the Wattenberg field.**

In the oil and gas industry, estimated ultimate recovery (EUR) is the most commonly used term for describing the approximate quantity of potentially recoverable oil or gas of a well. Many studies have been done to provide the best prediction of EUR since it is the most important criterion of a well. Today, many different methods and units can be used for calculating EUR. While most of the attentions were focused on the potential quantity of oil and gas, a lot of concerns have been raised upon the wastewater. Unfortunately, very limited studies were done regarding wastewater production from unconventional oil and gas field.

A framework will be proposed to estimate the volume of wastewater from horizontal shale oil and gas wells in the Wattenberg field. Water production prediction models will

be developed from different areas in the Wattenberg field, and the correlation between water production and locations of wells (or gas-oil-ratio value) will be investigated.

**2. Assessment of the variables in frac flowback and produced water volumes from shale oil and gas wells.**

In addition to the development of water production model, potential factors that could impact water production will also be studied. With the provided information from Noble Energy, Inc. following proposed sources of variability will be tested including time, location, wellbore length, type of frac fluids and the water source. For each variable, water production from two paired sets of wells will be compared with statistical analysis.

**3. Evaluation of the impacts on the characteristics and particle sizes of solids in early flowback water from the use of recycled water as fracturing fluid.**

When operators started increasing the number of fracturing jobs with recycled water, their biggest concern was the unknown impacts on well performance from organic compounds and high salts concentration in the recycled water. These impacts will be investigated through characterizing and comparing the solids in early flowback water collected from both fresh and recycled water fractured wells.

**4. Understanding of two hypothetical mechanisms of low salinity waterflood in unconventional shale wells: clay swelling and double layer expansion.**

Oil recovery has been enhanced by slightly increasing the total dissolved solids (TDS) concentration of the water used in conventional oil and gas field. It is still questionable whether the same result will be observed in unconventional shale formation. To understand how TDS affects oil recovery from unconventional oil and gas wells, two fundamental mechanisms for low salinity waterflood (LSF) are proposed to be evaluated:

clay swelling and double layer expansion. Shale cores from Niobrara formation in the Wattenberg field will be tested. These two mechanisms will be demonstrated separately through clay swelling test and real-time contact angle measurement and the applicability of LSF on shale cores will be evaluated by spontaneous imbibition test. All these tests will focus on how oil recovery rate is affected by the TDS concentration of brine. Furthermore, an optimal TDS concentration will be determined to give the highest oil recovery rate based on the test results.

**5. Understanding the impacts from organic matters on the interaction of TDS with the formation and subsequent oil recovery rate.**

To investigate the impacts on oil recovery from organic compounds in the recycled field water, lab modeled water will be used for spontaneous imbibition and contact angle measurements to compare with field water at various TDS concentrations.

## **4. Spatial Analysis of Horizontal Shale Well Water Production in the Wattenberg Field<sup>1</sup>**

### **4.1 Introduction**

In 2009, the U.S. Energy Information Administration (EIA, 2012) estimated the natural gas reserve of the Wattenberg field in the Denver-Julesburg Basin to be 195.3 billion cubic feet, and Raabe (2011) predicted a reserve of 1 to 2 billion barrels of oil equivalent in the Wattenberg field. As of February 2013, more than 22,000 active shale wells are producing about 100,000 barrels of oil and 740 million cubic feet of natural gas daily in the Wattenberg field (Colorado Oil and Gas Conservation Commission, 2013).

In Colorado, the average water use for hydraulic fracturing a 20-stage horizontal shale well is 2.8 million gallons or 68,357 barrels (Goodwin et al., 2013), and up to 30% of that water is recovered in the first year of production (Bai et al., 2015). With the significant volume of wastewater, known as frac flowback and produced water, generated during the first year of production, operators are motivated to reuse the wastewater for future hydraulic fracturing jobs. To reuse wastewater from the oilfield for hydraulic fracturing, a thorough understanding of both quality and quantity of the wastewater becomes essential. Water quality of flowback and produced water has been widely investigated in many studies (Benko and Drewes, 2008; Alley et al., 2011; Barbot et al., 2013; Li 2016) and showed that wells may clean out faster when recycled water is used as hydraulic fracturing fluids. However, due to the limitation and complexity of

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<sup>1</sup> **As Submitted to SPE Oil and Gas Facilities**

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production data, very few studies focused on the quantity of wastewater from oilfield (Clark et al., 2009; Kimball, 2011; Carlson, 2012; Bai et al., 2013). Bai (2015) demonstrated the use of the Arps equation for modeling wastewater from horizontal shale wells, and also showed that the volume of frac flowback can vary significantly in different locations.

In this study, a spatial analysis of water production from horizontal wells in the Wattenberg field was performed. Water production models were developed for wells in five sections of the Wattenberg field in northeastern Colorado, and the correlation between water production and the GOR value of each section was investigated.

## 4.2 Methods and Materials

### 4.2.1 Site Location

Locations of studied wells in the five sections are shown in Figure 4-1. Section 1 to 4 is within the traditional Wattenberg field, and section 5 is located approximately 20 miles northeast. All wells in this study are within Niobrara shale formation.

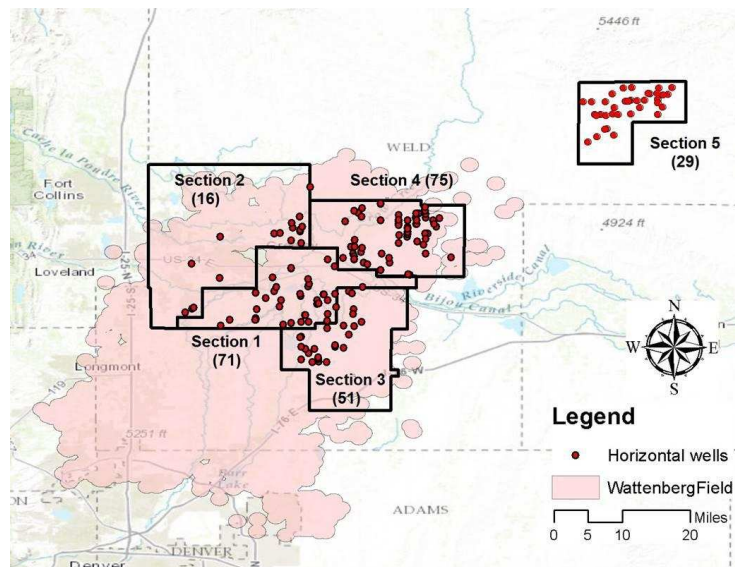


Figure 4-1. Location of wells in five sections with the number of wells in parenthesis

## **4.2.2 Analyzing Methods**

Daily water production data for one year was averaged from all studied wells in each field, and fit into three time periods: frac flowback, transition and produced water. The frac flowback period was the first 30 days of production, the transition period was the following 133 days, and water returned after the transition period was defined as produced water. Power decline and Arps equation were used for water production modeling. Water production volume from the five sections was compared to investigate the correlation between water production and GOR.

## **4.3 Results and Discussion**

### **4.3.1 Gas-Oil-Ratio of Five Fields**

The general GOR map of the five sections of the Wattenberg that were studied is shown in Figure 4-2. Wells with high GOR value are defined as gas wells so fewer liquids should be expected from these wells, and wells with low GOR value are typically oil wells with more liquids being produced. According to the GOR map, the five sections in this paper were divided into three GOR tiers: High GOR tier – section 1, middle GOR tier – sections 2 and 3, and low GOR tier – sections 4 and 5. Gas and oil production data from wells in five sections was collected from Colorado Oil and Gas Conservation Commission, and used for the calculation of GOR value of each individual well. The average GOR value of each section is calculated from all the wells within the field and summarized in Table 4-1.



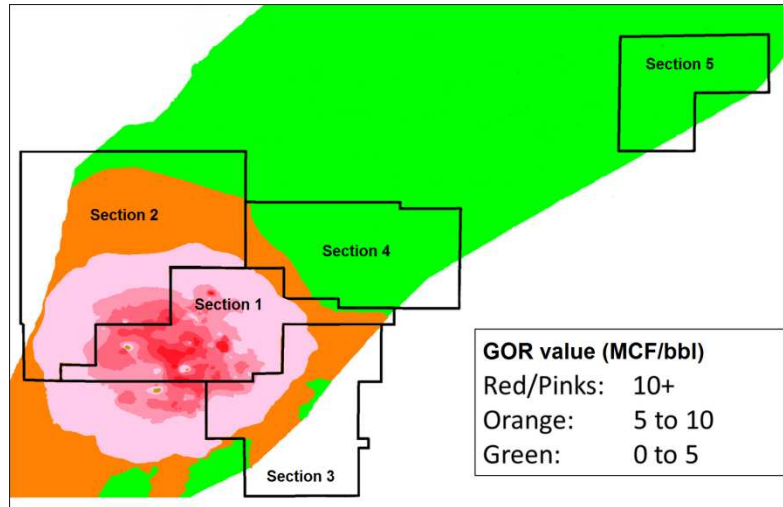


Figure 4-2. General GOR map of five sections across the northeastern Wattenberg field.

Table 4-1. Average GOR value of each section

Section #	# of wells	Average GOR (MCF/bbl)
1	71	11.56 ± 0.88
2	16	10.04 ± 1.02
3	51	10.75 ± 0.73
4	75	3.09 ± 0.17
5	29	2.78 ± 0.48

### 4.3.2 Water Production and Recovery

Daily water production models for each section are summarized in Table 4-2. All production data were modeled with the Arps equation except for frac flowback water from sections 1 to 3, which were fitted with the power decline function. In Table 4-2,  $q$  is the water production rate (bbls/day) at day  $t$ .

Table 4-2. Modeled water production equations for three time periods in five sections.

Section #	# of wells	Frac flowback (Day 1-30)	Transition (Day 31-163)*	Produced water (After day 164)**
1	71	$q = 1043.04t^{-0.721}$	$q = \frac{90}{(1 + 0.0529t)^{0.769}}$	$q = \frac{19.4084}{(1 + 0.00715t)^{0.588}}$
2	16	$q = 1406.48t^{-0.863}$	$q = \frac{74.65}{(1 + 0.011t)^{2.083}}$	$q = \frac{12.93}{(1 + 0.0039t)^{0.625}}$
3	51	$q = 1157.61t^{-0.725}$	$q = \frac{98.49}{(1 + 0.0693t)^{0.652}}$	$q = \frac{22.99}{(1 + 0.0119t)^{0.682}}$
4	75	$q = \frac{1516}{(1 + 0.0614t)^{2.092}}$	$q = \frac{176.33}{(1 + 0.0374t)^{1.006}}$	$q = \frac{29.39}{(1 + 0.00034t)^{1.112}}$
5	29	$q = \frac{1590}{(1 + 0.2492t)^{1.055}}$	$q = \frac{165.92}{(1 + 0.057t)^{0.7424}}$	$q = \frac{33.62}{(1 + 0.00837t)^{0.833}}$

Table 4-3 summarizes the averaged 1-year water volume with 95% confidence intervals from each time period. Also, a 20-year total water volume is calculated based on the models in Table 4-2. From Table 4-3, a major difference in water production volume exists in the first year of operation, while the total water volume from the following 19 years is predicted to be approximately 20,000 bbls. Boxplots of the first year water production volume are shown in Figure 4-3, and Figure 4-4 shows the boxplots of average water use for each field.

Table 4-3. Comparison of water production volume from five sections

Section #	1-year water volume (actual data) with 95% CI (bbl)				20-year total (predicted) (bbl)
	Frac flowback	Transition	Produced water	Total	
1	5,111 ± 602	4,334 ± 546	2,652 ± 421	12,097 ± 1,247	37,815
2	5,091 ± 1,262	3,491 ± 770	1,787 ± 376	10,369 ± 1,867	33,006
3	4,797 ± 580	4,511 ± 627	2,620 ± 413	11,928 ± 1,290	30,949
4	12,938 ± 762	7,310 ± 530	3,156 ± 528	23,404 ± 1,068	45,776
5	11,957 ± 1,076	6,315 ± 1,313	2,869 ± 671	21,141 ± 2,835	44,253

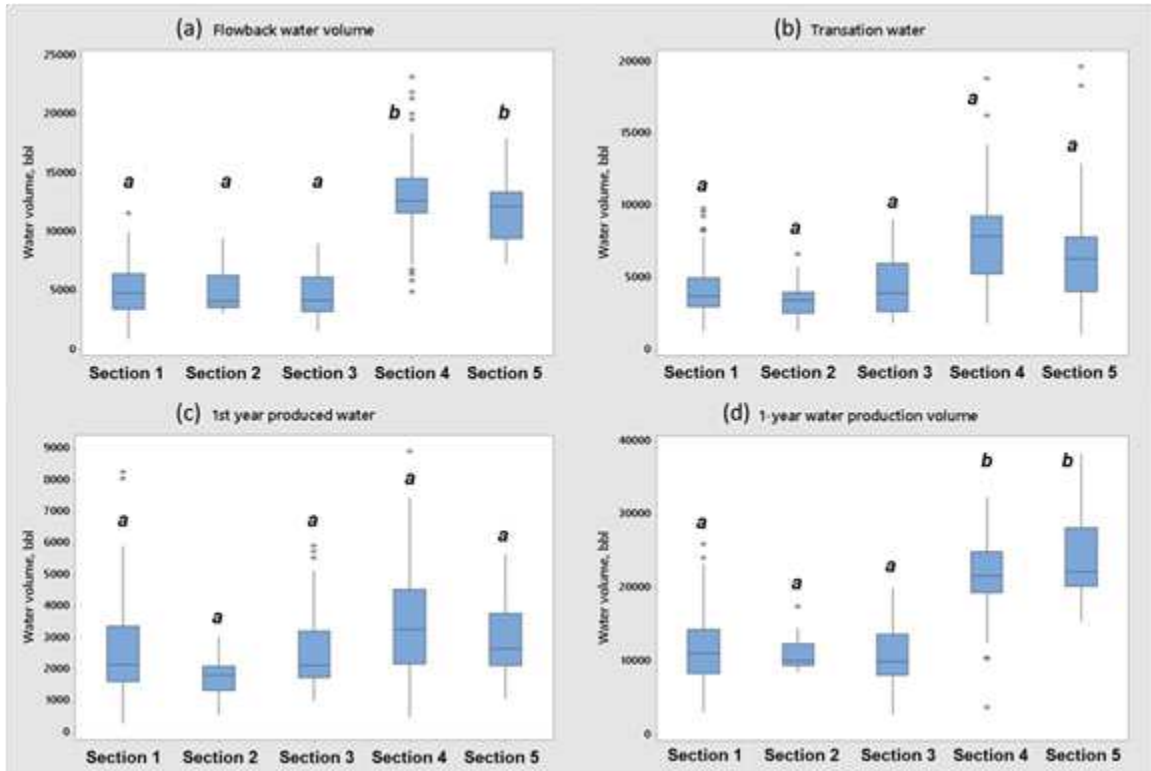


Figure 4-3. Boxplots and Tukey HSD post-hoc test of water volume in each time period from five sections: (a) frac flowback water, (b) transition water, (c) first year produced water and (d) 1-year total water volume. Within each graph, sections that do not share the same letter have significantly different means.

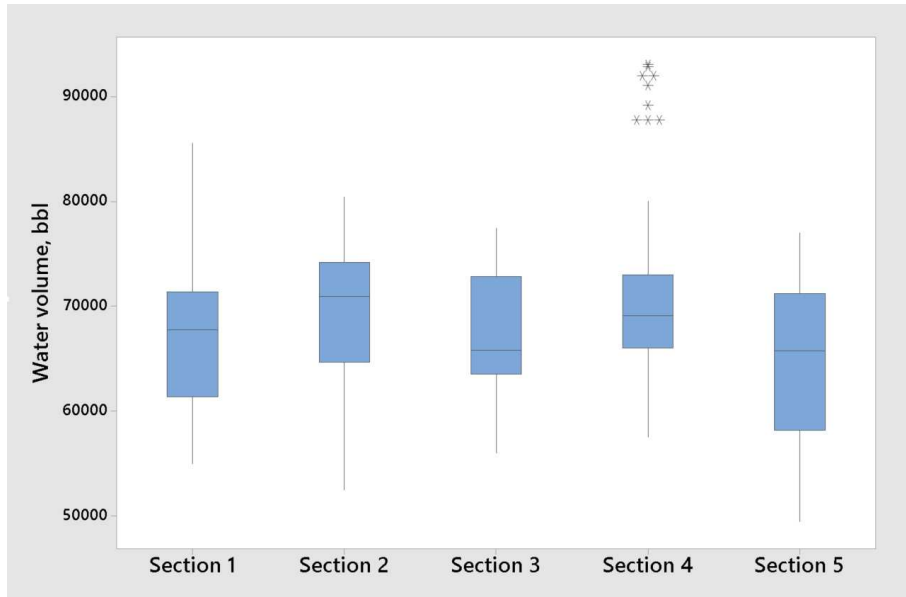


Figure 4-4. Boxplots of hydraulic fracturing water use for each section.

From Figure 4-3, sections 4 and 5 have significant higher frac flowback volume (ANOVA,  $p < 0.01$ ), but no significant difference is observed from transition water (ANOVA,  $p = 0.37$ ) and first year produced water (ANOVA,  $p = 0.15$ ). Meanwhile, according to Figure 4-4, no significant difference exists in water use among five sections (ANOVA,  $p = 0.54$ ). Results indicate that the difference in water production is mainly from frac flowback water. With low GOR value, sections 4 and 5 have higher water recovery during the first month of production. The average water recovery rate in each field is summarized in Table 4-4.

Table 4-4. Average water recovery rate from each section

Section #	Water Use with 95% CI (bbl)	Recovery rate=water volume/water use (%)			
		Frac flowback	Transition	Produced water	1-year total
1	68,214 ± 2,808	7.49	6.35	3.89	17.73
2	69,339 ± 3,943	7.34	5.03	2.58	14.95
3	66,931 ± 2,312	7.17	6.74	3.91	17.82
4	71,097 ± 1,366	18.20	10.28	4.44	32.92
5	65,337 ± 4,084	18.3	9.67	4.39	32.36

Water recovery rate from sections 4 and 5 is higher than the other three sections for the first year of production, and especially during the frac flowback period. Plots of water recovery against average GOR value of each section are shown in Figure 4-5, further proving that wells with low GOR value will have higher water production and water recovery rate.

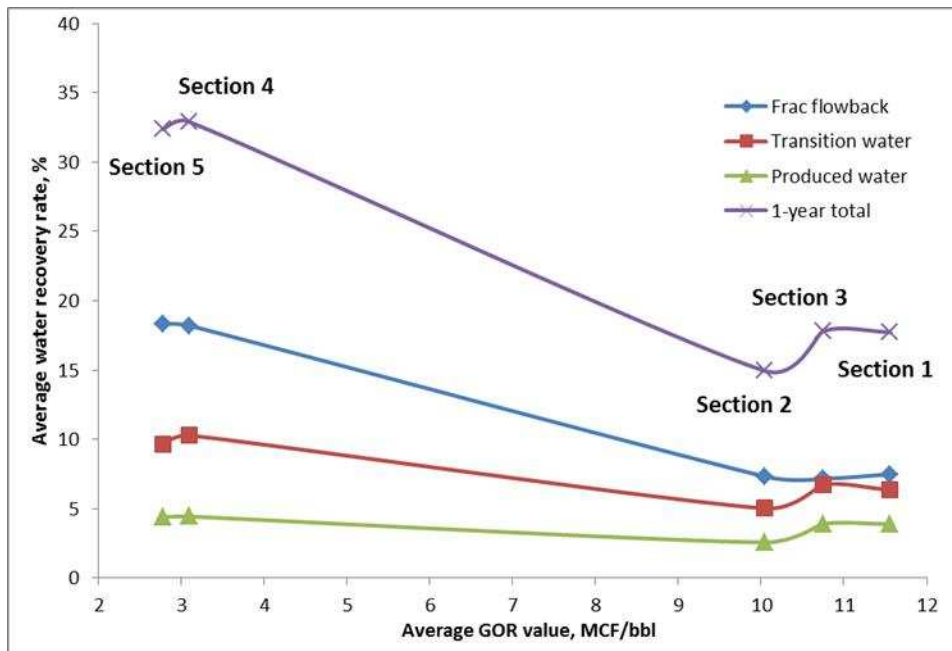


Figure 4-5. Correlation between GOR and water recovery for the first year of production.

## **4.4 Conclusion**

This study demonstrated a spatial analysis on water production from horizontal shale wells in five sections of the Wattenberg field. Water production models were developed for three time periods: frac flowback, transition water and produced water. After comparing the water production among the five sections, results show that GOR value of wells has a significant impact on water production, and furthermore, water recovery during the first year of production. Wells with low GOR value tend to produce more frac flowback during the first month. Therefore, location (or GOR value) is very important when it comes to estimating water production from shale oil and gas wells.

## **5. Sources of Variability in Flowback and Produced Water Volumes from Shale Oil and Gas Wells<sup>2</sup>**

### **5.1 Highlights**

- The focus is the Wattenberg Field, Denver-Julesburg basin (USA).
- Sources of variability in water production are examined.
- It provides factors for consideration when predicting water production in the future.

### **5.2 Keywords**

Variability; Frac Flowback; Produced Water; Wattenberg Field

### **5.3 Introduction**

Wastewater is the largest by-product in the shale oil and gas industry; about 21 billion bbls of water were produced in 2007 in the United States (Clark and Veil, 2009). Two major sources contribute to the production of wastewater: hydraulic fracturing water and formation or produced water. Hydraulic fracturing water, along with other chemicals that make up the frac fluids, is injected into the well to create fractures to allow hydrocarbons to be released (King, 2012). Water and sand make up 98 to 99.5 percent of the frac fluid, and the remaining 0.5 to 2 percent is comprised of chemical additives (FracFocus, 2013). Formation water is the solution naturally existing in the shale formation, typically with a high concentration of total dissolved solids (TDS) (U.S. Environmental Protection Agency, 2013).

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<sup>2</sup> **As Published in the Journal of Unconventional Oil and Gas Resources**  
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Northeast Colorado is in the midst of a shale oil and gas production boom. The proven total natural gas reserves in Colorado by the end of 2011 were 26,200 trillion cubic feet and Noble Energy alone has estimated its resources as 2.1 billion BOE (Stover, 2012). The majority of the shale oil and gas activity in Colorado is in the Greater Wattenberg field part of the Denver-Julesburg Basin. For drilling and hydraulically fracturing wells in the Wattenberg field, an average of 2.8 million gallons of water is used for 20-stage horizontal wells (Carlson, 2012; Goodwin and Douglas, 2012) resulting in production of high wastewater volumes. With the increased concern of water scarcity and environmental impacts such as soil and groundwater contamination, industry is working to optimize the management of wastewater from shale oil and gas wells. An essential component of an optimization strategy is recycling as much wastewater as possible for fracturing water. Therefore, it is important to understand the quantity and quality of the water produced so that treatment processes can be designed and sized for reusing the water (Kimball, 2011). Bai, et al. (2012) developed models to calculate and predict water production from the Wattenberg field using a limited set of data; however, it is still unclear what factors could impact the volume of flowback and produced water from shale oil and gas wells.

In this paper, water production from different horizontal wells in the DJ basin were analyzed and compared. Based on the data and information collected in this study, five potential sources of variability in the volume of water produced from shale oil and gas wells were examined and the results are summarized here.

#### **5.4 Methods and Materials**

Five potential sources of variability in water production volumes from oil and gas wells were examined in this paper; temporal, geospatial, wellbore length, type of frac fluid and water source. In order to evaluate these potential sources of variability, 149 Noble Energy horizontal



wells in the Denver-Julesburg basin were analyzed, including 86 wells in area A, 33 wells in area B and 30 wells outside these two areas (Figure 5-1).

Hydraulic fracturing water use for each well was collected from Noble Energy’s WellView® software (Peloton Computer Enterprises Ltd., Houston, TX). Daily water production data, frac fluid types and wellbore length (frac stages) data for each well was collected from Noble Energy’s Carte® program, which was part of the Merrick Systems Software (Merrick Systems Oil and Gas Technology Solutions, Houston, TX). The hydraulic fracturing water source data was collected from Noble Energy’s production engineers. Spatial data of all studied wells was collected from the GIS database of the Colorado Oil and Gas Conservation Commission (COGCC), and Figure 5-1 shows the locations of all studied wells in the Denver-Julesburg basin.

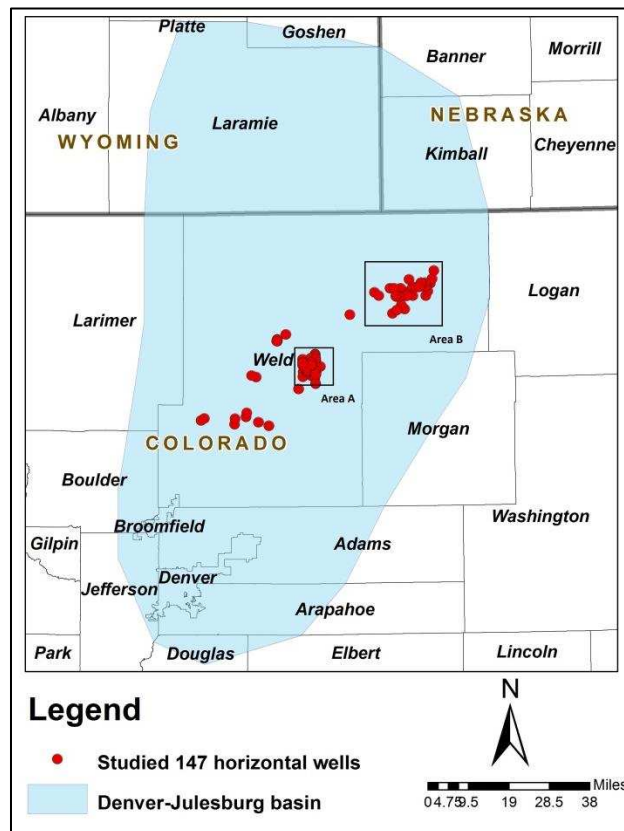


Figure 5-1. Locations of all studied wells in Denver-Julesburg Basin.

Temporal variability and wellbore length was evaluated with all the wells in area A, and spatial variability was studied with all the wells in area A and B. To examine how the type of frac fluid impacted water production, a sample of 28 wells was studied including 12 wells in area A, 6 wells in area B and 10 wells outside these two areas. The water source (fresh versus recycled) was also examined with 18 wells including 2 wells in area B and 16 wells outside these two areas.

Two tail t-tests were used to compare the difference between each subset of data, and significant differences were assumed to exist when the t-test p value was less than 0.05.

## **5.5 Results and Discussion**

### **5.5.1 Temporal Variability**

In oil and gas industry, water generated from shale wells is usually defined as two stages: frac flowback and produced water. Frac flowback water is referred to as the water that returned during the early stage of production, and it can last from several days to a few months. Due to the uncertainty in defining these two stages, in this study, wastewater from oil and gas wells was modeled over three consecutive time periods to improve modeling accuracy: frac flowback, transition and produced water. Water produced from the first 30 days after hydraulic fracturing was modeled as frac flowback, water produced during the following 133 days was modeled as transition water and water after the transition period ( $t > 163$  days) was modeled as produced water. The average daily water production was calculated for all wells in each area and fitted with the Arps equation (Poston, 2013; Bai 2012). For the Arps equation ( $q_{(t)} = q_0 / (1 + Dt)^{1/b}$ ), production rate at time  $t$  is a function of initial production rate ( $q_0$ ), initial decline rate ( $D$ ) and the degree of curvature ( $b$ ). The Arps equation becomes an exponential decay when  $b=0$ , and harmonic decay when  $b=1$ . Figure 5-2 shows an example model including each time period with

1 year of data for 86 wells in area A. Water production model equations in each period for both areas are shown in Table 5-1,  $q$  (bbls/day) is the water production rate at time  $t$  (days).  $R^2$  is greater than 0.99 for both frac flowback and transition water in two areas, and  $R^2$  is greater than 0.8 for produced water.

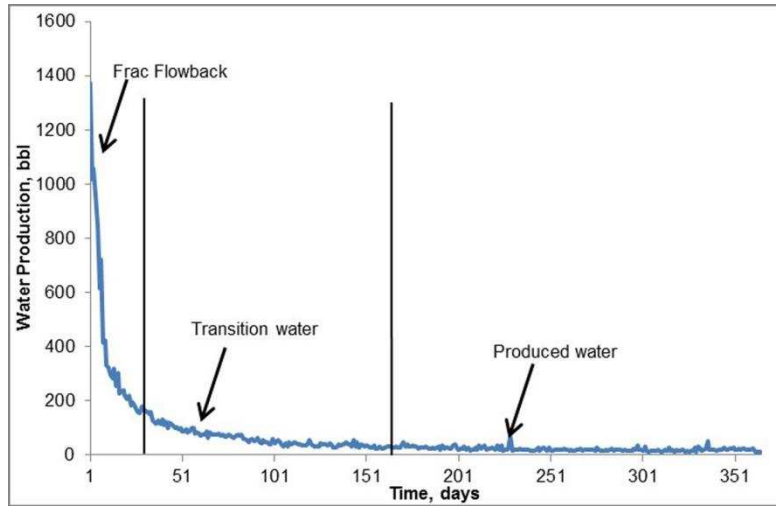


Figure 5-2. Definition of three time periods and average water production rate of 86 horizontal wells in area A.

Table 5-1. Water production models in each time period for areas A and B

Area	Frac flowback	Transition water	Produced water
A	$q = \frac{1,516}{(1 + 0.06138t)^{1/0.478}}$	$q = \frac{176}{(1 + 0.03738t)^{1/0.994}}$	$q = \frac{29}{(1 + 0.00341t)^{1/0.899}}$
B	$q = \frac{1,590}{(1 + 0.2492t)^{1/0.948}}$	$q = \frac{165.92}{(1 + 0.05701t)^{1/1.347}}$	$q = \frac{33.62}{(1 + 0.00837t)^{1/1.201}}$

### 5.5.2 Spatial Variability

When considering if geospatial (well location) variability impacts water production volume, data from two areas (A and B) were compared. Wells in both areas typically are completed in the same shale formation (Niobrara). A comparison of first year average water production volumes between the two areas is shown in Figure 5-3 and average water production

volume in each time period with 95% confidence intervals is summarized in Table 5-2. A two-tailed t-test was conducted on the average water production volume from the two areas. A significant difference was observed for frac flowback water volumes between the two areas (t-test;  $p < 0.05$ ), while no statistical difference was observed between transition water, produced water and total water production (t-test,  $p > 0.05$ ). The statistically relevant lower flowback water volumes from area B can be attributed to the significantly lower water volume used for hydraulic fracturing (t-test,  $p = 0.0001$ ). Average water use for hydraulic fracturing for wells in area A was 68,300 bbls while area B averaged 59,590 bbls. However, the average flowback water recovery was 20.6% (<30 days) for wells in both areas A and B.

In Figure 5-3, the curves in both cases differ slightly, but are not significantly different as shown in Table 5-2. The results showed that the volume of flowback water is proportional to the water used, which is related to the locations of the wells. Therefore, the location of the wells can impact the volume of frac flowback water by changing the water use patterns. However, the high degree of location dependence reinforces the need for more site-specific data.

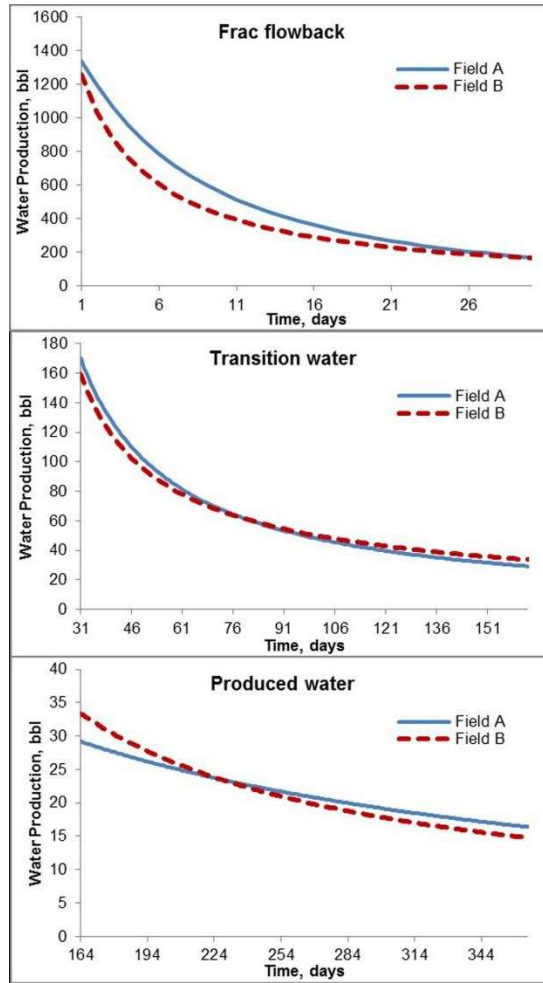


Figure 5-3. Comparison of one year water production rates between area A and B.

Table 5-2. Summary of average water production volumes in each period from area A and B.

<u>Time period</u>	Area A (bbls)	95% CI (bbls)	Area B (bbls)	95% CI (bbls)	Two tail t-test (p value)
Frac flowback	14,069	14,069 ± 1,195	12,279	12,279 ± 1,175	0.03
Transition water	8,286	8,286 ± 650	8,291	8,291 ± 1,535	0.94
Produced water	4,497	4,497 ± 623	4,517	4,517 ± 747	0.98
Total	26,853	26,853 ± 1,888	25,087	25,087 ± 2,836	0.54

### 5.5.3 Wellbore Length (Frac Stages)

Another potential source of variability is the length of the horizontal wellbore or the number of frac stages. Wells can be characterized as normal (shorter than 35 stages) and

extended (longer than 35 stages). Using these definitions, there were 6 extended wells in area A with an average wellbore length of 38 stages, and the other 80 wells had an average wellbore length of 20 stages that were characterized as normal length wells. Water production was compared between extended and normal wells but due to the limited production data of 6 longer wells, only a 327-day timeframe was analyzed. The average water production rate was calculated and is shown in Figure 5-4. Total volume of water produced in each period is summarized in Table 5-3, and two tail t-tests were conducted to compare normalized water production volume per stage between extended and normal wells.

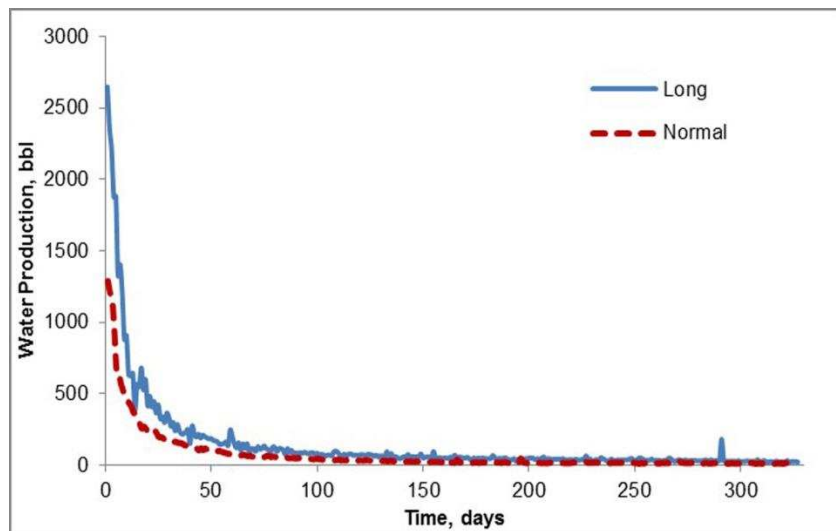


Figure 5-4. Comparison of 327-day water production between normal and extended wells in area A.

Table 5-3. Summary of average water production volumes in each period from wells of different wellbore length in area A.

<u>Time period</u>	Water production volume (bbls)		Water production volume per stage (bbls/stage)		Two tail t-test on water production volume per stage (p value)
	<u>Extended</u>	<u>Normal</u>	<u>Extended</u>	<u>Normal</u>	
Frac flowback	26,130	13,420	690	670	0.71
Transition water	14,750	8,340	390	420	0.66
Produced water	6,520	3,540	170	180	0.52
Total	47,400	25,300	1,250	1,260	0.51

From Figure 5-4, it is clearly observed that extended wells produce more water than normal wells, indicating that wellbore length or frac stages is a significant source of variability in water production from shale oil and gas wells. In addition, as shown in Table 5-3, the water production volume per stage is statistically equivalent for extended and normal bore lengths (p values of t-tests were greater than 0.05). This result indicates a good correlation between wellbore length (frac stages) and total water production volume. As a result, once stage-normalized water production is determined, water volume can be predicted based on the number of frac stages for a particular well.

#### 5.5.4 Type of Frac Fluid

Another potential source of variability in water production volume is the various types of fluid used in the hydraulic fracturing process. Two types of cross-linked gel frac fluids were used for fracturing wells examined in this study: a guar-based fluid with basic pH (Type I) and a non-guar based low pH fluid (Type II). 14 Type I wells in the Denver-Julesburg basin were geospatially paired with 14 Type II wells for the comparison, controlling for variability due to

location. Water production was compared between the Type I and II wells for a 164-day timeframe (Figure 5-5).

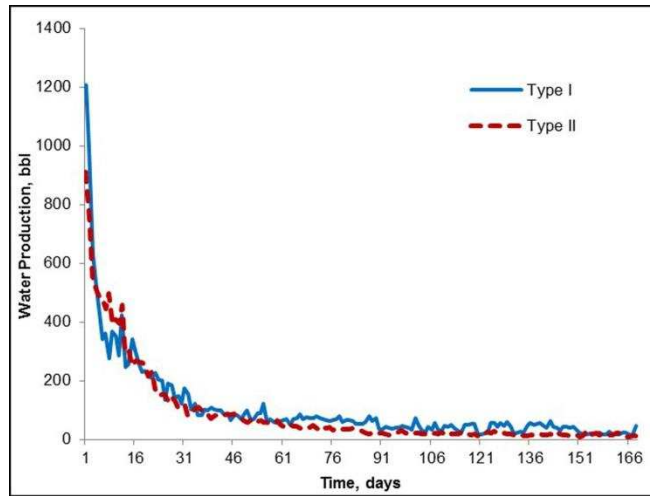


Figure 5-5. Comparison of average water production between Type I and Type II wells.

Average water production volumes are summarized in Table 5-4 along with the results of two tail t-tests. As shown in Table 5-4, Type I wells have higher average volume of flowback water than Type II wells, but not statistically significant at a 95% confidence level. For transition water and total water produced in 164 days, Type I had a higher volume of water produced than Type II wells and significant differences were observed (t-test,  $p < 0.05$ ). These results show that the type of frac fluid could have a significant influence on water production and should potentially be considered when developing a comprehensive model.

Table 5-4. Summary of average water production volumes in each period from two types of wells.

<u>Time period</u>	Type I (bbls)	Type II (bbls)	Two tail t-test (p value)
Frac flowback	8,800	7,950	0.44
Transition water	5,410	3,440	0.046
Total	14,210	11,400	0.04



### 5.5.5 Water Source

To understand the impact of the frac water source or quality (fresh versus recycled), 18 geospatially-paired wells (9 fresh water, 9 recycled water) were chosen controlling for location (all in the Niobrara formation), drilling time (all drilled within 6 months from December 2012 to May 2013) and frac fluid used (Type I was used for all wells in this part of the study). All the recycled wells were fractured using a recycled/fresh ratio of 1/7. Figure 5-6 shows the average water production rate trends and Table 5-5 summarizes the results for this analysis. Due to the limited timeframe of the data available for recycled wells, water production during the first 90 days was compared. Different water production rate decline curves were observed between recycled and fresh water wells with fresh water wells having significantly higher water production rates than recycled wells. The volume of both flowback water and transition water was significantly higher from fresh water wells. Meanwhile, the average water use was 3,217 bbls per stage of wellbore length [95% CI: 2,757, 3,677] for recycled wells and 3,118bbls [95% CI: 2,799, 3,436] for non-recycled wells; statistically equivalent frac water use (t-test,  $p=0.69$ ). Figure 5-7 shows the average water recovery ratio (water produced/water used) of both type of wells and the 95% confidence interval of the average water recovery ratio of recycled wells. Results show that the average water recovery ratio of non-recycled wells was significantly higher than recycled wells. Although it is not clear what aspect of recycled water leads to the different production rate, it appears that chemical characteristics can impact the water production rate and the source of water should be considered an important variable in any attempt to establish a more general model.

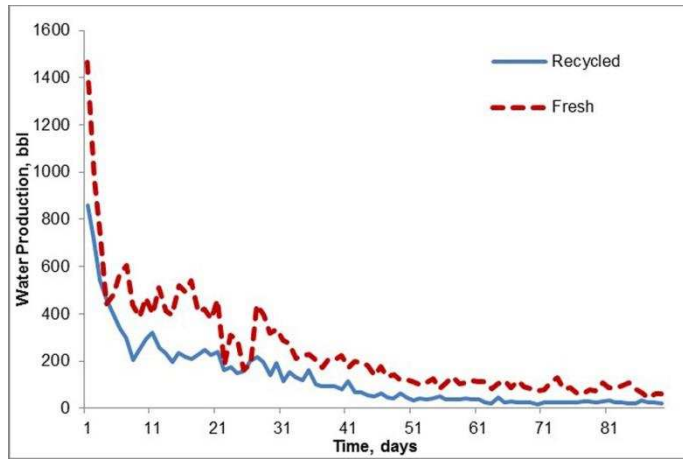


Figure 5-6. Comparison of average water production between recycled and non-recycled wells.

Table 5-5. Summary of average water production volumes in each period from recycled and non-recycled wells.

<u>Time period</u>	Recycled/Fresh Blend (bbls)	Fresh Water (bbls)	Two tail t-test (p value)
Frac flowback	7,620	10,438	0.04
Transition water	1,783	5,587	0.008
Total	9,403	16,025	0.002

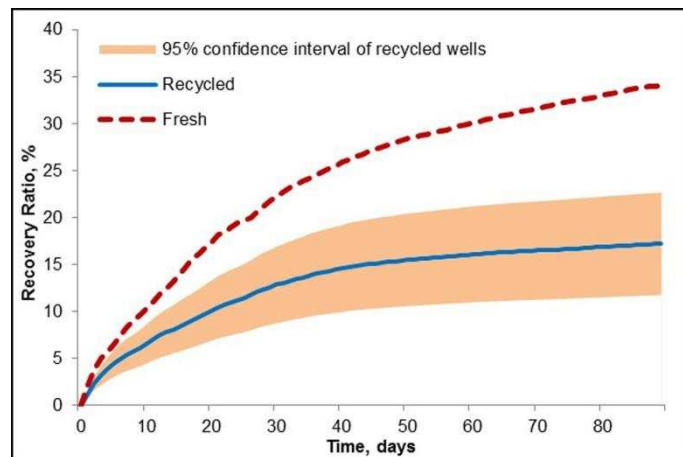


Figure 5-7. Water recovery ratio of recycled and non-recycled wells

## 5.6 Conclusion

Based on the study described in this paper, several conclusions are evident:

- Water production changes with time, but there is no standard definition of frac flowback and produced water. The introduction of transition water could help improve the accuracy when modeling water production from shale oil and gas wells. More accurate modeling of these stages could be developed through analyzing the change of water quality along with time; however, due to the lack of these data in this study, only flow rate was analyzed. Results showed various water production rates and volumes should be expected from different geospatial locations but the volume of water used was found to be more important.
- Water production volume was proportional to the lateral frac stages allowing predictions to be based on this parameter.
- The type of frac fluids can impact the water volume produced from shale oil and gas wells.
- The water used for hydraulic fracturing can also impact water production; higher water production rate and recovery ratio was observed from wells that were fractured with fresh water versus a 1/7 recycled/fresh blend.

This study examined five potential sources of variability in water production from shale oil and gas wells; however, this was not considered an exhaustive list and other sources may exist. The research outlines a protocol for predicting water production from shale wells accounting for major sources of variation and appropriate modeling parameters can be developed for other basins and formations.

## **6. Characterization of Solids in Produced Water from Wells**

### **Fractured with Recycled and Fresh Water<sup>3</sup>**

#### **6.1 Research highlights:**

- Understanding the size and composition of suspended solids in produced water.
- The difference in solids from wells fractured with fresh and recycled water was compared.
- Results indicate that wells fractured with recycled water tend to clean out faster.

**Key words: Produced water, Wattenberg Field, Solid characterization, Particle size, XPS**

#### **6.2 Introduction**

The Wattenberg field, lying in the northeast of the Denver-Julesburg Basin, is an unconventional shale play with an estimated 195.3 billion cubic feet (5.5 billion cubic meters) of wet natural gas reserve in 2009 (U.S. Energy Information Administration, 2012). Raabe (2011) also predicted that as much as 1 to 2 billion barrels of oil equivalent is reserved in the Wattenberg field, with 70% oil and 30% natural gas. There are five major formation layers in the Wattenberg field: J Sandstone, Codell Sandstone, Niobrara Formation, Hygiene Sandstone and Terry Sandstone (Weimer et al., 1986). By the end of February 2013, there are more than 22,000 active wells in the Wattenberg field, producing about 740 million cubic feet of natural gas and 100,000 barrels of oil per day (Colorado Oil and Gas Conservation Commission, 2013).

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To extract oil and gas from the deep shale formation, hydraulic fracturing has been widely performed all over the world, and a large amount of water is used during the hydraulic fracturing process to open up the target formation. Goodwin et al. (2013) estimated that each vertical and horizontal well in the Wattenberg field of Northern Colorado uses an average of 0.4 and 2.9 million gallons (1,500 and 11,000 cubic meters) of water, respectively. With oil-rich fields often located in water-scarce areas, the water demand of oil and gas production could add to the already-intense demand for water for municipal and agricultural purposes or even contribute to water shortages during severe drought conditions.

With the large amount of water being put into the wells for hydraulic fracturing, a significant volume of wastewater (as known as produced water) is generated with the production of hydrocarbon, and it has become crucial waste management and environment issues. The most common means of disposing wastewater from oil and gas production in the United States is through deep well injection—a practice that costs an average of 1 to 4 U.S. dollars per barrel (Clark and Veil, 2009). However, an increasing number of oil and gas companies are taking advantage of reusing treated produced water as fracturing fluid for new wells (Huang et al., 2006); this practice could help cutting down the demand for fresh water and, furthermore, the transportation and handling costs of the wastewater for deep well injection. Typically treated produced water (or recycled water in this study) is used to form fracturing fluids under different blend ratio with fresh water. Softening and coagulation are the most common treatment processes for operators to recycle the produced water. As a result, the reused produced water always has high total dissolved solid (TDS) concentration, and it is important to understand its potential impacts on the performance of wells that are fractured with recycled water.

The major compounds of produced water include dissolved salt and organic compounds, emulsified oil, fracturing chemical compounds, and suspended solid particles. Solids in produced water represent a wide range of materials, including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes (Fakhrul et al., 2009). Deng et. al. (2009) characterized suspended solid in produced water after water flooding at Daqing oilfield, China. The result showed the presence of inorganic substances such as SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and BaSO<sub>4</sub> in insolated solid samples, and authors recommend implementing fine filtration methods (fiber ball and membrane) for a successful suspended solid removal. With multiple studies focused on produced water qualities from shale wells fractured with fresh water (Benko and Drewes, 2008; Alley et al., 2011; Barbot et al., 2013), very few work has been done on recycled water fractured wells. In this study, produced water quality is compared between wells fractured with fresh and recycled water. Additionally, the suspended solids in produced water from these wells are characterized by gravimetric and particle sizing analyses, and their surface chemistry was tested through X-ray photoelectron spectroscopy (XPS). The understanding of solids properties and chemical composition will help guide the selection of the treatment technique that will improve wastewater treatment effectiveness and allow beneficial wastewater reuse.

## **6.3 Methods**

### **6.3.1 Well Location and Sampling Methods**

In this paper, two Noble Energy Inc. well pads in the Wattenberg field were studied: Crow Creek and Chandler State as shown in Figure 6-1. Five horizontal wells in the Niobrara formation, described in Table 6-1, were selected from these two pads, and wells from the same pad were parallel to each other and constructed at the same time. Water samples were collected from each well after flowback started. For all five wells, water was sampled daily for the first

two weeks, and then one sample every three days. All pre-flow and day 1 samples were collected at the wellhead, and the later samples were collected post separator. Particle size distributions were measured within 24 hours of sample collection and water quality analyses were finished within 7 days. Samples were kept at 4 °C at all times.

Table 6-1. Five wells selected for study

<b>Well Name</b>	<b>True vertical depth (ft)</b>	<b>Formation</b>	<b># of Stages</b>	<b>Fracturing source water</b>
Crow Creek State AC36-73HN	6,685	Niobrara	20	1:7 recycle: fresh
Crow Creek State AC36-76-1HN	6,742	Niobrara	20	100% fresh
Chandler State D15-72-1HN	6,750	Niobrara	23	100% fresh
Chandler State D15-73-1HN	6,750	Niobrara	23	1:7 recycle: fresh
Chandler State D15-74-1HN	6,750	Niobrara	23	1:5 recycle: fresh

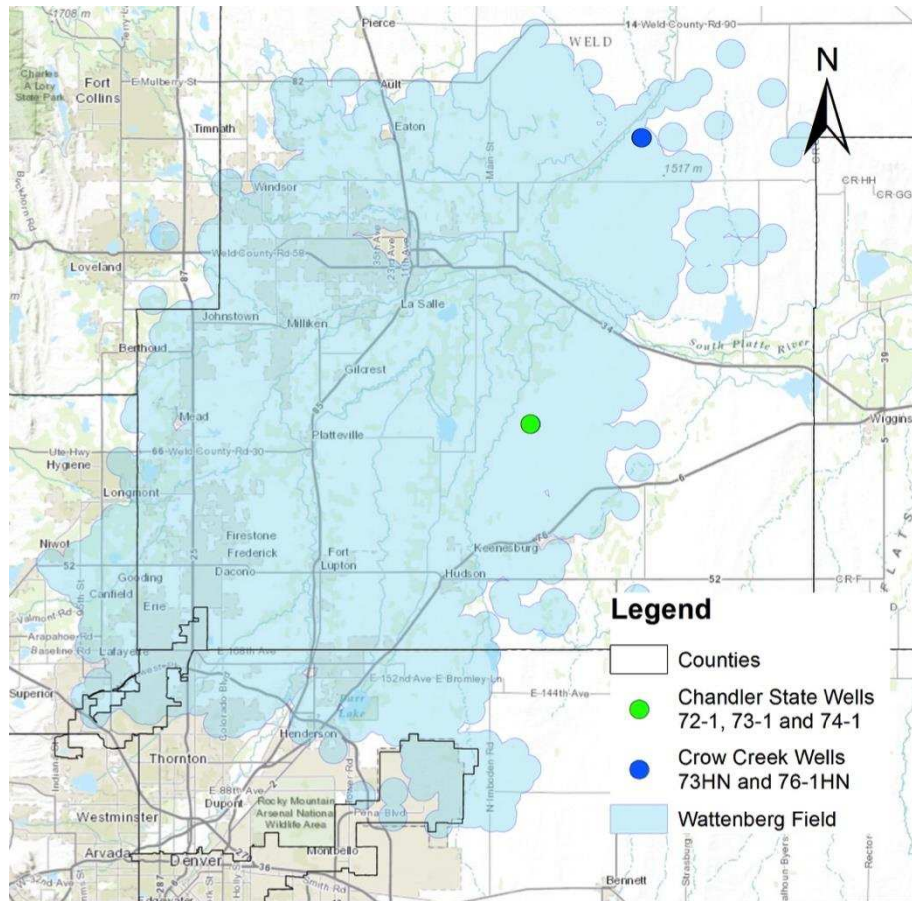


Figure 6-1. Location of studied wells within the Chandler State and Crow Creek pads

### 6.3.2 Produced Water Quality Measurement

Gravimetric analyses of solids were conducted according to Standard Method 2540 (APHA, 1995). Samples for total solids (TS), total dissolved solids (TDS), and total suspended solids (TSS) determination were dried at 105 °C; samples collected for total volatile solids (TVS), volatile dissolved solids (VDS), and volatile suspended solids (VSS) determinations were muffled at 550 °C. Ion concentration data were collected from Nalco Champion (Ecolab USA Inc.) and eAnalytics Laboratory (Loveland, CO) for Crow Creek wells and Chandler State wells, respectively.



### **6.3.3 Particle Sizing**

Particle size and particle size distribution (PSD) are the key properties describing colloidal and dispersed systems. In this study, a dynamic light scattering (DLS) method was applied to size particles, using a 90-Plus Particle Size Analyzer (Brookhaven Instruments, NY) at a fixed, scattering angle of 90° and temperature of 25 °C.

A multimodal size distribution (MSD) algorithm was used to represent PSD; the results of three runs were averaged to calculate the apparent hydrodynamic diameter of particles.

### **6.3.4 X-ray Photoelectron Spectroscopy (XPS)**

The surface chemistry of isolated suspended solids samples was analyzed by a PEI-5800 XPS-Auger spectrometer (Physical Electron, MN) at the Central Instrument Facility (CIF), Colorado State University. For each sample, ten surveys were scanned and averaged over the range of 0-1100 eV, at a resolution of 1 eV. High-resolution spectra of selected elements were acquired at a pass energy of 23.5 eV and a step-size of 0.1 eV. Binding energies were referenced to the C1s line of adventitious hydrocarbon at 284.8 eV.

To better capture suspended solids in produced water for XPS elemental testing, a solids separation protocol was developed. The following preparation steps were applied: 1) 200 mL of water sample was dried at 105 °C and then burned at 550 °C in a muffle furnace; 2) residuals were grounded and dissolved in 200 mL of deionized water; 3) the mixed solution was filtered through a 0.2- $\mu$ m silver filter (Sterlitech Corp. WA) under vacuum; 4) filter was then rinsed with 200 mL deionized water to wash off dissolved salts; 5) the filter was heated again at 550 °C and the sample was tested by XPS within one hour to prevent possible organic carbon contamination through air exposure.

## **6.4 Results and Discussion**

### **6.4.1 Produced Water Quality and Solids Distribution**

Table 6-2 summarizes the water quality of Crow Creek and Chandler State wells. While metal ions such as calcium, magnesium, iron, strontium, and zirconium were present, sodium chloride was found to be the dominant salt in all produced water samples. Sample pH averaged at approximately 7.5, and their buffer capacity was relatively high--suggesting that a significant amount of acid or base is required for softening if treatment was deemed necessary. Water quality was found to vary considerably from well to well, and organic and inorganic constituent concentrations of samples from Crow Creek wells were nearly all considerably higher than those of samples from Chandler State wells. Specifically, total organic carbon (TOC) and dissolved organic carbon (DOC) levels of Crow Creek samples were twice as high as those measured in samples collected from the Chandler State wells. Average TDS concentration of Crow Creek well samples was 40 percent higher than Chandler State well samples. The sulfate concentration averaged 368 mg/L and 29 mg/L in samples from Crow Creek wells and Chandler State wells, respectively. Because sulfate forces the precipitation of barium, barium was the only ion found to be at lower concentration in the Crow Creek well samples. Overall, the characteristics of inorganic constituents in produced water are primarily inherited from the shale formations with which the water had contact (Benko and Drewes, 2008). Consequently, the difference in inorganic constituent-related water quality between the wells is due, in part, to the geological variations across the Wattenberg field.

Table 6-2. Water Quality Summary for Crow Creek and Chandler State Wells

Wells	Crow Creek wells 73 and 76-1			Chandler State wells 72-1, 73-1 and 74-1		
Number of samples	60 Samples collected from day 1-54			66 Samples collected from day 1-57		
Parameters	Minimum	Maximum	Average	Minimum	Maximum	Average
<b>pH</b>	6.6	9.1	7.5	6.2	9.0	7.4
<b>Cond. (mS/cm)</b>	0.9	52.9	20.8	14.6	44.1	23.8
<b>TOC (mg/L)</b>	362	12,170	4,320	80	4,845	2,072
<b>DOC (mg/L)</b>	366	11,930	3,079	87	2,125	1,501
<b>Alkalinity (mg/L as CaCO<sub>3</sub>)</b>	234	2,264	1,301	432	1,488	994
<b>TS (mg/L)</b>	1,540	38,940	25,638	9,020	40,060	17,356
<b>TDS (mg/L)</b>	1,420	33,760	24,357	12,880	23,080	16,753
<b>TSS (mg/L)</b>	21	1,542	550	44	1,229	259
<b>TVS (mg/L)</b>	360	17,880	5,469	940	24,480	3,449
<b>VDS (mg/L)</b>	340	10,940	4,250	780	5,420	3,384
<b>VSS (mg/L)</b>	4	1,524	516	23	1,208	243
<b>Al (mg/L)</b>	0.1	16.0	5.4	0.1	1.4	0.6
<b>Ba (mg/L)</b>	0.1	5.6	2.1	1.5	15.5	6.4
<b>Ca (mg/L)</b>	43	435	269	54	186	104
<b>Fe (mg/L)</b>	4.2	171.1	44.0	0.5	60.4	29.8
<b>Mg (mg/L)</b>	21.3	57.7	37.1	7.5	25.1	14.9
<b>Na (mg/L)</b>	107	10,199	5,553	2,339	7,156	4,384
<b>Sr (mg/L)</b>	0.1	60.4	31.9	7.7	31.6	16.5
<b>Zn (mg/L)</b>	0.0	0.8	0.1	0.2	6.7	0.9
<b>Cl (mg/L)</b>	163	15,712	8,458	4,980	10,800	7,072
<b>HCO<sub>3</sub> (mg/L)</b>	63	3,660	1,190	512	1,476	955
<b>SO<sub>4</sub> (mg/L)</b>	316	446	368	1.1	268	29

Figure 6-2 details the solid distribution of dissolved and suspended portions. Consistent TDS values were observed within the same pad, suggesting that fracturing wells with some portion of recycled water might not result in higher TDS in produced water. As discussed above, effluent TDS concentrations are most likely influenced by the brine and the shale formation itself, and not by the water quality of fracturing source water.

Volatile solid study showed that about 13 to 46 percent of TS, and 9 to 25 percent of TDS, were volatile, indicating that a lot of organic compounds were present in the produced water. TSS also was found to be highly volatile, ranging from 88 to 99 percent. Possible sources

of the volatile content could be the emulsified oil and organic compounds in the fracturing package. Given the organic-rich nature of produced water, a new suspended solids isolation protocol was developed for better suitability of XPS testing, as discussed in Methods Section 6.2.4.

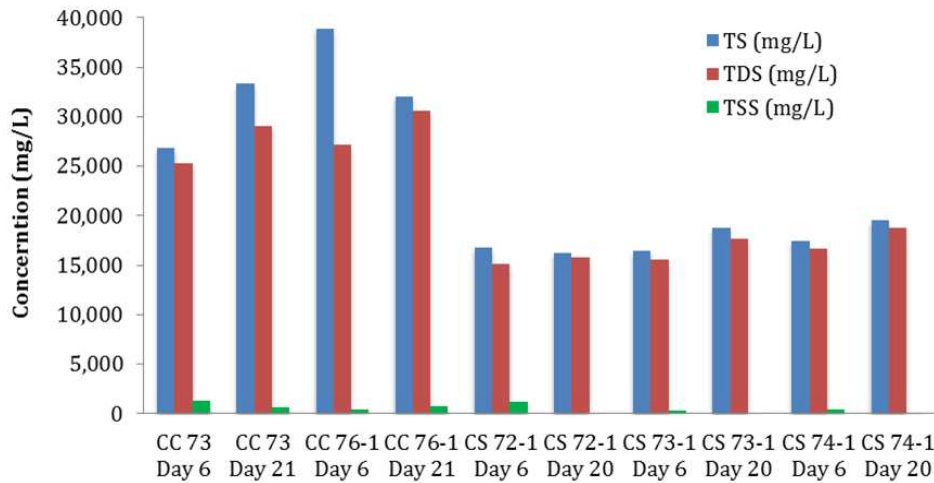


Figure 6-2. Solids distribution for Crow Creek wells on day 6 and day 21, and Chandler State wells on day 6 and day 20.

### 6.4.2 Particle Size Distribution

Effective particle diameter, illustrated in Figure 6-3, represents an average size of the particles in the sample. Higher particle sizes were captured in the pre-flow and day 1 samples, but that trend flattens out soon after production began. Large particles observed during the early-production period might have originated from clay content in the shale formation and/or the fracturing package (crosslinking gel, sand proppant, etc.). Once particle size stabilized, measurements showed the Chandler State wells had larger particle sizes than the Crow Creek wells. Particle sizes in Crow Creek pad samples stabilized at about 100 to 200 nm; most particles measured in Chandler State pad samples were greater than 400 nm in the first 20 days. However,

during the first week of production, the Crow Creek well fractured with fresh water well CC-76-1 was found to have larger particle sizes than the well fractured with recycled water (CC-73).

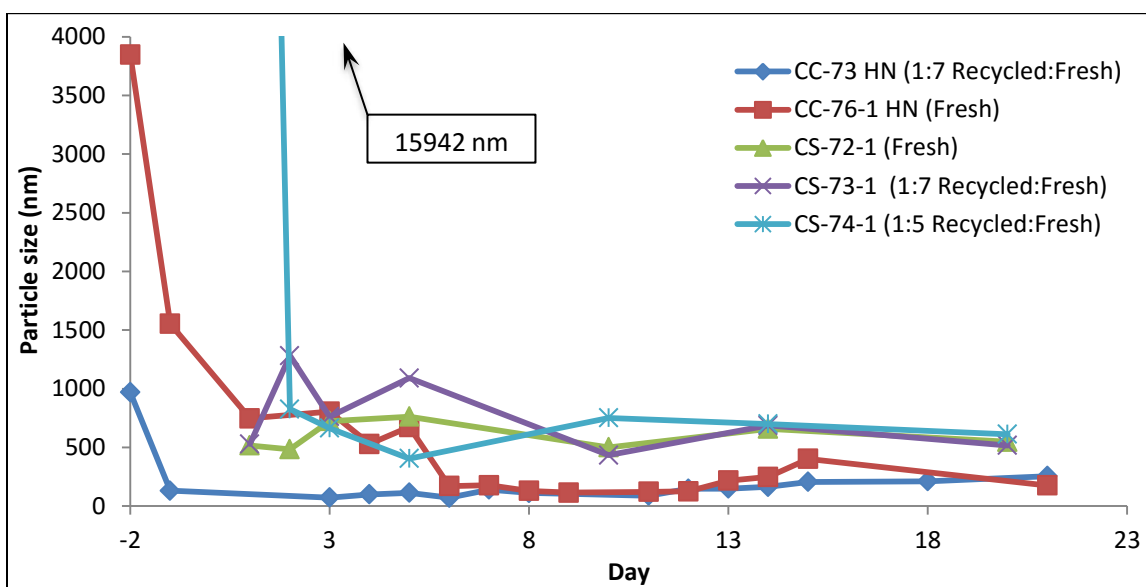


Figure 6-3. A summary of effective particle sizes for Crow Creek and Chandler State wells (Day -2 and -1 represent the pre-flow period before coiled tubing, and Day 1 refers to the production day.)

PSD profiles presented in Figure 6-4 show that early flowback samples contained a large variety of solids with particles ranging from 100 to 10,000 nm. Major difference in PSD patterns was found between well CC-73 and CC-76-1: well 76-1 particles showed a broader peak width and multiple peaks of size distribution, compared to well 73 that showed a smaller particle size and a uniform mono distribution peak after production. In general, CC-73 had smaller particle sizes than well CC-76-1, which suggests that well CC-73 tended to clean out much faster. One explanation is that recycled water has higher salinity and is more compatible with the shale formation; therefore, the mineral solubility equilibrium and chemical equilibrium can be established much faster. Yet, similar effects were not found in early Chandler State well samples, other than the extremely high particle size recorded in CS-74-1 day 1 sample, in which

noticeable particles were observed. Later XPS testing suggested these particles could be iron oxides

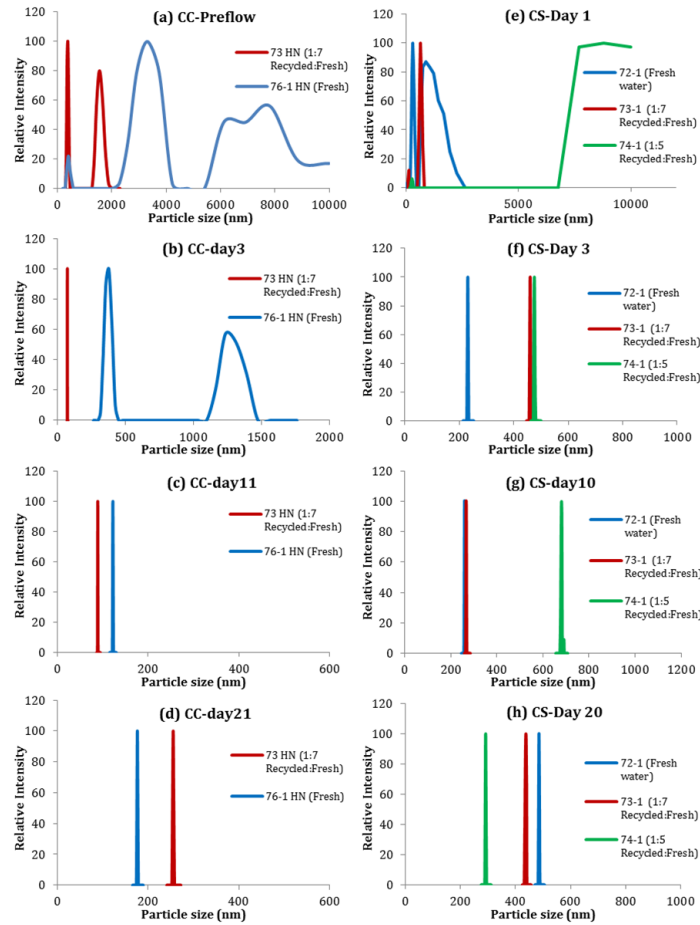


Figure 6-4. Particle size distribution (PSD) for Crow Creek wells: (a) pre-flow sample, (b) day 3 sample, (c) day 11 sample, (d) day 21 sample and Chandler State wells: (e) day 1 sample, (f) day 3 sample, (g) day 10 sample and (h) day 20 sample

### 6.4.3 X-ray Photoelectron Spectroscopy (XPS)

Analyzing the XPS spectra of peaks at different levels of binding energy allowed all elements present in the solid samples to be identified; the full list of elements and relative atomic percentages is presented in Table 6-3. For oxygen, carbon, silicon and magnesium, detailed temporal trends are provided in Figure 6-5.

Table 6-3. Atomic Percentage of All Elements for Chandler State Wells 72-1 HN, 73-1 HN and 74-1 HN, from Day 1 to Day 20 of production

Well No.	CS 72-1 HN					CS 73-1 HN					CS 74-1 HN				
Day	1	2	6	10	20	1	2	6	10	20	1	2	6	10	20
Oxygen	58.3	53.4	60.4	49.7	52.2	58.5	43.2	56.8	58.1	56.2	63.9	44.5	55.3	56.8	62.5
Carbon	6.6	13.2	6.2	16.2	10.4	6.7	13.1	5.8	6.2	4.1	4.1	11.8	8.6	5	5.9
Silicon	12.1	10.9	14.6	9.3	15	12.5	9.3	14.6	9	11.2	6.5	7.7	14.5	13.4	11.9
Calcium	3.6	-	1.4	2.8	5.1	-	-	2.6	4	2.9	7.1	2.8	3.7	2.8	1.8
Magnesium	1.5	3.8	1.3	3.1	3.1	3.6	18.2	4.3	4.5	5.7	10.1	15.5	5	5.2	5.6
Zirconium	1.7	2.7	1.3	0.7	-	1.8	2.3	1.2	0.9	1	-	2.3	0.8	1	1
Iron	2.5	1.8	1.6	1.5	4.1	2.3	1.9	1.7	2.3	2.9	2.9	1.2	-	1.6	3.5
Iodine	-	0.6	-	3.9	2.1	-	2.4	1.5	0.5	4.6	-	1.8	0.6	2	-
Sodium	12.8	11.9	12.2	7.5	5.0	14.6	7.5	9.1	12.7	7.1	0.9	8.4	8.4	10	5.6
Chlorine	1	0.9	0.4	0.9	-	-	0.6	1	1.3	1.1	-	0.9	1.1	1	1.1
Nitrogen	-	-	0.6	2.1	-	-	-	-	-	-	-	1.6	1.3	-	-
Barium	-	-	-	-	-	-	-	-	-	0.1	-	0.2	0.2	-	0.1
Silver	-	0.7	-	2.2	3	-	1.5	1.4	-	3.1	-	1.4	0.5	1.2	-
Sulfur	-	-	-	-	-	-	-	-	-	-	2.7	-	-	-	-
Strontium	-	-	-	-	-	-	-	-	0.5	-	-	-	-	-	-
Phosphorus	-	-	-	-	-	-	-	-	-	-	1.8	-	-	-	-

The data in Table 6-3 show that the most abundant element was oxygen, with an atomic percentage of 40 to 60 percent, followed by carbon and silicon. Because solid samples were burned at 550 °C, only inorganic carbon was expected to remain in the residuals. It can be deduced that major chemical components were calcium/magnesium, carbonate mineral, and quartz/clay. Figure 6-5 shows all three wells followed similar temporal trends in atomic percentage of oxygen and silicon. Magnesium spiked at day 2 in wells CS-73-1 and CS-74-1, fractured with recycled water, and their atomic percentages were continuously higher than those of well CS-72-1, which was fractured with fresh water. Iron presence was constant at about 2 to 4 percent of atomic percentage; divalent ions such as barium and strontium were detected only sporadically. The relative abundance of zirconium (Zr) peaked at day 2 in all three wells. Since zirconium is generally considered insoluble in crustal fluids and only trace amounts of Zr-bearing mineral are found in shale formations (Werne et al., 2002; Odoma et al., 2015), Zr

detected in produced water more likely originates from the zirconate-based cross-linker in the fracturing package. As polymer gel is broken down, Zr is expected to be released and gradually cleaned out from the well bore. Temporal trend of Zr reflected the gel break-down/well clean-out process. The relative abundance of Zr decreased after day 2 for all three wells indicated a quicker well clean out. Silver spectra were identified occasionally because silver filters were used in this study; the use of silver filters was meant to eliminate interference of silicon spectra that might occur when using fiberglass filters.

Figure 6-6 presents XPS core-level spectra on selected elements. Core-level XPS of carbon and oxygen confirm that most of the suspended solids were composed of carbonate-based minerals and metal oxides. Multivalent iron species were identified, and Fe 2p<sub>3/2</sub> XPS spectra were fitted into three peaks at 710.2, 711.6, and 713.4 eV for Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>FeO<sub>4</sub>, respectively (Deng et al., 2009).

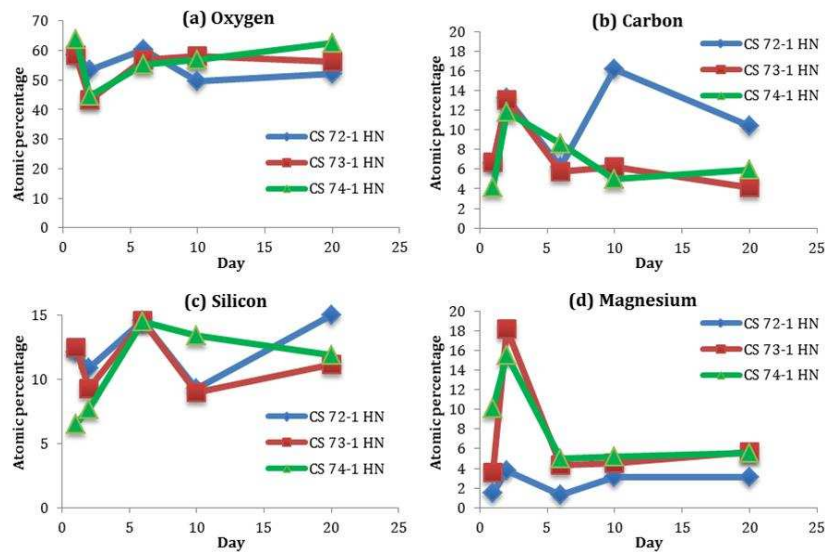


Figure 6-5. Temporal trending of oxygen, carbon, silicon and magnesium in samples from Chandler State wells 72-1 HN, 73-1 HN and 74-1 HN, from day 1 to day 20 of production: (a) Oxygen, (b) Carbon, (c) Silicon and (d) Magnesium



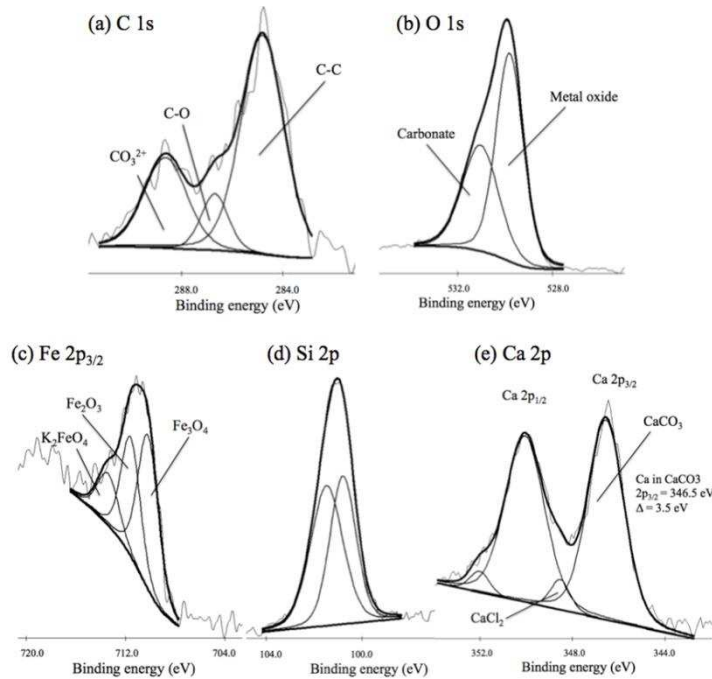


Figure 6-6. Core-level XPS spectra for isolated suspended solids from well CS 72-1 at Day 20: (a) C 1s, (b) O 1s, (c) Fe 2p<sub>3/2</sub>, (d) Si 2p and (e) Ca 2p

As discussed previously, silicon is expected to be associated with silicate minerals. However, the high-resolution XPS spectra of silicon showed peaks at 100.8 and 101.5 eV that did not match reference binding energy values for silica or silicate at around 103 eV. The 100.8 and 101.5 eV peaks measured represent, instead, SiC and Si<sub>3</sub>N<sub>4</sub>, respectively (Parrill and Chung, 1991). Nevertheless, SiC and Si<sub>3</sub>N<sub>4</sub> are highly unlikely to be present in suspended solids in produced water. Silicon carbide and silicon nitride are rarely found in terrestrial mineral environments (Di Pierro et al., 2003), and natural occurrences are reported primarily in meteorite cases. A possible explanation for this lower binding energy shift could be that silica or silicate was bonded with metal ions. For example, Vempati et al. (1990) discovered that when ferrihydrite co-precipitated with silica, the binding energy of silicon was shifted lower to 100.8 eV. Moreover, a study done by Gonzalez-Elipe et al. (1988) showed that, in the phyllosilicate minerals framework, substitution of Al or Mg for Si conferred net negative charge to the

tetrahedral sheet, thus lowered the photoelectron binding energies of silicon and oxygen. While these are possible explanations, the complex nature of solids isolated from produced water make it difficult to determine its exact chemical composition.

Figure 6-6(e) shows the Ca 2p spectra. The main component at the binding energy of 346.5 eV was attributed to CaCO<sub>3</sub>, while a smaller peak at 350 eV can be assigned to CaCl<sub>2</sub> (Demri and Muster, 1995). The spin orbit splitting between Ca 2p<sub>3/2</sub> and Ca 2p<sub>1/2</sub> was found at 3.5 eV, which also matched literature values (Chastain and King, 1992; Demri and Muster, 1995).

## **6.5 Conclusions**

Suspended solids in flowback water from horizontal shale wells were successfully isolated and characterized by gravimetric analysis, particle sizing, and XPS. Gravimetric analyses showed that dissolved and suspended solids concentrations were similar for wells in the same pad. Major differences were found between the wells fractured with fresh water and recycled water with respect to particle size and PSD during the first week of production. The smaller and mono-distribution of particle size identified suggests that recycled water is more compatible with shale formation and that wells fractured with recycled water clean out faster. XPS tests confirmed the presence of major elements, including oxygen, carbon, and silicon, and some minor elements such as calcium, magnesium, zirconium and iron. Core-level scanning confirmed that the isolated suspended solids were composed primarily of carbonate-based minerals and metal oxides; several iron compounds with different valences were also found in these samples. These results indicate that the solids likely originated in the formation and were not due to the frac fluid additives.

# **7. Investigating the Mechanisms of Low Salinity Waterflood on Niobrara Shale with Contact Angle Measurement and Spontaneous Imbibition<sup>4</sup>**

## **7.1 Introduction**

Wastewater management from shale oil and gas field has been a hot topic in recent years and deep well injection is the most common practice for handling wastewater from oil and gas wells. However, with the emergence of new regulations and technologies, oil and gas operators are seeking alternative wastewater management approaches including recycling. The beneficial reuse of oil and gas wastewater as hydraulic fracturing fluids has been considered as the most cost-effective practice. Historically only fresh water was used for hydraulic fracturing, therefore, it is unknown whether the use of recycled wastewater from oil and gas wells will affect the performance of newly drilled shale oil wells. In conventional oil and gas fields, a technology called low salinity water flooding (LSF) was introduced to improve oil recovery (Jadhuanandan, 1990; Jadhuanandan and Morrow, 1991, 1995; Lager, et al., 2008). By adding low concentration of salts into the base water, an average of 5 – 15% increase in oil recovery was observed (Henthorne, et al., 2013).

The same mechanisms that enhance oil recovery in conventional wells could provide benefits to unconventional oil and gas fields, but only very few studies have been done. A 10-year study of reusing frac flowback and produced water for hydraulic fracturing in Canada

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<sup>4</sup> **As Submitted to SPE Journal**  
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showed that gas production from wells that were fractured with recycled water was statistically higher than wells fractured with fresh water (Monroe, et al, 2013). Nguyen (2015) also reported that brine salinities have a significant impact on oil recovery from liquids-rich shale plays, with low salinity brine showing better hydrocarbon recovery. Morsy (2014) reported that oil recovery from Eagle Ford shale was enhanced by alkaline flooding, with the wettability altered to strongly water-wet after low alkaline flooding. No other similar reports have been published since the reuse of frac flowback and produced water is still in its early stages.

Many laboratory tests have been done to investigate the mechanisms of LSF. Researchers believe that wettability alteration of rocks contributes to increased oil recovery when using LSF (Buckley, et al., 1998; Berg, et al., 2010; Nasralla, et al, 2011; Yousef, et al., 2011; Zekri, et al., 2011). Vledder et al. (2010) also provided a proof of wettability change at a field scale. Al-Shalabi (2013) and Mahani (2015) illustrated that double layer expansion was one of the mechanisms contributing to LSF effect, and a new method for wettability measurement was introduced by Mahani (2015). In his study, the contact angle of oil drops on clay surface in different solutions was measured real-time and the change in oil shapes was used to characterize the alteration of wettability of the clay surface.

## **7.2 Theories and Definitions**

Two theories are proposed in this study:

1. Clay swelling and diffused double layer (DDL) compression are the two major mechanisms contributing to effects of salinity on oil recovery.
2. TDS play a critical role in low salinity hydraulic fracturing and an optimum value or range exists for optimal oil recovery from shale depending on geochemical characteristics of the formation.

### **7.2.1 Clay Swelling**

Clay minerals such as smectites and mixed-layer illites can usually expand in volume up to 20 times through absorption of water between clay cells, resulting in a reduction of formation permeability (Civan and Knapp, 1987). In the oil and gas industry, clay swelling has been a major cause of formation damage, and it can also lead to a closure of hydraulic fractures and decrease in hydrocarbon production. To prevent clay swelling in the formation, high concentrations of clay stabilizers may be added to hydraulic fracturing fluids. For example, the concentration of a commonly used clay stabilizer, potassium chloride (KCl), was recommended at between 2% (TDS=20,000 mg/L) and 7% (TDS=70,000 mg/L) based on the clay content (Gdanski, 2000).

### **7.2.2 DDL Compression**

Double layer compression and expansion has been considered one of the major mechanisms of improved oil recovery from LSF (Al-Shalabi et al., 2013; Nasralla et al., 2014; Mahani, et al., 2015), and it is a significant factor for wettability alteration of shale rock. Studies show low salinity water will cause cores to become mixed-wet (less oil-wet), and mixed-wet cores typically have lower residual oil saturations or higher oil recoveries than strongly oil-wet cores (Morrow, 1990; Morrow et al., 1998). Niobrara shale is normally either mix-wet or strongly oil-wet, and the surface tension between oil and rock surface is dependent on the ionic strength, in other words, the thickness of the DDL. Surface tension reduces with expansion of the DDL, and increases when the DDL is compressed (Figure 7-1). Theory predicts that DDL expands in low salinity solutions and as a result, the surface tension becomes weaker and oil is easier to be detached from the rock surface (Mahani, et al., 2015).

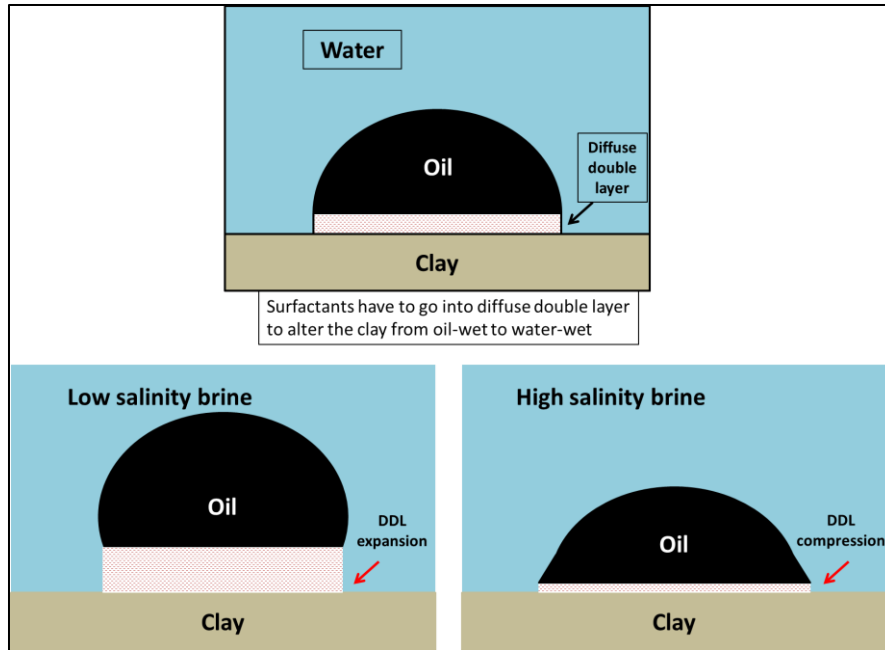


Figure 7-1. Schematic of changes of DDL in low and high salinity brine. DDL is expanded in low salinity brine and compressed in high salinity brine.

As a combined result of these two opposite mechanisms (clay swelling and double layer compression), oil recovery from shale formation can be impacted by the TDS concentration of the base fluids used as fracturing fluids. Figure 7-2 shows the theoretical relationship between oil recovery and TDS concentration of the fracturing fluids. An optimal TDS concentration exists for highest oil recovery from Niobrara shale formation, and this could be the explanation if TDS control is important to oil recovery in unconventional shale plays.

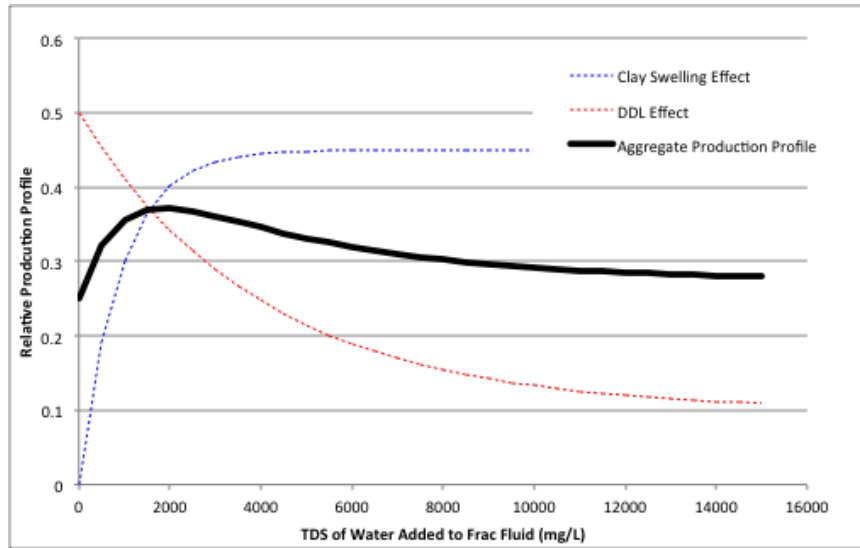


Figure 7-2. Theoretical relationship between oil recovery rate and TDS through combined effects from clay swelling and DDL compression

### 7.3 Materials and Methods

This study focuses on three experiments: clay swelling tests, contact angle measurements, and spontaneous imbibition of oil from Niobrara formation core plugs.

#### 7.3.1 Cores, Crude Oil, Brine, and Clay

Cleaned and dried shale cores were collected from wells of a large oil and gas operator in the Wattenberg field, Northern Colorado. All cores were extracted from the Niobrara formation, and across two formation benches: Niobrara B chalk and Niobrara B marl. All core samples were 1 inch in diameter and 1.5–2 inches in length. Crude oil was collected from the same well pad where the cores were extracted. Raw brine (TDS=20,000 mg/L, total organic carbon (TOC) =1,100 mg/L), also called high TOC brine (HTB), was treated produced water collected from on-site treatment facilities in the same field. Low TOC brine (LTB) was obtained after running HTB through granular activated carbon (GAC), and it has a TDS of 13,000 mg/L and TOC of 85 mg/L. Fresh pond water (TDS=400 mg/L) was used to blend both HTB and LTB to form

different TDS concentrations. Lab modeled water was also used for spontaneous imbibition and contact angle measurements to investigate the impacts from residual organic compounds in the recycled water, and it was modeled based on the inorganic composition of recycled water. Due to the very low smectite (swellable clay) percentage of the Niobrara core plugs (1–5%), for clay swelling tests, only powdered bentonite (PB) with 91% and 45% of smectite were used.

### 7.3.2 Clay Swelling Test

To understand how TDS affects clay swelling, powdered bentonite (PB) was tested for swelling with LTB of various TDS concentrations. The property of the PB is summarized in Table 7-1, and all the procedures followed the standard method ASTM D5890 – 11. The TDS concentrations of brine in this test were: 0 (DI water), 1,000, 2,000, 4,000, 8,000 and 13,000 mg/L.

Table 7-1. Property of powdered bentonite (PB) used for clay swelling test

Property	Standard	Average Value of Type [No. trials]
Specific Gravity	ASTM D 854	2.71
Principle Minerals (%)		
Smectite	XRD results from Mineralogy, INC. (Tulsa, OK)	91
Quartz		2
Plagioclase Feldspar		3
Illite/Mica		2
Gypsum		1
Calcite		1
Swell Index, SI (mL/2g)	ASTM D 5890	32 [5]

### 7.3.3 Contact Angle Measurement

Real-time contact angle measurement of oil drops on formation rock was performed to verify the DDL theory that has been reported in literature (Al-Shalabi et al., 2013; Nasralla et al., 2014; Mahani, et al., 2015; Teklu, et al., 2015). This protocol measures the contact angle between oil droplets and a pulverized shale powder surface when submerged in different brines. The experimental setup is shown in Figure 7-3. In order to coat the shale patches onto the glass



slides, core samples were ground into a fine powder and then mixed with deionized water at a concentration of 100 mg/L. The mixed suspension was gently stirred to prevent sedimentation, and approximately 2  $\mu\text{L}$  of suspension was pipetted onto the clean glass slides to form one shale patch. After the patches were dried completely, another 2  $\mu\text{L}$  of suspension was pipetted on the dried patch. By repeating the steps above 10 times, shale patches were created and adhered to the glass naturally without requiring any glue or synthetic adhesives, even when exposed to brine. Additional details of the procedure can be found in the work of Mahani (2015). After the crude oil drops were carefully introduced on the clay patches, 150 mL of LTB was slowly injected into the cell to fully submerge the oil drops. The shapes of oil drops were recorded and analyzed by Kruss® Drop Shape Analyzer, and the first photos were taken after 24 hours of stabilization. After the photos of the drops were taken, 150 mL of fresh water was then slowly injected into the system to dilute the brine in the cell. The shapes of the oil drops were carefully monitored during the flow of fresh water to make sure no interference on the oil drops occurred due to the flow. The next photos were taken 24 hours after the injection of fresh water was completed. The Niobrara B chalk samples were used for contact angle measurement.

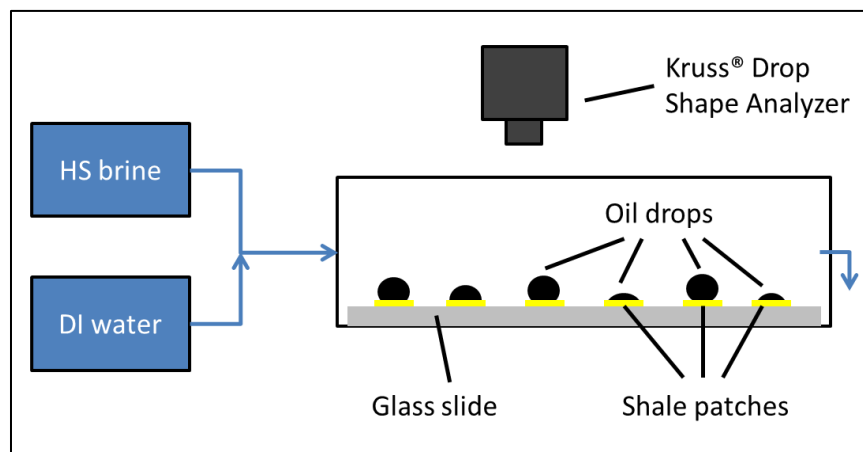


Figure 7-3. Side-view sketch of the experimental setup

### 7.3.4 Spontaneous Imbibition

14 Core plugs from each formation bench were tested for spontaneous imbibition. Since all cores were pre-cleaned and dried, an oil saturation process was conducted before the spontaneous imbibition. All cores were vacuum-desiccated for 24 hours and weighed for initial weight. After another 24-hour of vacuum desiccation, crude oil was then sucked into the desiccator to fully submerge cores. All cores were saturated with crude oil for 1 month and weighed again before the spontaneous imbibition testing after wiping off the free oil on the surface. The weight difference was the initial oil saturated in each core sample, and was converted to volume by simply dividing the density of the crude oil. Since recycled water usually has high concentrations of organic matter (McFarlane, et al., 2002), to understand whether these compounds affect oil recovery, both recycled water and lab model water were used as brine for spontaneous imbibition. Brine with various TDS concentrations was created by blending high TDS brine with fresh water at different blend ratios. Table 7-2 summarizes materials and criteria for the spontaneous imbibition tests.

Table 7-2. Summary of materials used in two parts of spontaneous imbibition tests

Testing criteria	
Raw brine TDS (mg/L)	20,000
Lab modeled brine TDS (mg/L)	19,600
Fresh water TDS (mg/L)	400
Number of tested TDS points	7
Tested TDS concentration (mg/L)	400, 1,500, 3,000, 4,500, 7,500, 10,000, 20,000
Formation benches	Nio B chalk, Nio B marl
Crude oil density at 20 °C (g/ml)	0.796

Amott cells were used for spontaneous imbibition, and all tests were performed in an oven at a constant temperature of 190 °F to simulate downhole thermal conditions. All imbibition tests lasted for 14 days when no additional imbibed oil was observed in the amott cells after 14 days. The volume of the oil imbibed out from the cores was measured by both

gravimetric and volumetric methods, and the average of two results was used. Oil recovery rate was calculated as: oil recovery rate (%) = oil imbibed (mL) / oil saturated (mL) × 100%.

All core plugs were reused once: after the first round of spontaneous imbibition, core plugs were dried in an oven at 105 °C for 7 days, followed by vacuum desiccation for 24 hours. The core plugs were weighed and then saturated with crude oil again for 1 month followed by the second round of tests. No core plug was reused more than once.

## **7.4 Data and Results**

### **7.4.1 Clay Swelling Test**

The swell index (mL/2g) of the PB in different brine is summarized in Table 7-3. When the TDS concentration of brine increased from 0 to 13,000 mg/L, the swell index decreased from 32 to 10 for PB with 91% smectite and from 16 to 5 for PB with 45% smectite. Figure 7-4 shows a decline of swell index when the TDS concentration increases. According to Table 7-3 and Figure 7-4, the swell index follows a linear function with the percentage of smectite in the powdered bentonite. Although it is very difficult to test swell index with actual core samples due to the low smectite percentage, it can be projected from the results of powdered bentonite and should follow a similar pattern. The results of clay swelling testing also supported many literature studies that show by increasing the TDS of the brine, less clay swelling will happen, and oil recovery will be improved (Santos, et al., 1996; Zhou, et al., 1996; Zhou, et al., 1997; Sanaei, et al., 2016).

Table 7-3. Swell index of the PB in brine of different TDS concentrations.

TDS (mg/L)	Swell index (mL/2g)	
	PB (91%)	PB (45%)
0	32	16
1,000	20	10
2,000	18.5	9.5
4,000	15	7.5
8,000	12.5	6
13,000	10	5

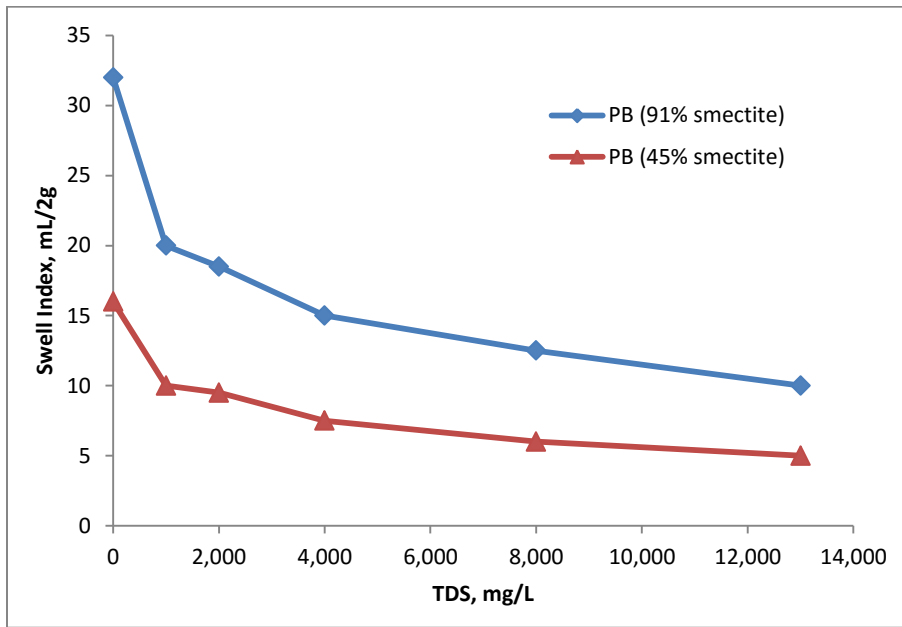


Figure 7-4. Change of swell index of powdered bentonite with the increase of TDS concentration

### 7.4.2 Contact Angle Measurement

High-resolution images of oil droplets were captured as the TDS concentration was varied from 13,000 mg/L to 1,000 mg/L. 26 oil droplets in total were measured with 13 for each type of brine (recycled water and model water). Figure 7-5 shows example images of six oil droplets at varying TDS concentrations. The average contact angle of all oil droplets in two types of brine with 95% confidence interval is summarized in Table 7-4. Two tail t-test result shows significant difference exists between recycled water and lab model water, and contact angles in

recycled water were statistically greater than that in modeled water. The results indicate the residual organic compounds in recycled water, even at low concentration (TOC=85 mg/L), still significantly reduce the surface tension between oil droplets and shale surface. The change of average contact angle with TDS concentration is shown in Figure 7-6.

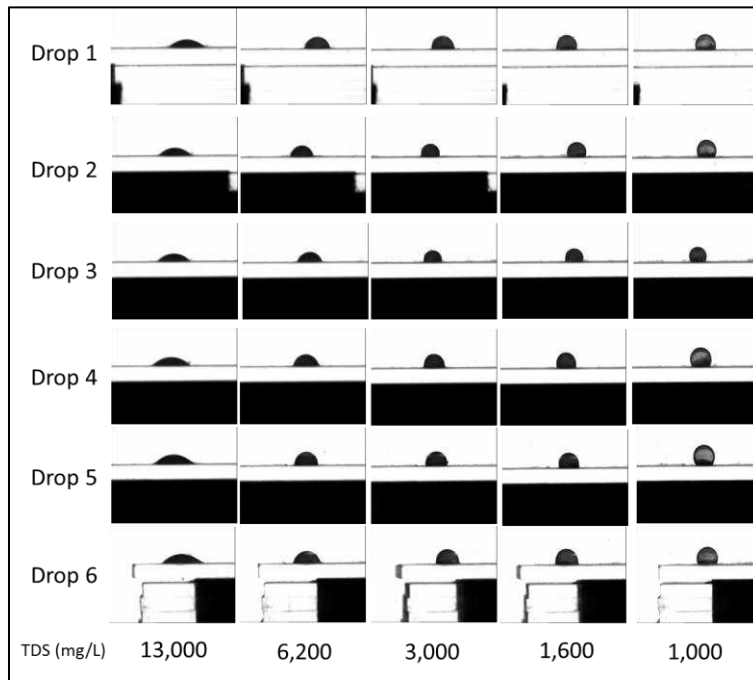


Figure 7-5. Sample images of six oil droplets under various concentrations of brine. (TDS concentration from left to right: 13,000, 6,200, 3,000, 1,600 and 1,000 mg/L)

Table 7-4. Average contact angle of all oil droplets with 95% CI, n=13 for each type of water

TDS (mg/L)	Recycled water with 95% CI	Modeled water with 95% CI	Two tail t-test <i>p</i> value
13,000	37.53 ± 2.58	27.36 ± 2.71	< 0.01
7,500	73.46 ± 1.96	62.74 ± 3.26	< 0.01
3,700	95.28 ± 2.06	81.96 ± 2.82	< 0.01
2,000	112.47 ± 2.85	94.49 ± 1.1	< 0.01
1,000	123.58 ± 3.52	101.96 ± 0.87	< 0.01

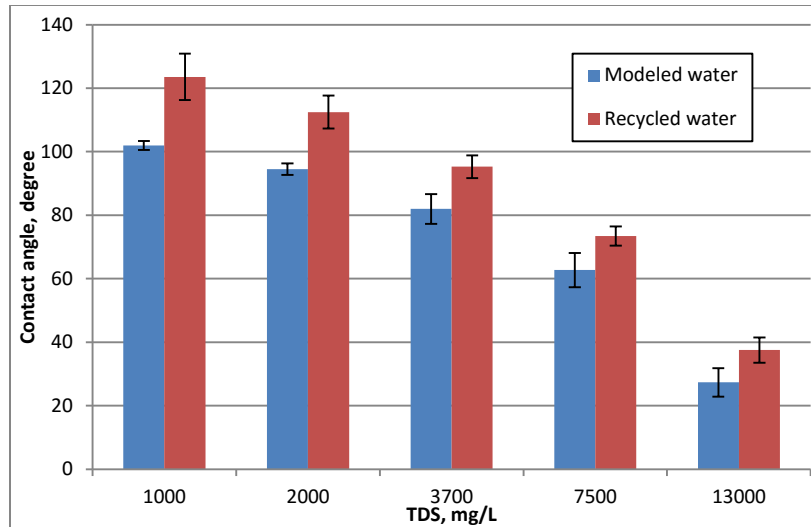


Figure 7-6. Change of average contact angle with the increase of TDS concentration. Error bars represent the standard deviation of 13 data points of each water type.

Results from both recycled and model water indicate that contact angle between oil droplets and ground core powder surface increases with the decrease of TDS concentration. At lower TDS concentration oil is easier to detach from the rock surface, leading to an increase in oil recovery. This experiment supports the double layer expansion theory and its importance for improved oil recovery in shale formations. These results, when combined with the increased clay swelling at low TDS concentrations, support the hypothesis that optimum oil recovery will occur at salinity values between fresh and brackish water (Figure 7-2).

### 7.4.3 Spontaneous Imbibition

The results of oil recovery (%) versus brine TDS are summarized in Table 7-5. Two rounds of spontaneous imbibition tests were performed on all plugs. The average oil recovery from two formation benches is plotted in Figure 7-7 and Figure 7-8.

Table 7-5. Oil recovery rate from spontaneous imbibition with shale core plugs

Brine TDS (mg/L)	Oil Recovery Rate (%) with recycled water				Oil Recovery Rate (%) with modeled water			
	Niobrara B chalk		Niobrara B marl		Niobrara B chalk		Niobrara B marl	
	Round 1	Round 2 (reused)	Round 1	Round 2 (reused)	Round 1	Round 2 (reused)	Round 1	Round 2 (reused)
400	6.05	8.3	7.92	2.76	5.6	4.28	4.38	7.11
1,500	5.98	6.02	8	4.76	12.16	3.02	8.58	6.42
3,000	9.06	10.91	8.53	5.25	23.91	7.8	22.7	9.63
4,500	8.43	6.68	9.86	8.7	18.39	7.91	20.82	27.96
7,500	5.24	5.94	18.47	11.01	9.11	12.49	24.75	28.78
10,000	5.76	4.89	17.08	6.9	7.72	10.98	20.92	12.16
20,000	5	4.97	3.67	2.5	7.37	7.16	5.54	8.6

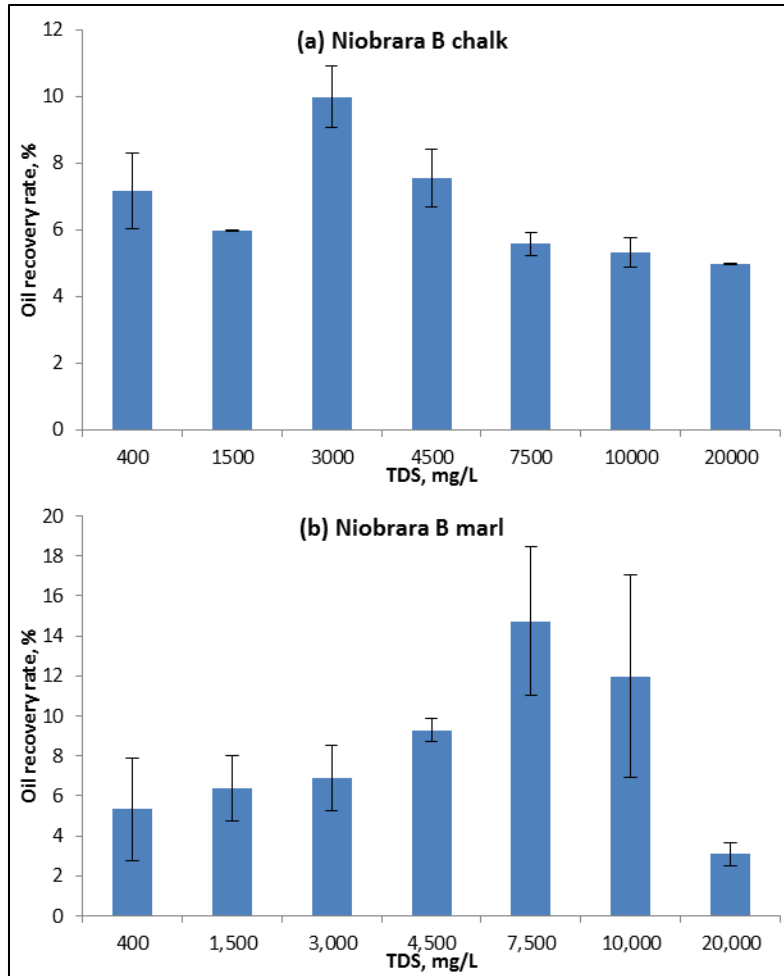


Figure 7-7. Average oil recovery rate from spontaneous imbibition tests with recycled water for two formation layers: (a) Niobrara B chalk and (b) Niobrara B marl. Error bars represent the range of result from two rounds of tests.



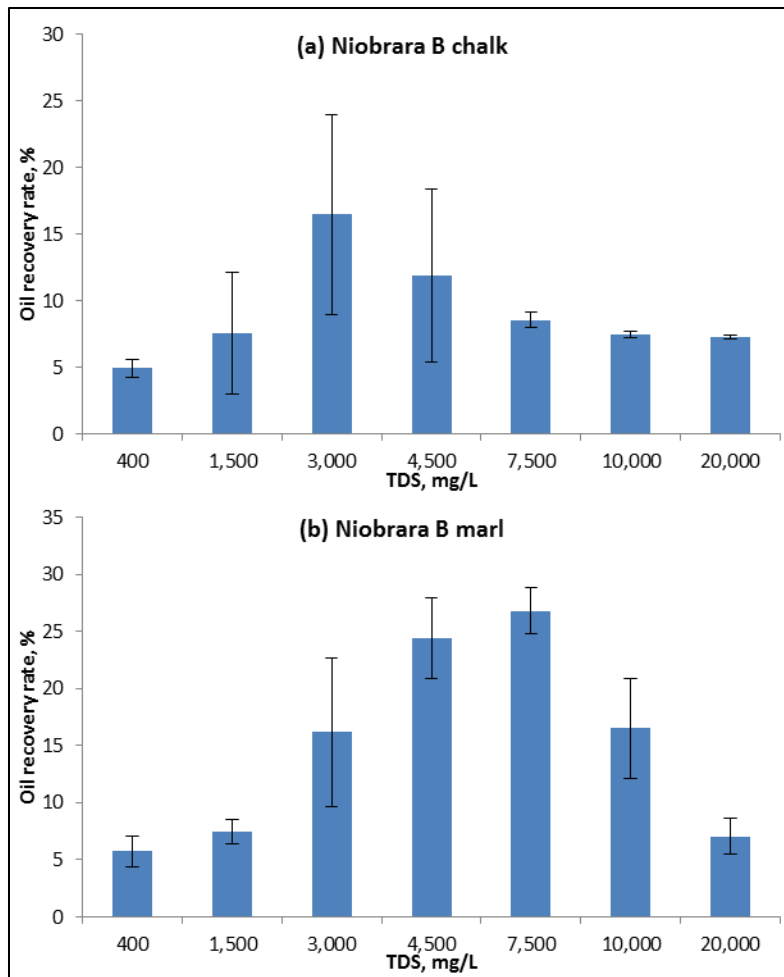


Figure 7-8. Average oil recovery rate from spontaneous imbibition tests with modeled water for two formation layers: (a) Niobrara B chalk and (b) Niobrara B marl. Error bars represent the range of result from two rounds of tests.

Figure 7-7 and Figure 7-8 show that oil recovery peaked when the TDS of brine was between 0 and 10,000 mg/L. For both recycled and model water, the highest oil recoveries were observed at a TDS of 3,000 mg/L for Nio B chalk plugs and 7,500 mg/L from Nio B marl plugs. Neither fresh water nor high salinity brine gave the highest oil recovery. X-ray Diffraction (XRD) results showed that the average smectite percentage was 3.39% in Nio B marl plugs, while it was only 1.74 % in Nio B chalk plugs. The difference in expandable clay fractions may explain why

the peak oil recovery rate was observed at a higher TDS value for the Nio B marl plugs, since a higher salinity brine is required to minimize clay swelling.

Results from the spontaneous imbibition tests indicate that similar to the effects documented for low salinity flooding of conventional wells, TDS of the water used for hydraulic fracturing of unconventional wells can significantly impact shale oil recovery. According to this study, there will be a TDS concentration for optimal oil recovery dependent on the smectite concentration of the formation rock.

## **7.5 Conclusions**

Based on the study described in this paper, the following conclusions can be drawn:

- Clay swelling and diffused double layer compression and expansion are two important mechanisms that will influence oil recovery in unconventional shale oil plays.
- Higher TDS is preferable to minimize clay swelling in shale formations.
- Lower TDS makes it easier for oil to be detached from shale rock surface by expanding the double layer between oil and shale rock surface, and residual organic compounds in recycled brine can significantly reduce the surface tension.
- Spontaneous imbibition results indicate that controlled salinity may be for increasing oil recovery in unconventional shale oil wells.
- Depending on formation rock geology, optimal oil recovery can be achieved with TDS values between fresh water (approximately 400 mg/L) and brackish water (approximately 10,000 mg/L).

## 8. Conclusion

The overall objective of this dissertation is to:

**Model and quantify the wastewater production from horizontal shale wells in the Wattenberg field, and evaluate the applicability of LSF to enhance oil recovery from unconventional shale formation.**

Chapter 4 and 5 illustrated the development of water production models for horizontal shale wells in the Wattenberg field. In chapter 4, water production models were developed for five well fields with different GOR values. Results show that the GOR value of field has a significant impact on water production from horizontal shale wells. With higher GOR value, wells typically have fewer fluids production including both oil and water. In chapter 5, 5 variables in frac flowback and produced water production from shale wells was examined. Results show that water production could be impacted by the locations of wells, the horizontal length of wells, the type of fracture fluid used, and the type of water used (fresh or recycled).

To investigate the impacts on flowback water quality from the use of recycled water as hydraulic fracturing fluid, chapter 6 focused on comparing the solids in produced water from fresh and recycled wells. Results show that recycled water is more compatible with the formation, and wells fractured with recycled water tend to clean out much faster than those fractured with fresh water.

Chapter 7 focused on investigating the impacts on oil recovery from the use of recycled water as hydraulic fracturing fluid. Historically low salinity water flooding has been adapted as one of many EOR methods in conventional wells, hence, the same idea was brought into

unconventional shale formation and the mechanisms were studied in this chapter. Two major mechanisms of LSF were proposed: clay swelling and DDL compression. Results show that both mechanisms were impacted by the TDS of the brine. Spontaneous imbibition tests further proved that highest oil recovery was observed at TDS of 3,000 mg/L for Nio B chalk plugs and 7,500 mg/L for Nio B marl plugs from both field and lab modeled brine. Neither fresh water nor 100% recycled water is best for oil recovery.

Unfortunately, it was unable to compare the impacts on oil recovery from the existence of organic compounds in the recycled field water. However, the contact angle results indicate that the residual organic compounds in recycled field water can significantly reduce surface tension, and allow oil to be detached from shale surface faster.

The findings and results from this dissertation will provide oil and gas operators the ability to model and quantify wastewater volume from given well fields so a better management practice could be achieved. More importantly, the results in this dissertation indicate that low salinity water flooding could also be applied to unconventional shale wells to improve oil recovery.

## 9. Future work

In Chapter 4, water production from horizontal shale wells in five sections in the northeastern Wattenberg field was modeled and compared. Results suggested that location of wells could have important impacts on water production. However, this study only focused on a relatively small study area compared to the entire Wattenberg field. It is still know whether the same trend will be observed from other fields, hence, continuous study could be done on a larger field with more sample numbers to provide better understanding of the correlation between water production and location/GOR value of shale wells.

In Chapter 5, five variables in frac flowback and produced water production were investigated. With the rapidly changing technologies in unconventional well development, more factors may become important in water production from shale wells, such as different formation geology and new types of frac fluids. The continuous study could focus on investigating new variables with larger data sample across the field.

Chapter 6 focused on comparing solids sizes and characteristics in flowback water between fresh and recycled wells. However, only early flowback water from five wells was studied, and no conclusion was drawn in this study. In order to understand how water quality differs from the use of different fracturing water, future research could focus on increasing number of wells and developing better sample collection and measurement protocols.

In Chapter 7, two mechanisms of LSF in shale wells were proposed and proved. Results indicated that LSF could also improve oil recovery from low permeability unconventional shale formation. However, a lot of variables existed during the experiments. To thoroughly understand the applicability of LSF, and best use of it to enhance oil recovery in shale wells, further

investigations are needed. Other mechanisms should also be investigated such as fine mobilization; multicomponent ion exchange and PH change during LSF. An XRD database or map across the field could be developed for operators to optimize hydraulic fracturing jobs. Also in this dissertation, TDS was the only studied factor in the LSF of shale cores, and very little study was done to demonstrate how residual organic matters in produced water can impact the LSF process. Therefore, future research can focus on analyzing the composition of organics and how they could affect low salinity waterflood in shale wells. Studies on how different compositions of inorganic salts (TDS) could impact LSF are also needed for continuous research.

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## Appendix B. Decline Curve Analysis

The Arps Equation used for the decline curves fitting is shown below:

$$q(t) = \frac{q_i}{(1+D_i t)^{1/b}} \quad \text{where} \quad q(t) = \text{Future production rate}$$

$q_i$  = Initial production rate

$D_i$  = Initial decline rate

$t$  = time

$b$  = Degree of curvature

When  $b = 0 \implies q(t) = q_i e^{D_i t}$  (Exponential Decline Curve)

(Low Production Scenario)

When  $b = 1 \implies q(t) = \frac{q_i}{1+D_i t}$  (Harmonic Decline Curve)

(High Production Scenario)

In real production cases, the  $b$  value can always be up to 2.

# Appendix C. Figures and Maps of Hypothetical Development Plan from the ArcGIS Modeling Tool.

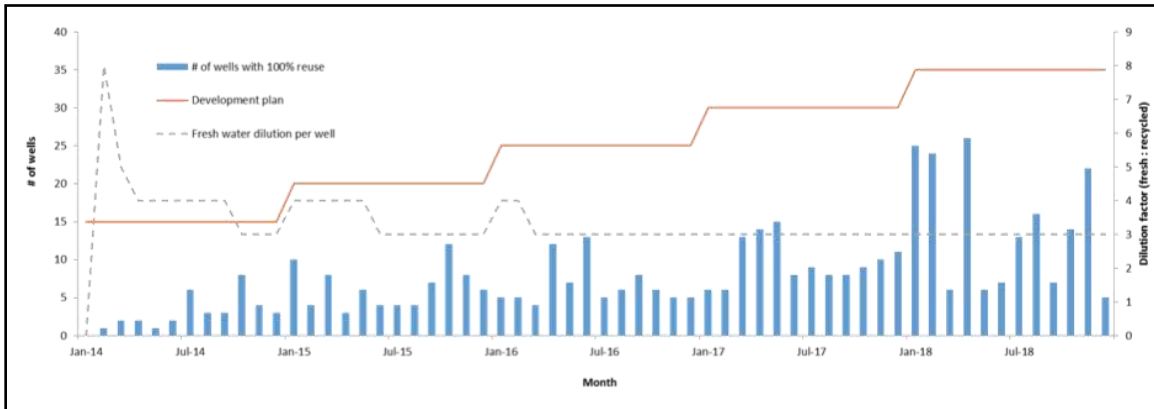


Figure C-1. Figure of water reuse potential

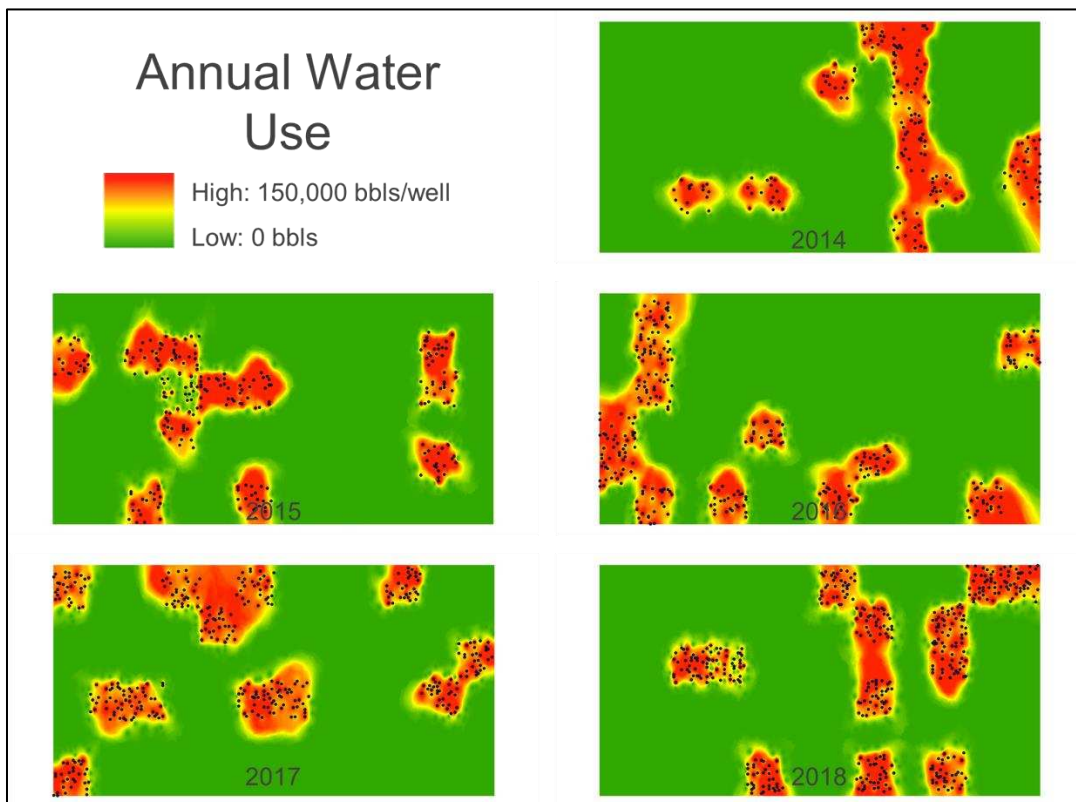


Figure C-2. Map of annual water use across the hypothetical development field

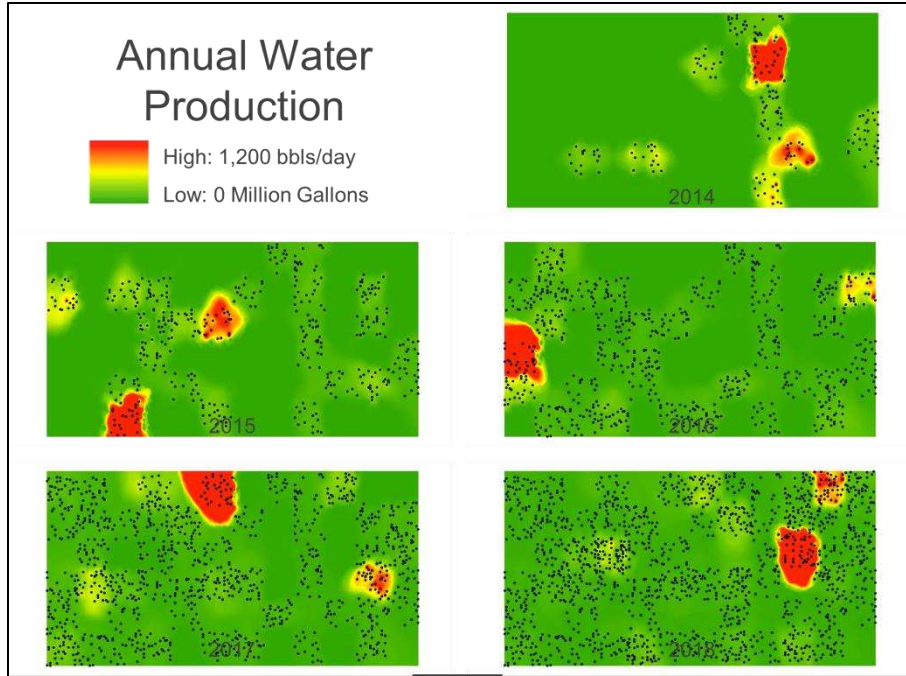


Figure C-3. Map of annual water production across the hypothetical development field

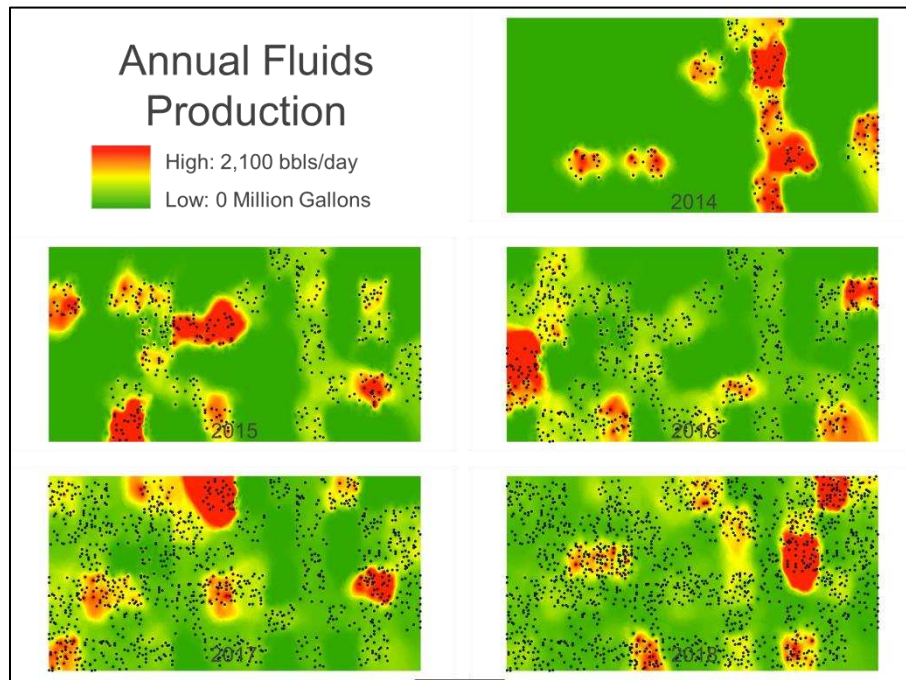


Figure C-4. Map of annual fluids (oil and water) production across the hypothetical development field

# Appendix D. XPS Results of Particles in Produced Water from Noble Energy

Figure D-1 to Figure D-4 show XPS results of particles in produced water from two wells: Crow Creek State AC36-76-1HN (fresh) and Crow Creek State AC36-73HN (recycled).

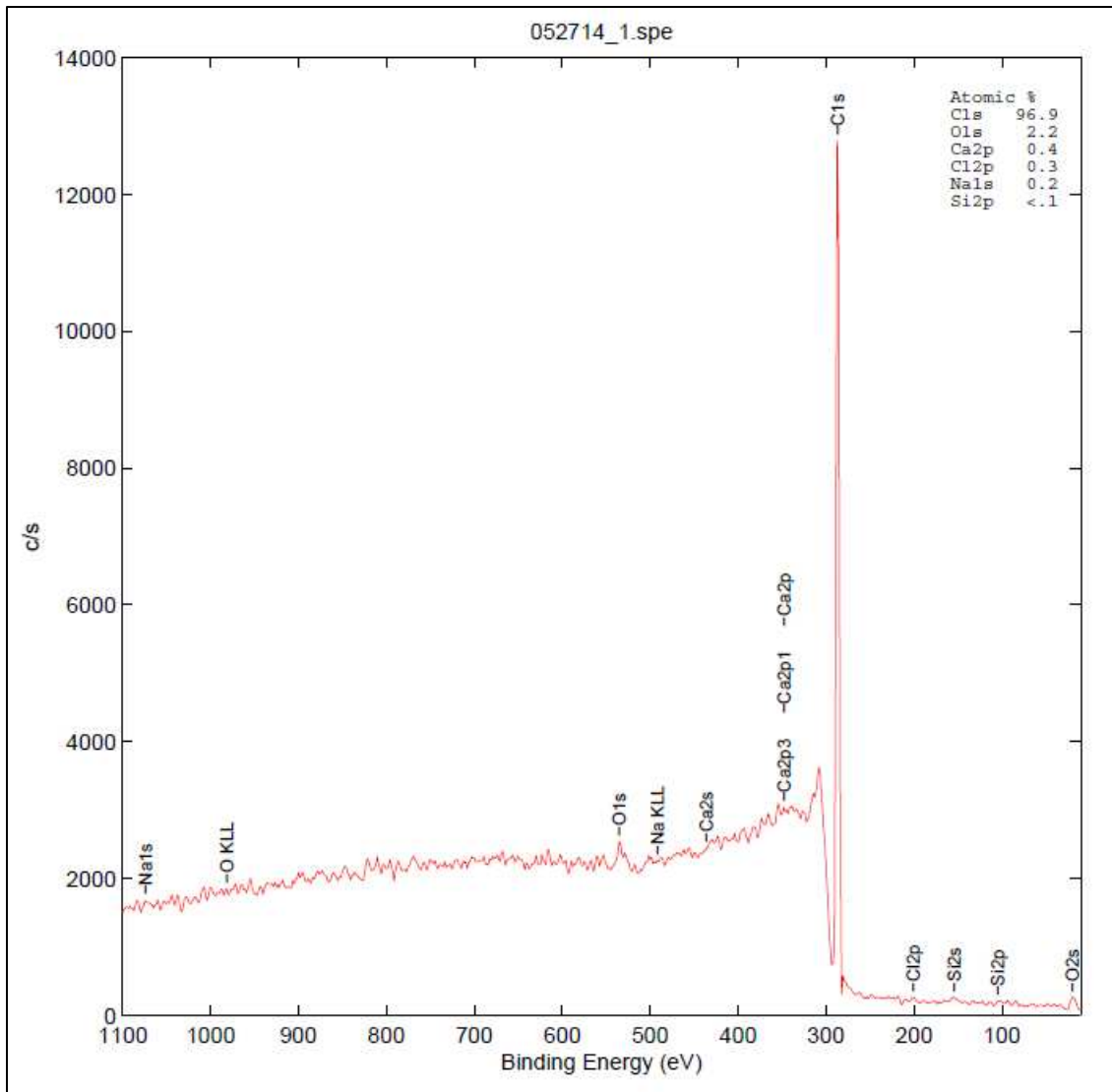


Figure D-1. XPS of sample Crow Creek State AC36-76-1HN

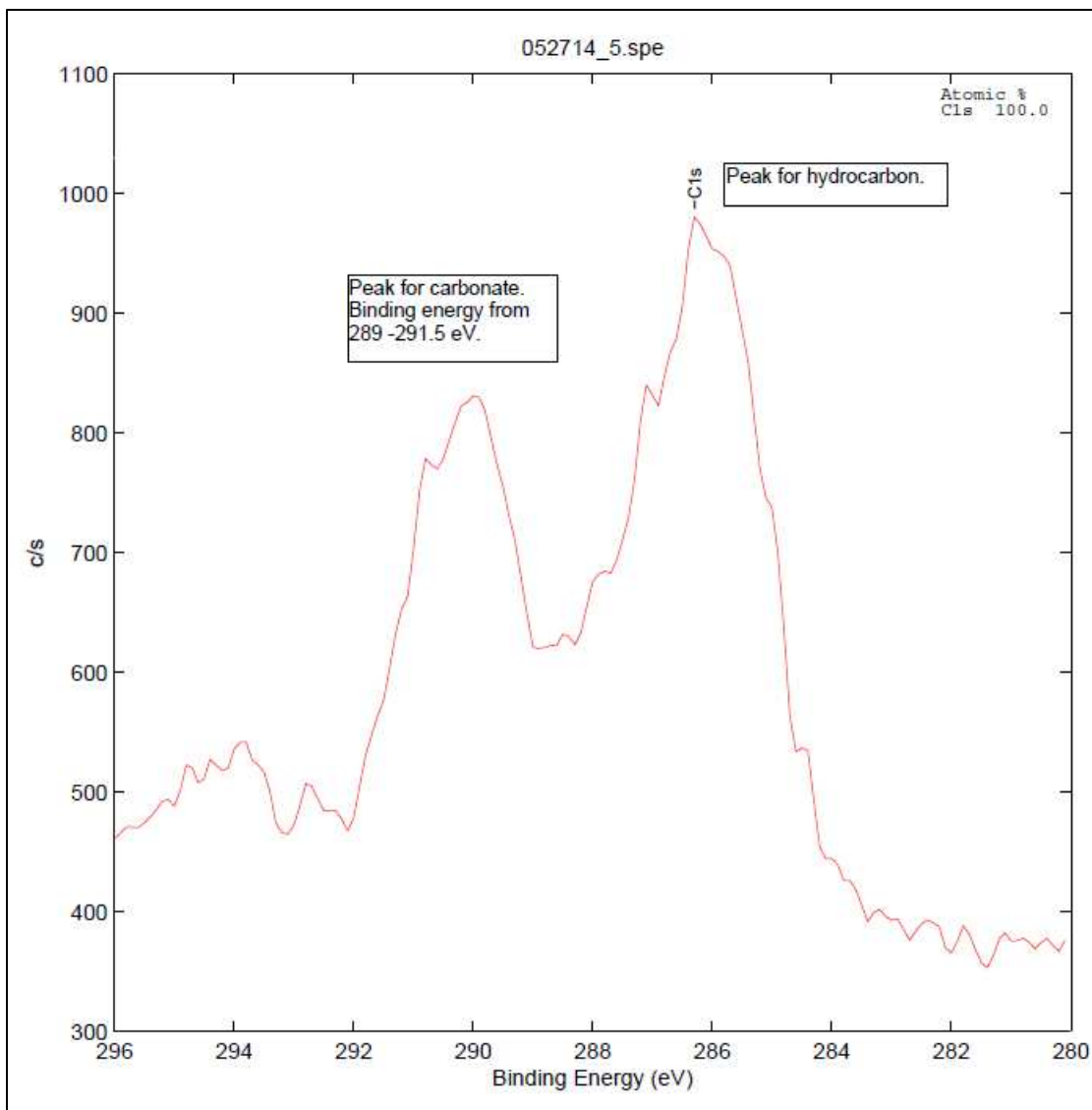


Figure D-2. XPS of inorganic carbon of sample Crow Creek State AC36-76-1HN



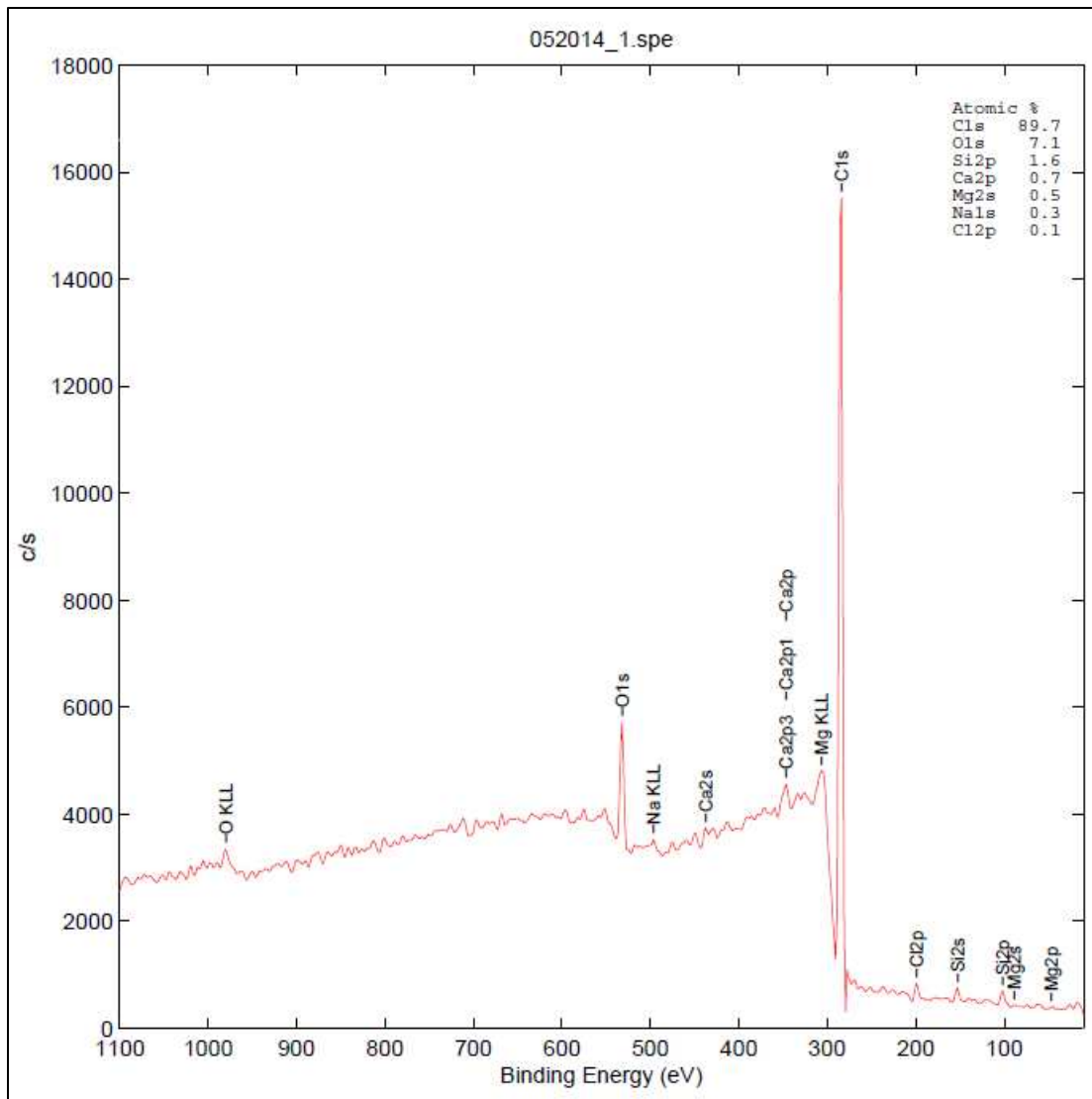


Figure D-3. XPS of sample Crow Creek State AC36-73HN

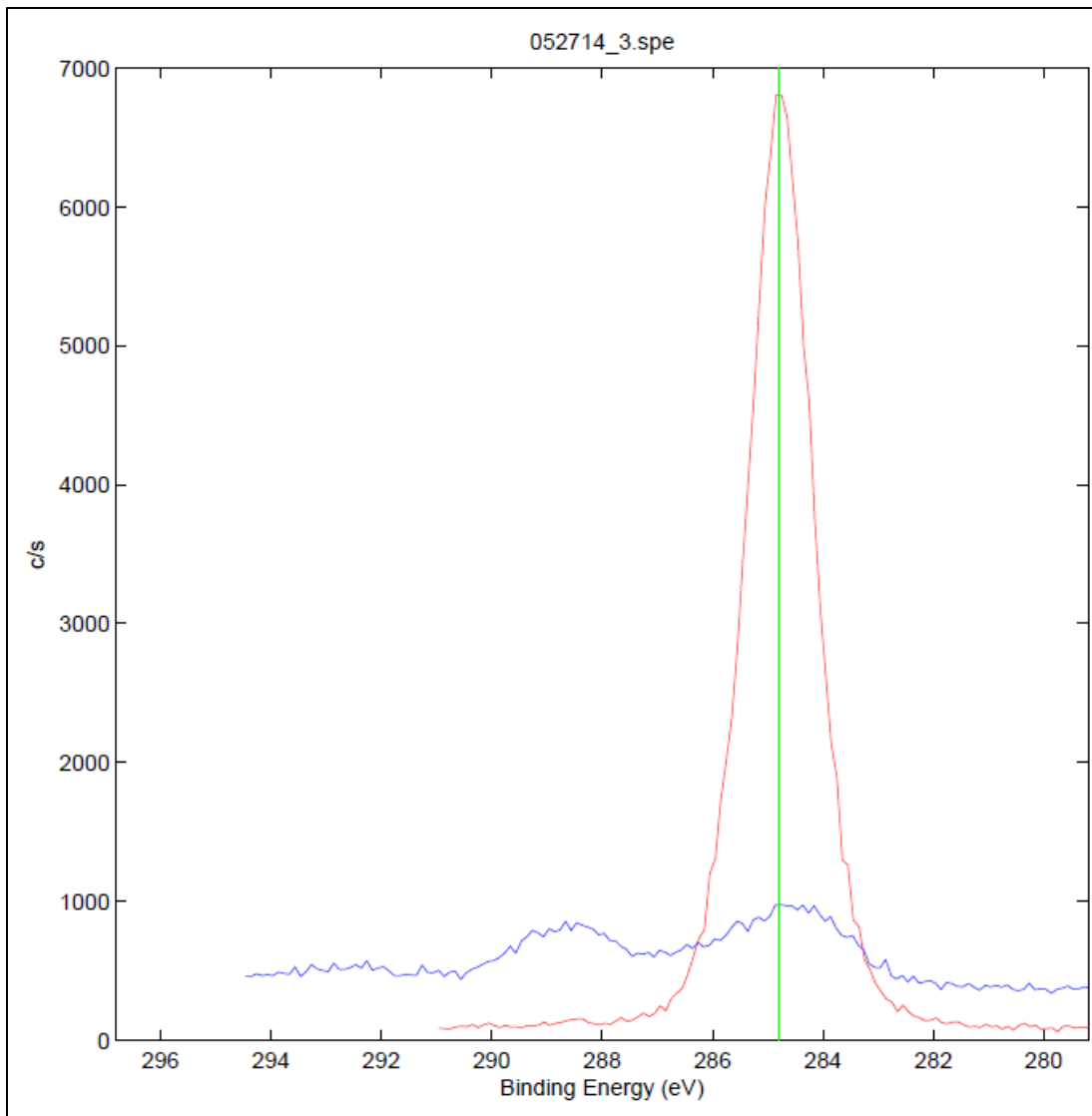


Figure D-4. XPS of inorganic carbon of sample Crow Creek State AC36-73HN

## Appendix E. Theories of Low Salinity Waterflood and Mechanisms of Clay Swelling and Diffused Double Layer Expansion

### E.1 Clay Swelling

Figure E-1 shows the theoretical relationship between oil recovery rate and TDS through the effect of clay swelling.

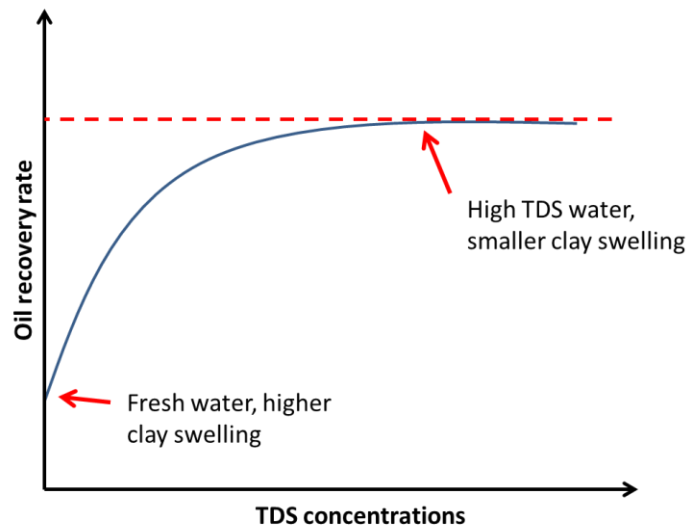


Figure E-1. Theoretical relationship between oil recovery rate and TDS through the effect of clay swelling.

### E.2 Diffused Double Layer Compression

Niobrara shale is normally either mix-wet or strongly oil-wet, and surfactants are added to the fracturing fluids to alter the wettability to water-wet to allow oil to be detached from the clay surface. The surfactants are used to reduce the surface tension between the oil and clay surface (Figure E-2).

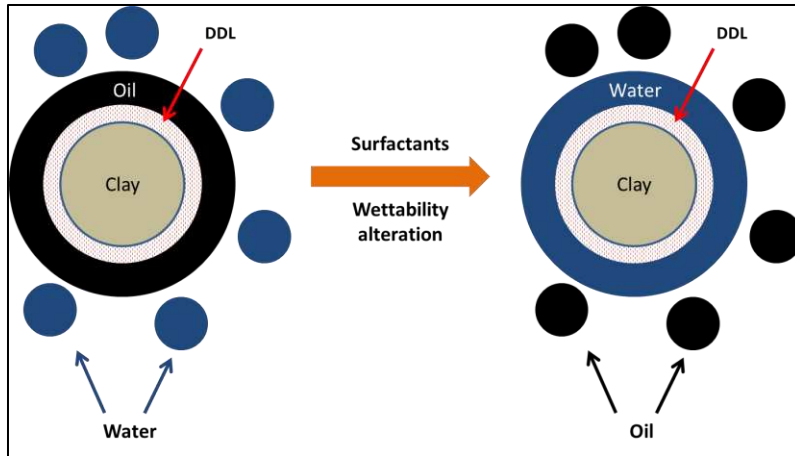


Figure E-2. Shale clay wettability alteration by surfactants from oil-wet to water-wet.

Oil is easier to detach from the clay surface when the bonding force is low between clay and oil, and the clay is easier to be altered to water-wet. Since the bonding force is formed from the ions in DDL, it is highly relative to the thickness of the DDL (Figure E-3).

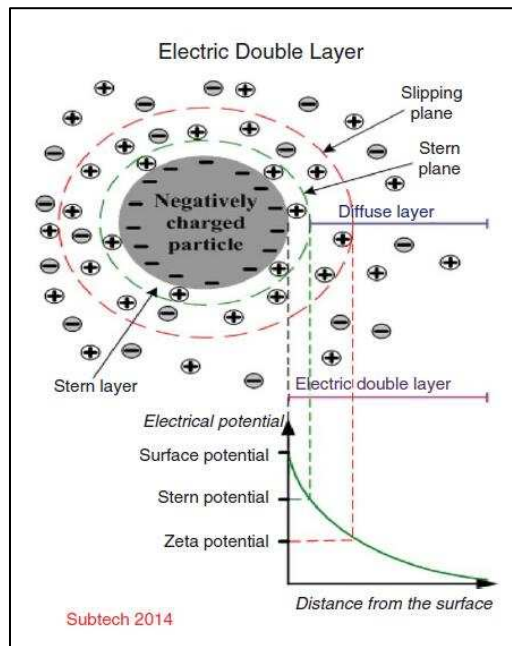


Figure E-3. A schematic of DDL

A theoretical relationship between oil recovery rate and TDS through the effect of DDL compression is shown in Figure E-4.

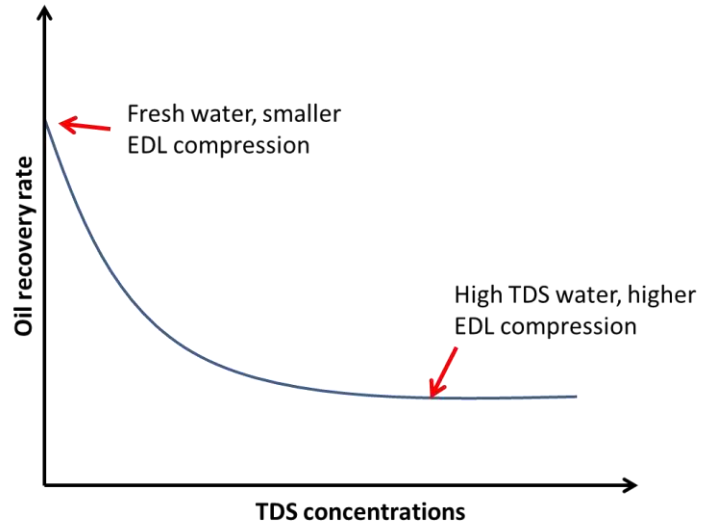


Figure E-4. Theoretical relationship between oil recovery rate and TDS through the effect of DDL compression

## Appendix F. X-ray Diffraction (XRD) Results

In order to simulate the composition of core samples for clay swelling test, X-ray diffraction (XRD) was performed on two core samples from Marie: one from B marl at a depth of 6,706 feet, and one from C chalk at a depth of 6,785 feet. The XRD analysis was conducted by Mineralogy, INC. (Tulsa, OK), and the results were shown in Table F-1. According to the results, calcite, quartz, and illite/mica are the dominant minerals in both samples. From the list, the percentage of smectite will be used for simulating the clay swelling test, which is 3-5 % in both samples.

Table F-1. XRD results showing the mineralogy of two core samples from Marie

	Sample ID	Sample #1 - B Marl	Sample #2 - C Chalk
	Lab ID	14491-01	14491-02
Mineral Constituents	Chemical Formula	Relative Abundance (%)	
Quartz	SiO <sub>2</sub>	12	9
Plagioclase Feldspar - Ab <sub>71</sub> An <sub>29</sub>	(Na <sub>0.82</sub> Ca <sub>0.17</sub> )AlSi <sub>3</sub> O <sub>8</sub>	2	1
Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>	1	<0.3
Calcite	CaCO <sub>3</sub>	50	58
Dolomite	(Ca,Mg)(CO <sub>3</sub> ) <sub>2</sub>	7	2
Pyrite	FeS <sub>2</sub>	3	2
Fluorapatite	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub>	<0.5	<0.3
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>		<0.3
Chlorite	(Mg,Al) <sub>6</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	<0.3	<0.3
Illite/Mica	KAl <sub>2</sub> (Si <sub>3</sub> AlO <sub>10</sub> )(OH) <sub>2</sub>	14	15
Mixed-Layered Illite/Smectite	K <sub>0.5</sub> Al <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> · 2H <sub>2</sub> O	11	13
<b>TOTAL</b>		100	100
% Illite Layers in ML Illite/Smectite	+/- 5%	75%	70%

Table F-2 summarizes the XRD results of Wells Ranch core plugs for spontaneous imbibition tests.

Table F-2. XRD results of two formation layers of core plugs used for spontaneous imbibition in chapter 7

Sample #		1	2
Formation		B chalk	B marl
<b>CLAYS</b>	Chlorite	Tr	Tr
	Kaolinite	Tr	Tr
	Illite	1.08	1.66
	Mx I/S*	5.82	11.29
<b>CARBONATES</b>	Calcite	87.00	74.00
	Dolomite	Tr	0.00
	Dolomite (Fe/Ca+) <sup>1</sup>	0.00	1.00
	Siderite	0.00	0.00
<b>OTHER MINERALS</b>	Quartz	3.00	9.00
	K-spar	Tr	1.00
	Plag.	2.00	2.00
	Pyrite	1.00	Tr
	Marcasite	Tr	Tr
<b>SMECTITE (calculated from Mx I/S)</b>	0.2	1.16	2.26
	0.3	1.74	3.39

## Appendix G. Raw Data from Clay Swelling Tests

### G.1 Clay Swelling Tests Setup

The setup of the clay swelling test is shown in

Figure G-1 and Figure G-2.

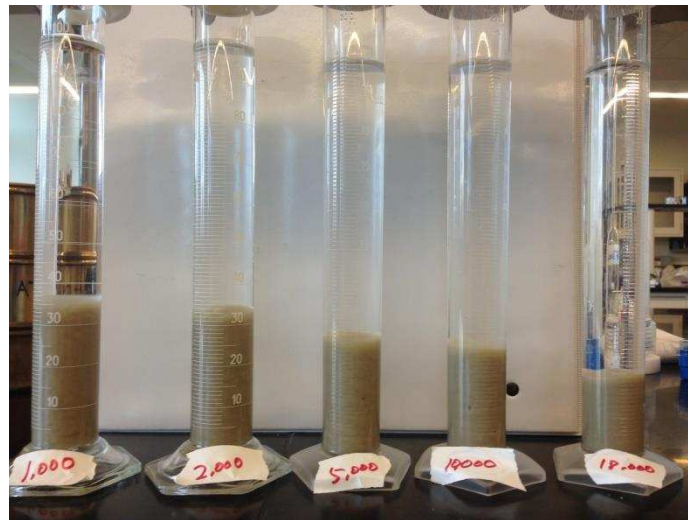


Figure G-1. Clay swelling test set up with TDS from 1,000 to 18,000 mg/L



Figure G-2. Clay swelling test set up with TDS from 25,000 to 40,000 mg/L



Results from clay swelling test with NaCl solution is shown in Figure G-3.

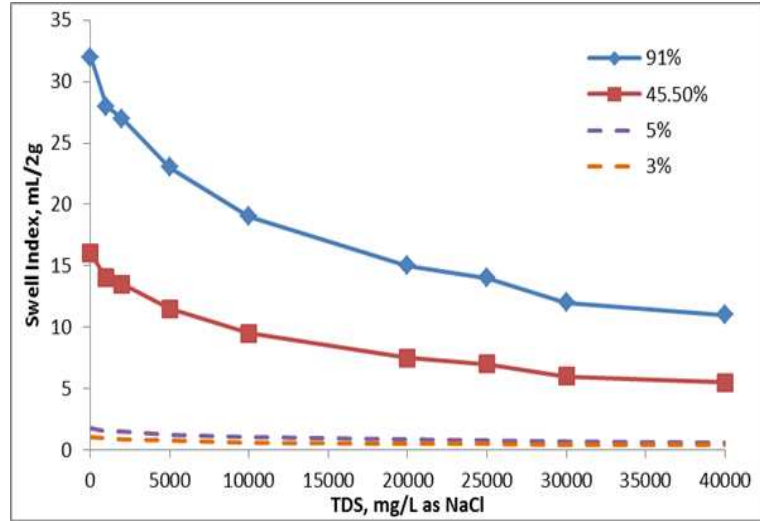


Figure G-3. Clay swelling test with NaCl solution

## G.2 Clay Swelling Test with Recycled Produced Water

In order to investigate how recycled produced water affects the swelling of the bentonite, this round of clay swelling test was performed with recycled water with different TDS concentrations. Results are shown in Figure G-4.

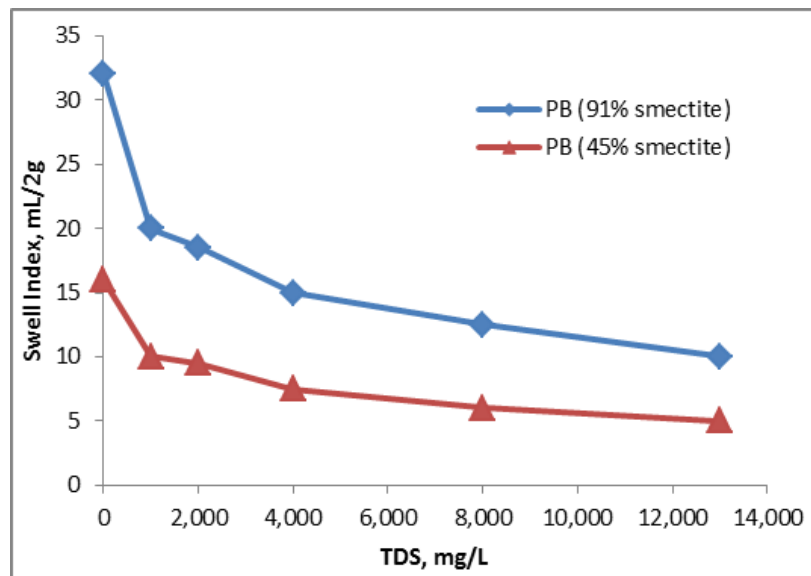


Figure G-4. Clay swelling test with recycled water.

## Appendix H. Raw Data from Contact Angle Measurements

The setup of the contact angle measurement equipment is shown in Figure H-1.

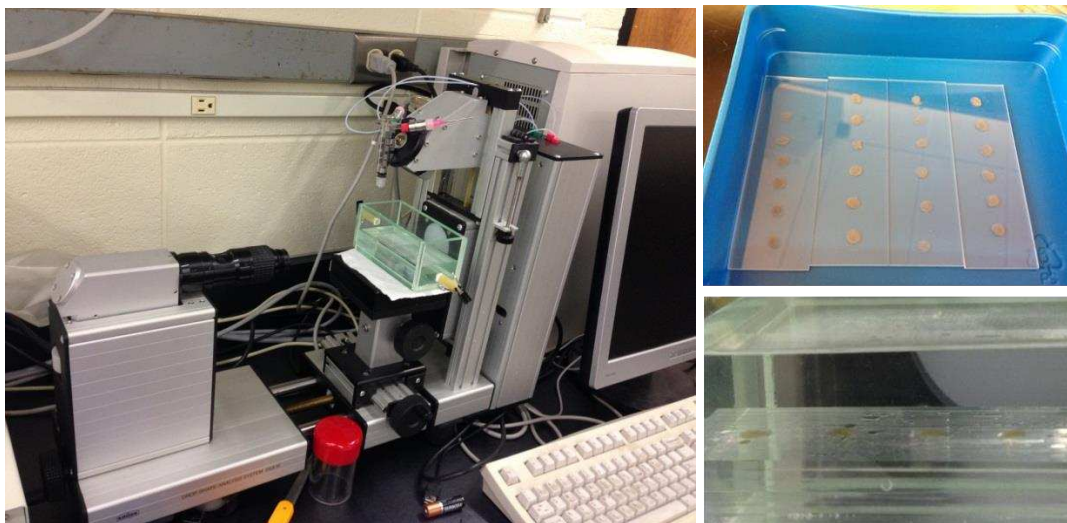


Figure H-1. Real-time contact angle measurement experimental setup. (Left: Kruss® Drop Shape Analyzer. Top right: clay coated glass slides; Bottom right: Oil drops on the clay patches on the glass slides submerged in water.)

### ***Run #1. Niobrara B marl core powder in NaCl solution.***

Sodium Chloride (NaCl) solution was used as brine for the first round of test. The experiment started with 50 mL of high concentration NaCl solution at 16,500 mg/L, and the contact angle was measured after the oil droplets were submerged in the brine for 24 hours. After the measurement was done, 50 mL of DI water was slowly pipetted into the glass cell to dilute the brine for 24 hours. Before measuring the contact angle, 50 mL of brine was carefully pipetted out for TDS reading. The Same procedure was repeated and the contact angle between oil droplets and clay patches was measured at each TDS concentration (Figure H-2 shows the change in three oil droplets' shape with the decrease of TDS concentration).

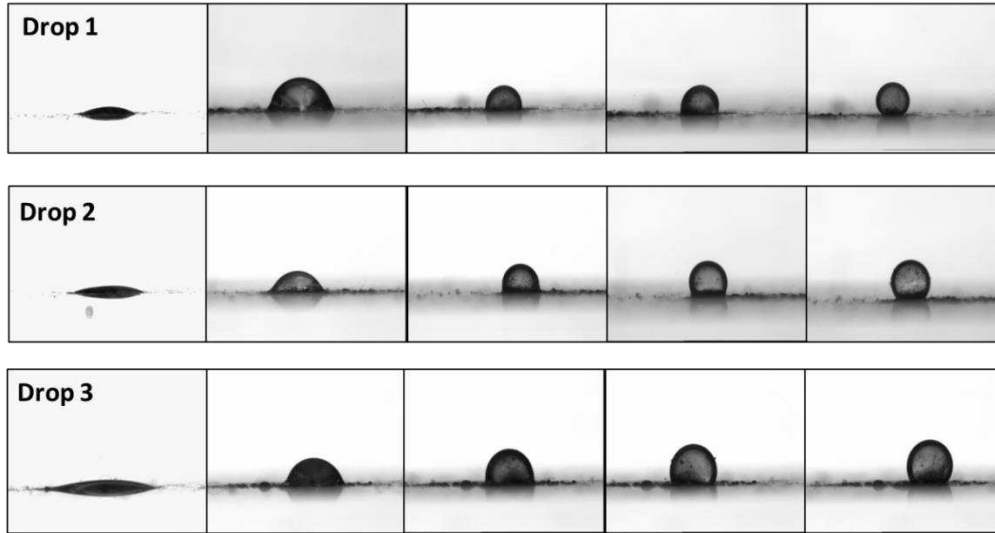


Figure H-2. Shape of three oil droplets under different TDS concentrations. (TDS concentration from left to right: 16,000, 7,000, 5,000, 2,500 and 1,000 mg/L)

Table H-1 summarizes the contact angle of three droplets, and no statistical difference existed among three droplets (ANOVA:  $n=3$ ,  $p=0.9947$ ). The contact angle and TDS concentration followed a linear relationship with  $R^2=0.9884$ , as shown in Figure H-3.

Table H-1. Contact angles ( $^{\circ}$ ) of three oil droplets

TDS	16,500	7,000	5,000	2,500	1,000
Drop 1	7.75	80.11	102.55	114.14	137.42
Drop 2	6.91	69.43	111.65	125.82	141.62
Drop 3	5.4	77.6	105.69	118.48	132.95
Average	6.69	75.71	106.63	119.48	137.33

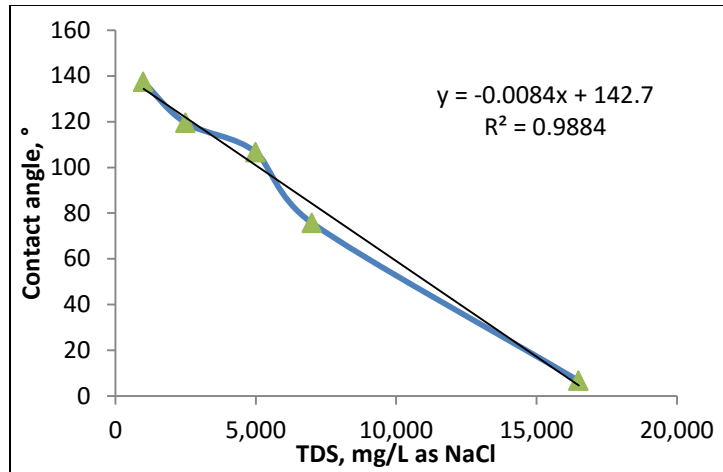


Figure H-3. Change of average contact angle from three oil droplets with the change of TDS concentration.

**Run #2. Niobrara B chalk core powder in NaCl solution.**

Niobrara B chalk core powder was obtained from one core plug from well Wells Ranch USX AA27-64-1HNX and NaCl solution was used as brine. Shape of each oil droplet and their contact angle at different TDS concentrations are summarized in Figure H-4 and Table H-2.

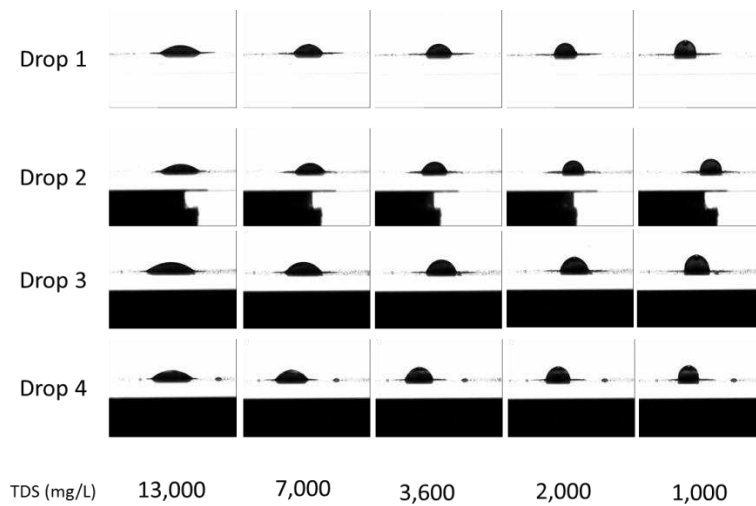


Figure H-4. Shape of four oil droplets under different TDS concentrations.

Table H-2. Contact angles (°) of four oil droplets

TDS	13,000	7,000	3,600	2,000	1,000
Drop 1	30.87	61.4	76.81	92.62	102.3
Drop 2	30.1	59.06	75.92	93.25	100.62
Drop 3	30.33	59.41	79.84	91.86	100.61
Drop 4	31.17	62.05	82.3	94.02	105.32
Average	30.77	60.48	78.72	92.94	102.21

Average contact angle from four oil droplets are plotted in Figure H-5, and it follows a linear function with the TDS concentration of the brine.

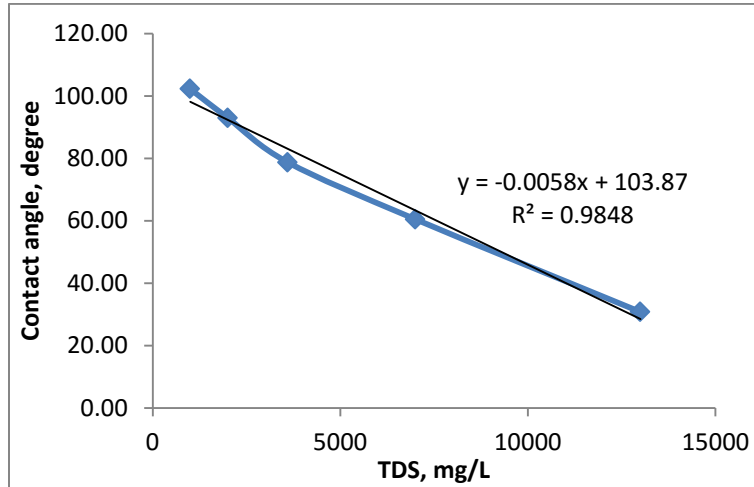


Figure H-5. Change of average contact angle from four oil droplets with the change of TDS concentration.

**Run #3. Niobrara B chalk core powder in NaCl solution.**

This round is the repeated test of Run #2, and the results are shown in Figure H-6, Table H-3 and Figure H-7. A linear function between contact angle and TDS of NaCl solution was also observed.

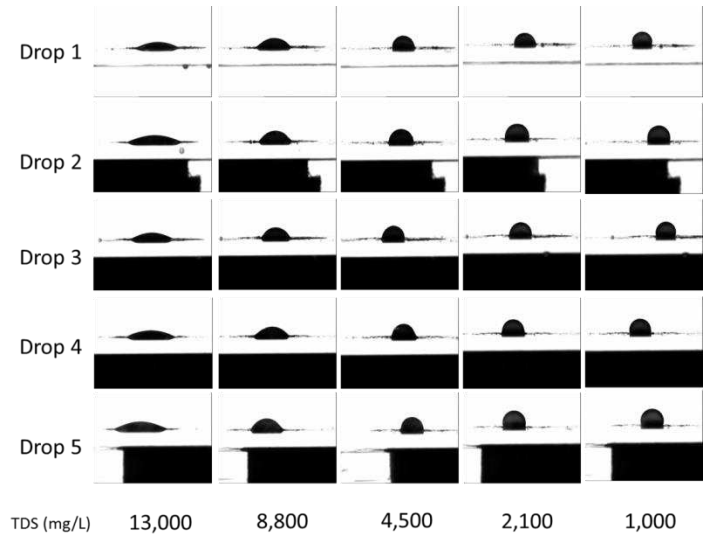


Figure H-6. Shape of five oil droplets under different TDS concentrations.

Table H-3. Contact angles (°) of five oil droplets

TDS	13,000	8,800	4,500	2,100	1,000
Drop 1	29.44	54.39	83.66	96.93	115.84
Drop 2	27.67	65.82	83.01	99.90	116.69
Drop 3	32.03	63.98	84.38	97.15	121.05
Drop 4	29.68	54.98	84.76	99.17	114.59
Drop 5	28.94	62.04	82.23	103.81	119.68
Average	29.55	60.24	83.61	99.39	117.57

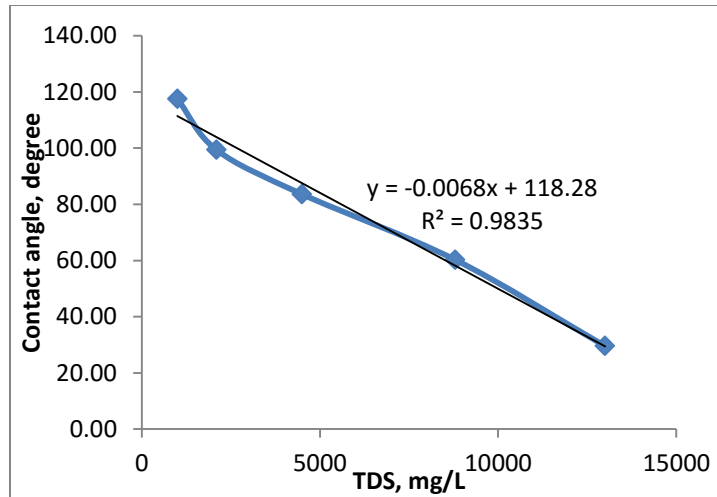


Figure H-7. Change of average contact angle from five oil droplets with the change of TDS concentration.

***Run #4. Niobrara B chalk core powder in recycled produced water.***

In order to compare the impacts on contact angle from organic compounds in real recycled produced water, treated produced water was used in this round of test. The raw was has a TDS of 13,000 mg/L and TOC of 85 mg/L. Results are summarized in Figure H-8, Table H-4 and Figure H-9. A linear function between contact angle and TDS of recycled water was also observed.

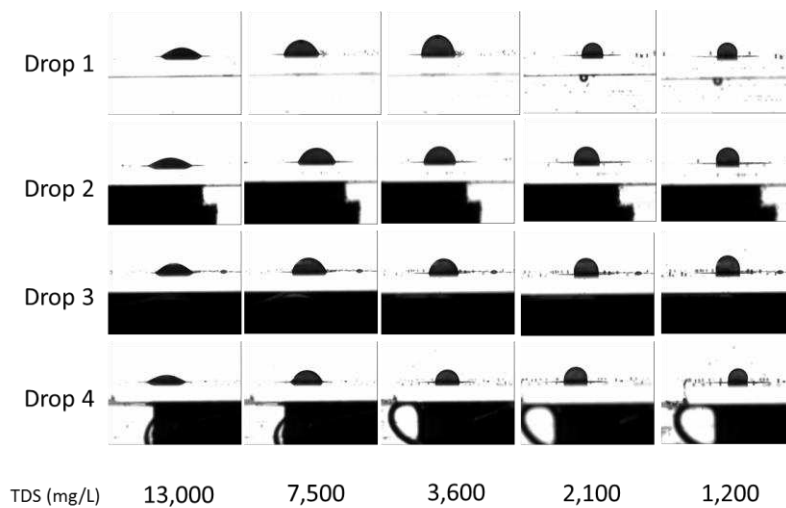


Figure H-8. Shape of four oil droplets under different TDS concentrations of recycled water.

Table H-4. Contact angles (°) of four oil droplets

TDS	13,000	7,800	3,800	2,300	1,200
Drop 1	43.93	74.99	92.763	102.23	111.45
Drop 2	38.94	72.07	89.15	103.89	110.55
Drop 3	45.18	76.1	87.193	107.92	114.06
Drop 4	38.1	71.81	93.27	105.19	108.38
Average	41.54	73.74	90.59	104.81	111.11

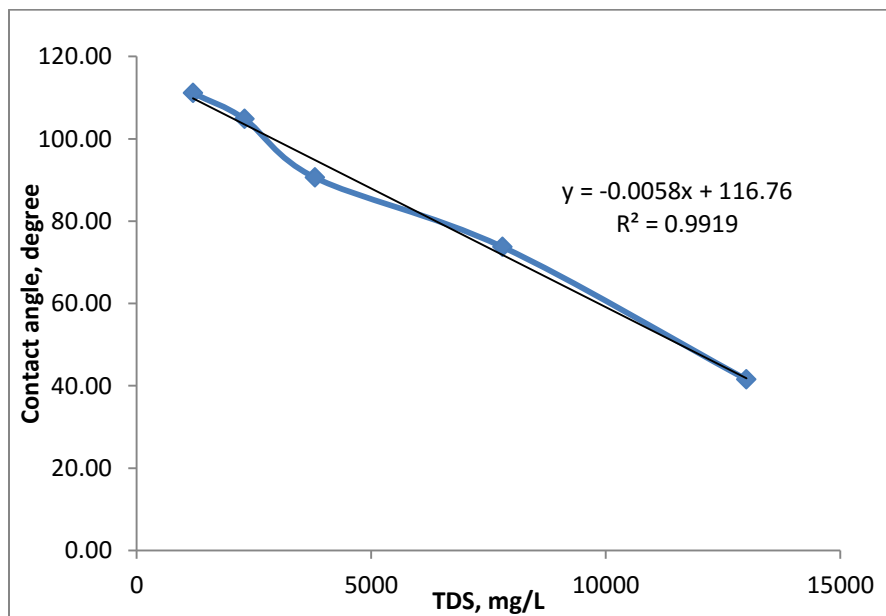


Figure H-9. Change of average contact angle from four oil droplets with the change of TDS concentration.

***Run #5. Niobrara B chalk core powder in recycled produced water.***

This round is the repeated test of Run #4, and the results are shown in Figure H-10, Table H-5 and Figure H-11. A linear function between contact angle and TDS of NaCl solution was also observed.



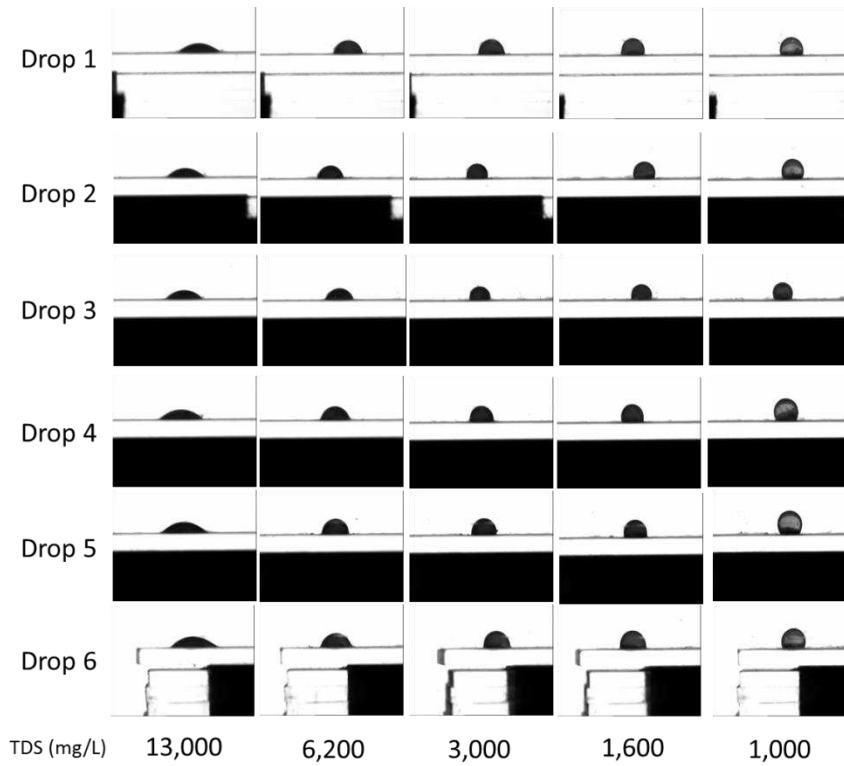


Figure H-10. Shape of six oil droplets under different TDS concentrations of recycled water.

Table H-5. Contact angles (°) of six oil droplets

TDS	13,000	6,200	3,000	1,600	1,000
Drop 1	38.42	71.77	96.93	110.47	120.26
Drop 2	38.66	74.04	98.79	114.06	122.28
Drop 3	39.78	76.6	98.16	115.75	123.44
Drop 4	39.49	73.94	98.37	107.71	121.91
Drop 5	38.69	80.92	97.21	112.22	125.31
Drop 6	38.04	70.8	94.26	110.55	124.59
Average	38.85	74.68	97.29	111.79	122.97

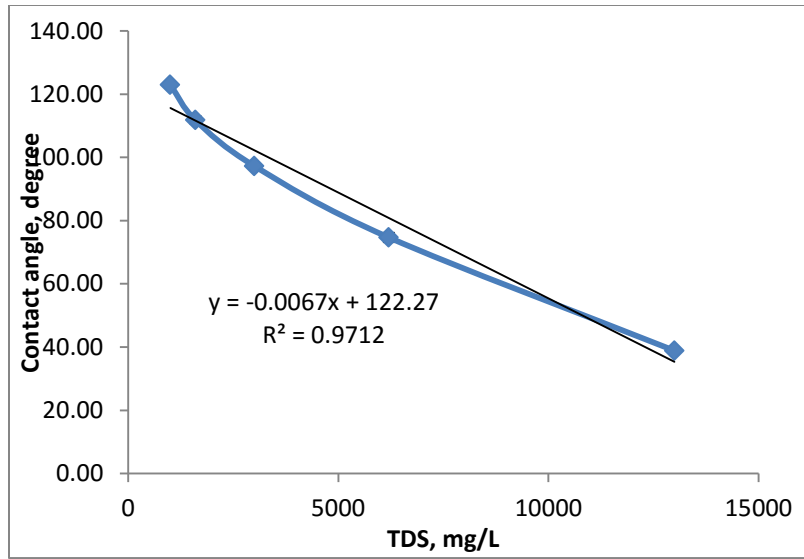


Figure H-11. Change of average contact angle from six oil droplets with the change of TDS concentration.

**Run #6. Niobrara B chalk core powder in recycled produced water.**

This round is the repeated test of Run #5, and the results are shown in Figure H-12, Table H-6 and Figure H-13. A linear function between contact angle and TDS of NaCl solution was also observed.

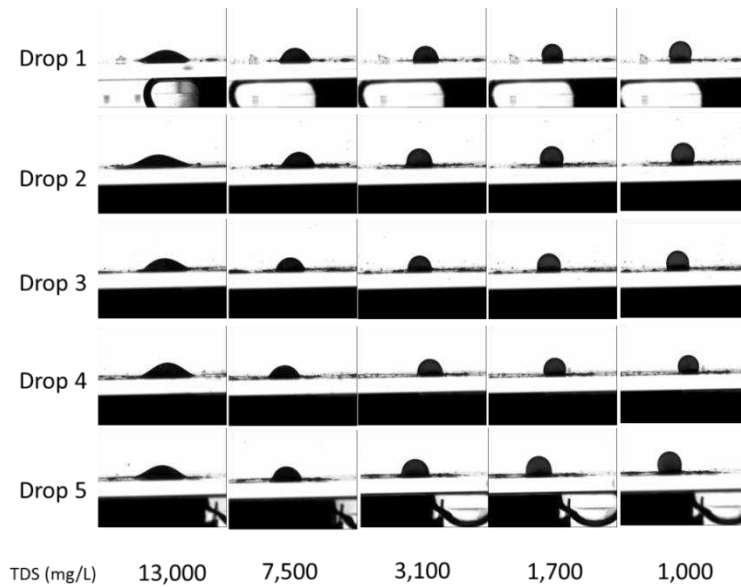


Figure H-12. Shape of five oil droplets under different TDS concentrations of recycled water.

Table H-6. Contact angles (°) of five oil droplets

TDS	13,000	7,500	3,100	1,700	1,000
Drop 1	34.36	70.13	96.25	119	131.77
Drop 2	31.38	69.69	98.8	118.02	126.42
Drop 3	33.35	69.55	95.2	112.34	127.83
Drop 4	35.19	73.63	92.08	116.6	126.93
Drop 5	31.48	72.82	92.62	115.23	130.27
Average	33.15	71.16	94.99	116.24	128.64

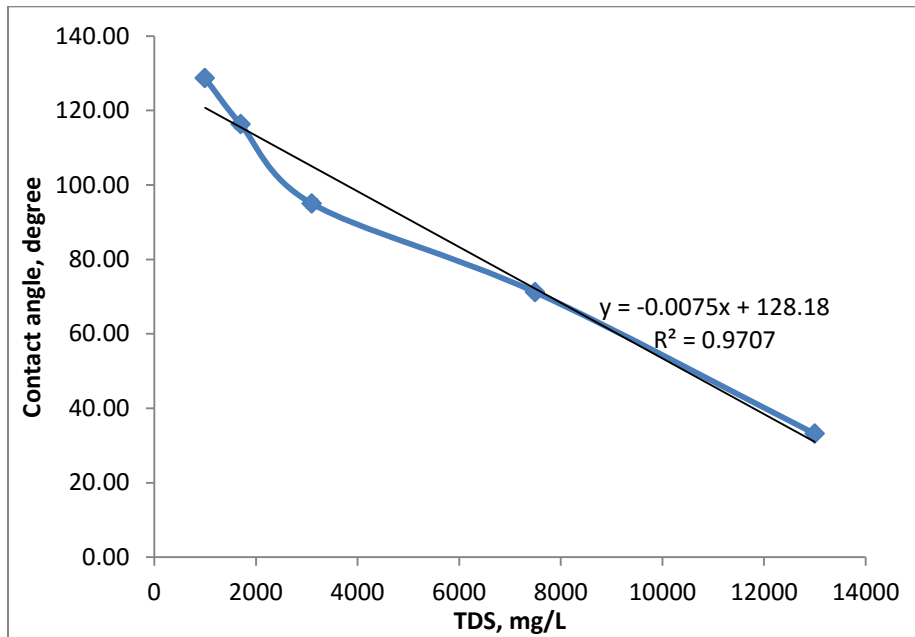


Figure H-13. Change of average contact angle from five oil droplets with the change of TDS concentration.

Figure H-14 summarized all the contact angle results from six rounds of experiments. Results show that contact angles from recycled water are generally greater than them from NaCl solution, indicating the existence of organic compounds in recycled water may serve as surfactants, which could accelerate the detachment of oil droplets from shale clay surface.

However, due to the very low concentration of organic compounds in recycled water (TOC = 85 mg/L) in these tests, no significant difference is observed.

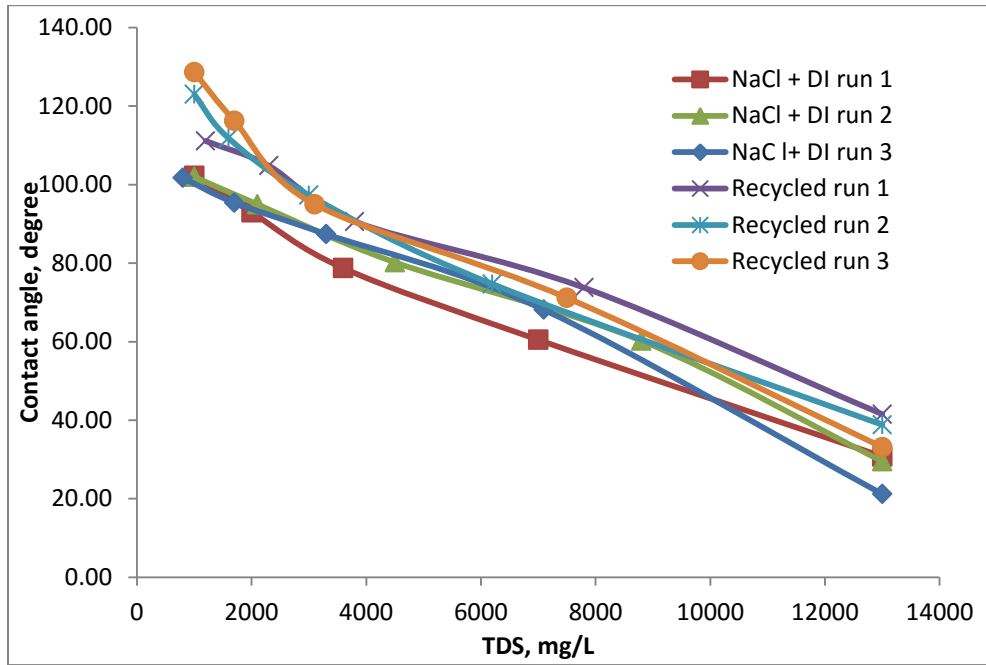


Figure H-14. Comparison of contact angles from six rounds of experiments.

## Appendix I. Raw Data from Spontaneous Imbibition Tests

### I.1 Imbibition Test Part I – Core Plugs from Two Wells in Mustang IDP (Marie D04-74-1HN and Sater CC18-72-1HN)

First three rounds of spontaneous imbibition tests were conducted in this part of test. Based on the formation log of each well, 20 cores were tested. Table I-1 summarizes the number of cores in each formation layer. Two base fluids were used in this study: fresh pond water (as fresh water) and treated produced water (as recycled water). Two recycle/fresh blend water was tested at TDS of 3,000 and 10,000 mg/L. The test criteria and number of runs are shown in Table I-2. All tests were performed at 190 °F, and the volume of oil recovered was recorded.

Table I-1. Distribution of core samples from two wells in Mustang IDP

Formation Layer	Marie	Sater	Total
Niobrara B Chalk	0	3	3
Niobrara B Marl	4	6	10
Niobrara C Chalk	5	2	7

Table I-2. Spontaneous imbibition test criteria and number of runs, all water with various TDS values are fresh/recycled blended water

Test Criteria		B Marl (10 cores)	C Chalk (7 cores)	B Chalk (3 cores)
Water	Fresh pond water	2	2	1
	100% recycled	2	1	1
	TDS 3,000	2	2	1
	TDS 10,000	2	2	

**Run #1 – B marl cores.**

Before saturation with crude oil, all cores were dried in vacuum desiccator for 24 hours and weighed. All cores were then saturated with crude oil for 10 weeks and weighed again. 8 cores from B marl were tested with water for the first run of spontaneous imbibition, and their weights before and after saturation were summarized in Table I-3. At the same time, the density of the crude oil as well as four imbibition water was measured.

The volume of oil recovered was recorded after 11 days of imbibition when no more oil was imbibed out. Photos of each imbibition cell were taken after 1 day of imbibition (Figure I-1) and 11 days of imbibition when the volume of oil stabilized (Figure I-2). From Figure I-1, oil showed up first in fresh water cells, and almost no oil was observed from the cells with 30,000 mg/L TDS water. From Figure I-2, it is evident that with the increase of TDS concentrations in the water, the darker the oil became.

Table I-3. Summary table of 8 cores for the first run of spontaneous imbibition (all group-a samples are from Sater and group b samples are from Marie)

Imbibition Water (TDS: mg/L)	Group	Core weight (g)		Oil adsorbed (% weight)
		Before saturation	10 weeks saturation	
Fresh WR pond water (TDS=400)	a	33.0877	33.737	1.96
	b	32.3219	33.6753	4.19
R/F 1/10 blend (TDS=3,000)	a	33.9668	34.8608	2.63
	b	35.5274	36.7057	3.32
R/F 1/2 blend (TDS=10,000)	a	34.3523	35.5099	3.37
	b	30.769	31.9929	3.98
High Sierra water (TDS=30,000)	a	34.02	35.3552	3.92
	b	36.6936	37.3732	1.85

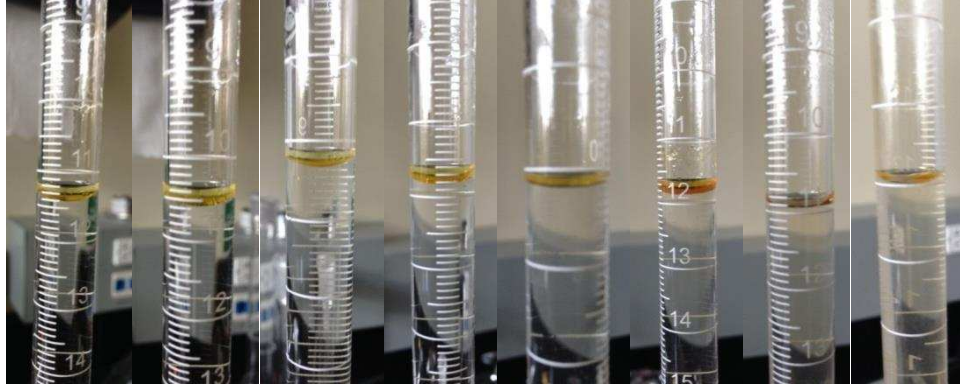


Figure I-1. Oil recovered from shale cores after 1 day of imbibition.  
 (Left to right: fresh a, fresh b, TDS 3,000 a, TDS 3,000 b, TDS 10,000 a, TDS 10,000 b, TDS 30,000 a, TDS 30,000 b)

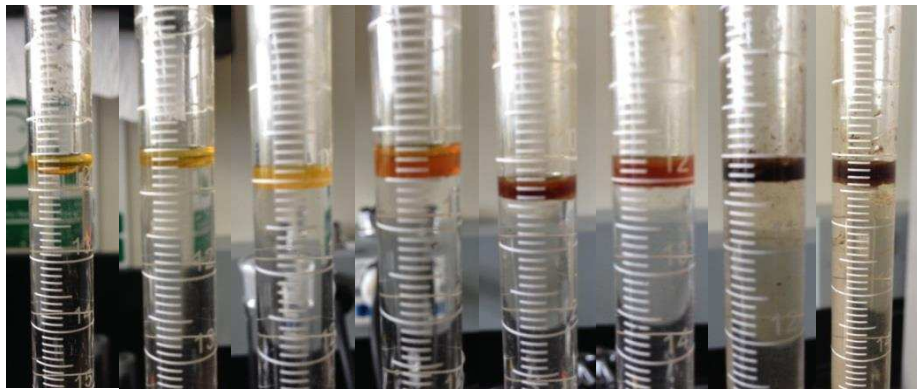


Figure I-2. Oil recovered from shale cores after 11 days of imbibition.  
 (Left to right: fresh a, fresh b, TDS 3,000 a, TDS 3,000 b, TDS 10,000 a, TDS 10,000 b, TDS 30,000 a, TDS 30,000 b)

After 11 days of imbibition, oil from each cell was taken out for measurement. Two methods were applied when measuring the volume of oil: by reading the volume of oil with 1 ml x 0.01 ml measuring pipet, and by calculation from the total weight of 1 ml of oil and water mixed solution.

Table I-4 summarized the results of oil volume from two types of measuring methods, and average oil recovery rate from B marl was calculated and plotted in Figure I-3.

Table I-4. Summary table of the volume of oil measured from two methods (all group-a samples are from Sater and group b samples are from Marie)

Imbibition #	Oil volume by 1ml measuring pipet (ml)	Oil volume by weight calculation (ml)	Average oil volume (ml)	Average oil recovery rate (%)*
TDS 400 a	0.11	0.07	0.09	11.03
TDS 400 b	0.23	0.21	0.22	12.88
TDS 3,000 a	0.14	0.12	0.13	11.57
TDS 3,000 b	0.21	0.20	0.205	13.76
TDS 10,000 a	0.18	0.13	0.155	10.66
TDS 10,000 b	0.15	0.17	0.16	10.36
TDS 30,000 a	0.16	0.17	0.165	9.84
TDS 30,000 b	0.08	0.09	0.085	10.18

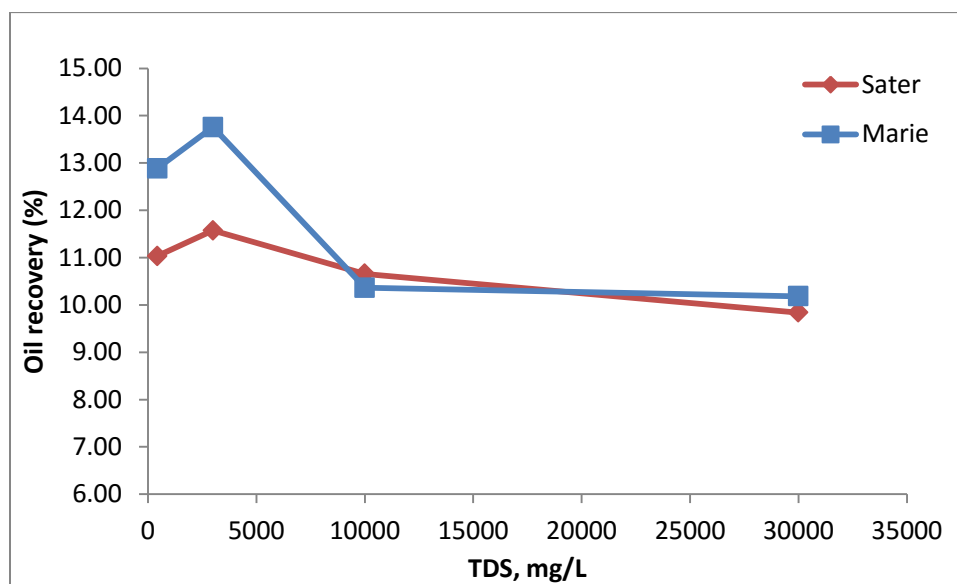


Figure I-3. Average oil recovery rate vs. TDS of imbibition water from B marl between well Sater and Marie

**Run #2 – C chalk cores.**

Followed the exact same steps in the first run of spontaneous imbibition, the second



round of imbibition used 7 cores from C chalk. Table I-5 and Table I-6 summarized the oil adsorbed from saturation and recovered after imbibition.

Table I-5. Summary table of 7 cores for the second run of spontaneous imbibition (all group-a samples and sample TDS 3,000 b are from Sater, and other two group b samples are from Marie)

Imbibition Water (TDS: mg/l)	Group	Core weight (g)		Oil adsorbed (% weight)
		Before saturation	10 weeks saturation	
Fresh WR pond water (TDS=400)	a	35.001	35.7464	2.13
	b	32.6678	33.81	3.5
R/F 1/10 blend (TDS=3,000)	a	34.9361	36.0695	3.24
	b	36.5721	37.3066	2.01
R/F 1/2 blend (TDS=10,000)	a	33.26	34.3603	3.31
	b	36.7232	37.8604	3.1
High Sierra water (TDS=30,000)	a	32.1675	33.4801	4.08

Table I-6. Summary table of the volume of oil measured from two methods (all group-a samples and sample TDS 3,000 b are from Sater, and other two group b samples are from Marie)

Imbibition #	Oil volume by 1ml measuring pipet (ml)	Oil volume by weight calculation (ml)	Average oil volume (ml)	Average oil recovery rate (%)
TDS 400 a	0.09	0.05	0.07	7.48
TDS 400 b	0.05	0.08	0.065	4.43
TDS 3,000 a	0.23	0.25	0.24	16.86
TDS 3,000 b	0.14	0.18	0.16	17.53
TDS 10,000 a	0.19	0.15	0.17	12.3
TDS 10,000 b	0.15	0.13	0.14	9.77
TDS 30,000 a	0.11	0.1	0.105	6.37

The results of the second round of imbibition were plotted in Figure I-4, and the oil recovery rate followed the same trend as in the first run of experiment with 8 cores from B marl. Although only four TDS values were tested in two rounds of spontaneous imbibition, the average oil recovery rate followed the hypothesis that an optimal TDS value may exist between the TDS of 400 and 30,000 mg/L.

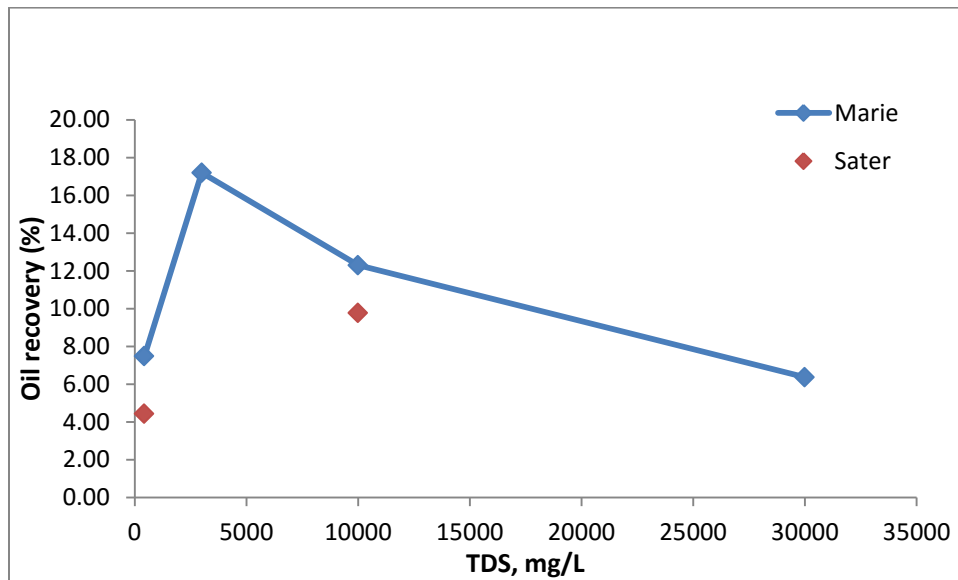


Figure I-4. Average oil recovery rate vs. TDS of imbibition water from C chalk between well Sater and Marie. Data of TDS 3,000 was the average of group a and b since both two cores were from well Marie.

***Run #3 – Check repeatability with B marl and C chalk cores.***

Same cores in the first two runs were tested again in this round of imbibition test. Four cores were tested with exact same water to check the repeatability of the result, and the other cores were tested with different TDS water to check if the results still fall into the same trend. Figure I-5 and Figure I-6 show the results of these two rounds of spontaneous imbibition tests.

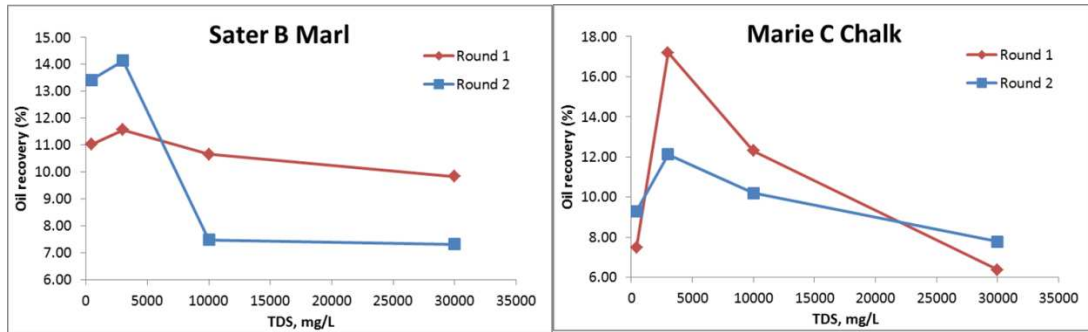


Figure I-5. Repeatability check with cores from B marl and C chalk.

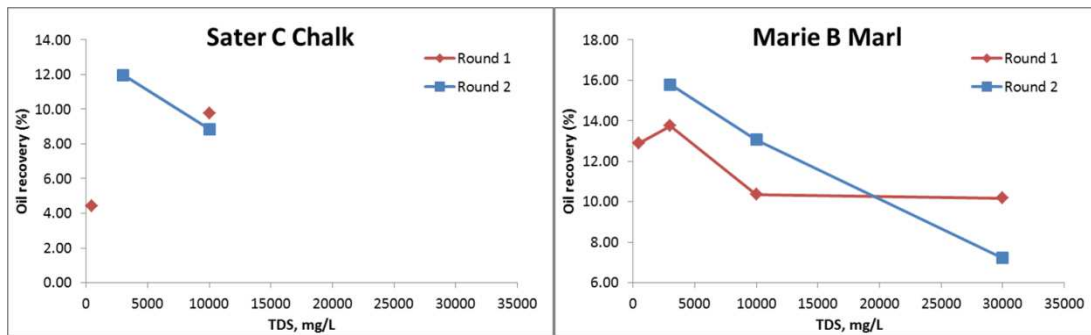


Figure I-6. Oil recovery from mixed up cores and TDS concentrations from B marl and C chalk.

The Same trend of oil recovery rate was observed from both B marl and C chalk in the repeatability check. Oil recovery rate peaked both at 3,000 mg/L of TDS again; however, the uncertainty needs to be narrow down with more runs of tests. Also, no final conclusion could be drawn from the other two runs of spontaneous imbibition due to the limited number of cores.

## I.2 Imbibition Test Part II – Core Plugs from Wells Ranch IDP (Wells Ranch USX AA27-64-1HNX)

Spontaneous imbibition tests were conducted on shale core plugs from Wells Ranch USX AA27-64-1HNX with detailed information summarized in Table I-7. All imbibition tests were performed at 190 °F for two weeks (14 days) with no further imbibition of oil was observed. For all four rounds of imbibition tests, water with 7 Total Dissolved Solids (TDS) concentration was

investigated: 400, 1,500, 3,000, 4,500, 7,500, 10,000 and 20,000 mg/L. Fresh water (TDS=400 mg/L) was collected from the Windsor Lake on December 4th, 2015, and stored in the fridge at 4 °C. Recycled water (TDS=20,000 mg/L) was lab treated flowback/produced water collected from Central Process Facility (CPF) of Wells Ranch IDP. Raw water was treated through Electric coagulation and Ultra Filtration, and the effluent was used for spontaneous imbibition with Total Organic Carbon (TOC) of 1,100 mg/L. All imbibition water was blended with fresh water and treated CPF water to form different TDS concentration. Crude oil from Wells Ranch CPF was also collected and used for core plug saturation. The density of crude oil is 0.796 g/ml. For all cleaned core plugs, a 24-hour vacuum desiccation was performed before saturation started. 7 of uncleaned core plugs were tested without saturation of crude oil in the first round of spontaneous imbibition; however no free oil was imbibed out from these plugs after 3 weeks of imbibition. As a result, these plugs and all the unclean plugs were dried in the oven at 105 °C for a week before vacuum desiccation and oil saturation. All the plugs were saturated with crude oil for at least one month before they can be tested for spontaneous imbibition. All plugs were weighed before and after saturation, and the difference is the oil saturated into the plugs.

Table I-7. Core plugs used for spontaneous imbibition tests with Wells Ranch plugs

<b>SI test Run#</b>	<b>Core plugs info</b>	<b>Formation</b>
1	Uncleaned plugs, not saturated with crude oil	B chalk
2	Cleaned plugs, saturated with crude oil	B chalk
3	Cleaned plugs, dried and saturated with crude oil	B chalk
4	Cleaned plugs, dried and saturated with crude oil	B marl

Core plugs are reused after the imbibition tests, if not broken during the tests. All reused plugs were dried in oven at 105 °C for a week, vacuum desiccated for 24 hours and submerged under crude oil for saturation.

**Run #1 – Uncleaned B chalk cores without crude oil saturation**

As mentioned above, no free oil was imbibed out from uncleaned unsaturated plugs after 3 weeks of imbibition tests. Instead, the TOC of imbibition water after the tests was measured and compared (Table I-8). Figure I-7 shows the increase of TOC concentration of imbibition water after 3 weeks of tests.

Potential explanations for the results could be: evaporation of hydrocarbon (oil and gas) from the core plugs during the long storage time period; stabilization and solidification of hydrocarbon inside the core plugs; very low TOC concentration of the plugs that could not be imbibed out by spontaneous imbibition.

Table I-8. TOC of imbibition water before and after 3 weeks of spontaneous imbibition

TDS (mg/L)	Base TOC (mg/L)	TOC after SI (mg/L)	TOC increase (mg/L)
400	3.294	3.32	0.026
1500	70.46724	68.61	-1.86
3000	148.6075	153.3	4.69
4500	232.5056	232.7	0.19
7500	400.5757	396.6	-3.98
10000	540.6799	551.6	10.92
20000	1100	1151	51

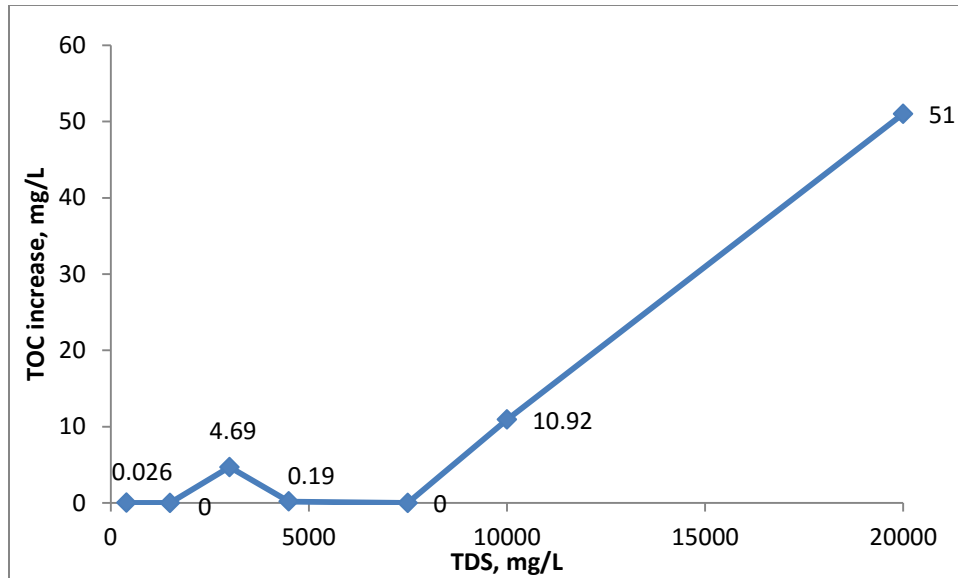


Figure I-7. Increase of TOC concentration of imbibition water after 3 weeks of spontaneous imbibition. All negative values were represented as 0 in the figure.

Results from this round of imbibition suggested that uncleaned core plugs cannot be tested directly. Although there could be the residual hydrocarbon in these plugs, they are unable to be imbibed out. So an oven dry and oil saturation process will be applied to all uncleaned plugs.

***Run #2 – cleaned B chalk cores***

This round of spontaneous imbibition was performed with cleaned core plugs saturated with crude oil from B chalk. The results are summarized in Table I-9, and the oil recovery is plotted in Figure I-8. From Figure I-8, average oil recovery rate is peaked at TDS of 3,000 mg/L, and the oil recovery at TDS of 4,500 mg/L is also higher than the rest of five TDS concentration.

Table I-9. Results of the 2<sup>nd</sup> round of spontaneous imbibition with cleaned B chalk core plugs.

TDS mg/L	Plug #	Oil saturated ml	Oil imbibed			Average oil recovery %
			Weight g	Volume ml	Average ml	
400	111B	1.57	0.07	0.1	0.09	6.05
1500	106B	2.28	0.11	0.14	0.14	5.98
3000	110B	1.86	0.12	0.18	0.17	9.06
4500	104B	2.12	0.13	0.2	0.18	8.43
7500	94B	2.39	0.09	0.14	0.12	5.24
10000	96B	1.98	0.09	0.12	0.11	5.76
20000	112B	1.58	0.06	0.08	0.08	5.00

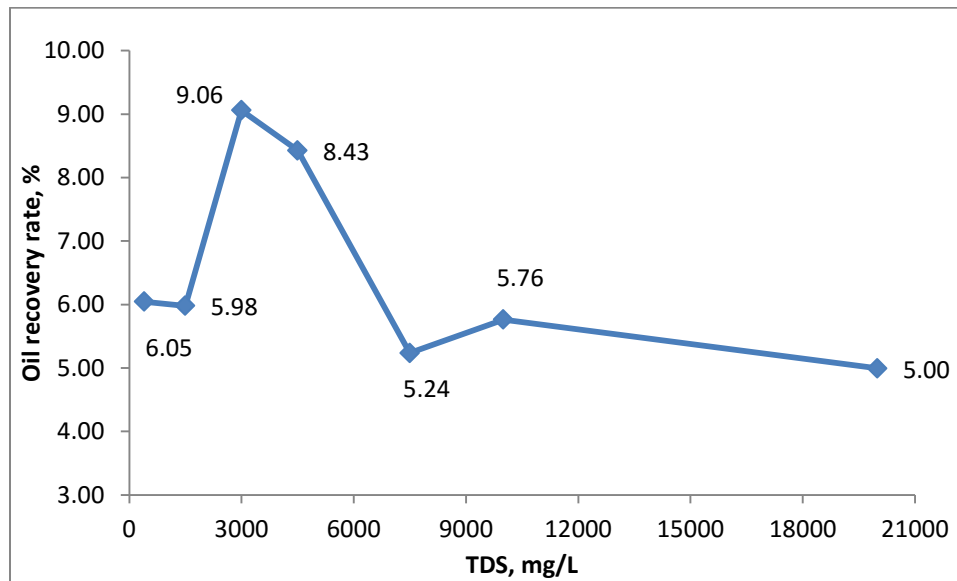


Figure I-8. Average oil recovery rate vs. TDS of imbibition water from cleaned B chalk plugs.

**Run #3 – cleaned B chalk cores**

This round of spontaneous imbibition was performed with cleaned core plugs saturated with crude oil from B chalk. The results are summarized in Table I-10, and the oil recovery is plotted in Figure I-9. From Figure I-9, average oil recovery rate is also peaked at TDS of 3,000

mg/L, and the fresh water (TDS=400 mg/L) comes as the second highest recovery point. The decline at TDS of 1,500 mg/L indicates the uncertainty of this set of results, and further tests will be needed.

Table I-10. Results of the 3<sup>rd</sup> round of spontaneous imbibition with cleaned B chalk core plugs.

TDS mg/L	Plug #	Oil saturated ml	Oil imbibed			Average oil recovery %
			Weight g	Volume ml	Average ml	
400	112A	0.82	0.05	0.07	0.07	8.30
1500	91A	0.67	0.04	0.03	0.04	6.02
3000	95A	0.76	0.07	0.08	0.08	10.91
4500	110A	1.18	0.06	0.08	0.08	6.68
7500	100A	0.70	0.04	0.03	0.04	5.94
10000	111A	1.14	0.05	0.05	0.06	4.89
20000	101A	0.95	0.04	0.04	0.05	4.97

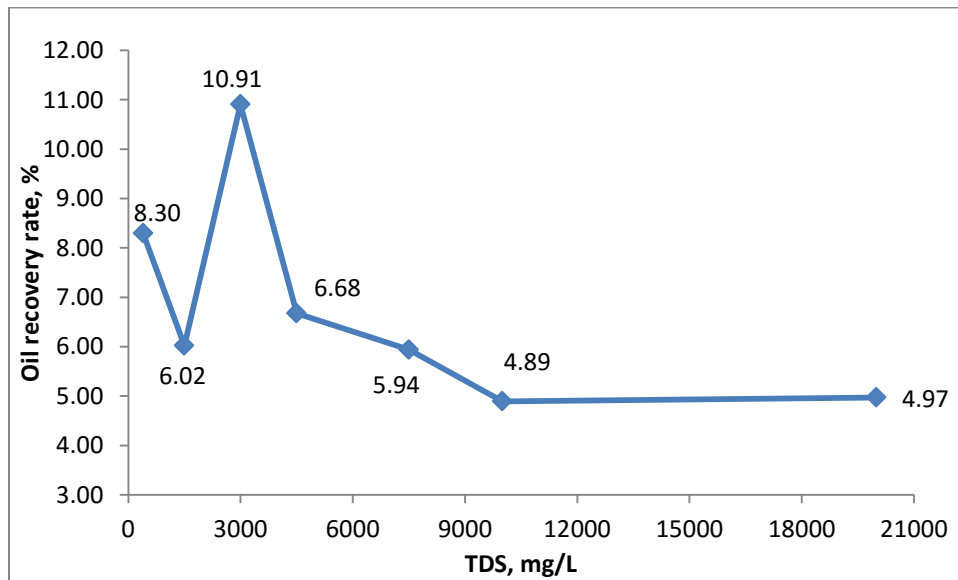


Figure I-9. Average oil recovery rate vs. TDS of imbibition water from cleaned B chalk plugs.



**Run #4 – cleaned B marl cores**

This round of spontaneous imbibition was performed with cleaned core plugs saturated with crude oil from B marl. The results are summarized in Table I-11, and the oil recovery is plotted in Figure I-10. From Figure I-10, average oil recovery rate is peaked at TDS of 7,500 mg/L, and the oil recovery at TDS of 10,000 mg/L is also higher than the rest of five TDS concentration. A different trend of oil recovery rate is observed, and it may due to the different formation layer of the plugs used. Additional tests are needed for further prove the results.

Table I-11. Results of the 4<sup>th</sup> round of spontaneous imbibition with cleaned B marl core plugs.

TDS mg/L	Plug #	Oil saturated ml	Oil imbibed			Average oil recovery %
			Weight g	Volume ml	Average ml	
400	112A	0.82	0.05	0.07	0.07	8.30
1500	91A	0.67	0.04	0.03	0.04	6.02
3000	95A	0.76	0.07	0.08	0.08	10.91
4500	110A	1.18	0.06	0.08	0.08	6.68
7500	100A	0.70	0.04	0.03	0.04	5.94
10000	111A	1.14	0.05	0.05	0.06	4.89
20000	101A	0.95	0.04	0.04	0.05	4.97

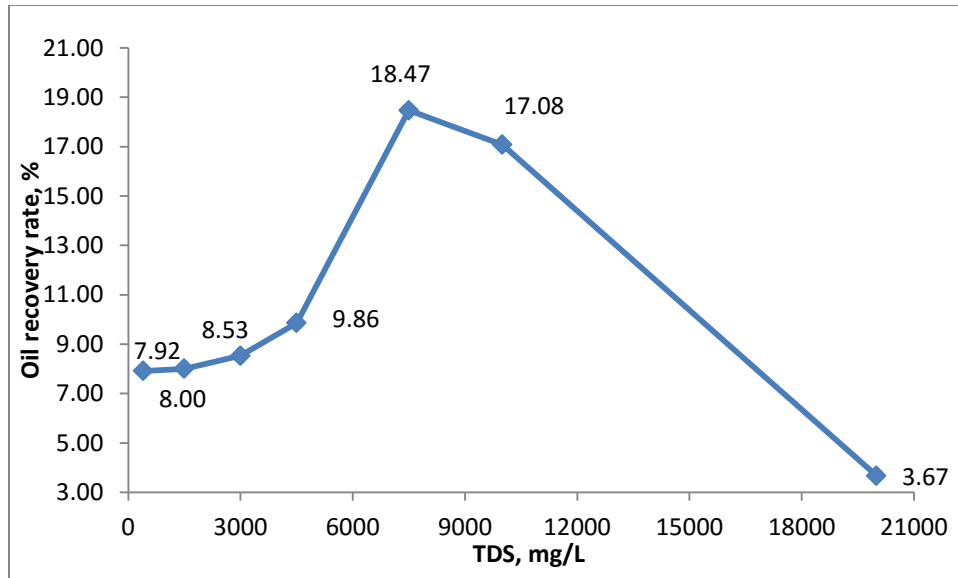


Figure I-10. Average oil recovery rate vs. TDS of imbibition water from cleaned B marl plugs.

***Run #5 – cleaned B marl cores***

This round of spontaneous imbibition was performed with cleaned core plugs saturated with crude oil from B marl. The results are summarized in Table I-12, and the oil recovery is plotted in Figure I-11. From Figure I-11, average oil recovery rate is peaked at TDS of 7,500 mg/L, and the oil recovery at TDS of 4,500 mg/L is also higher than the rest of five TDS concentration. A different trend of oil recovery rate is observed, and it may due to the different formation layer of the plugs used. Additional tests are needed for further prove the results.

Table I-12. Results of the 5<sup>th</sup> round of spontaneous imbibition with cleaned B marl core plugs.

TDS mg/L	Plug #	Oil saturated ml	Oil imbibed			Average oil recovery %
			Weight g	Volume ml	Average ml	
400	112A	0.82	0.05	0.07	0.07	8.30
1500	91A	0.67	0.04	0.03	0.04	6.02
3000	95A	0.76	0.07	0.08	0.08	10.91
4500	110A	1.18	0.06	0.08	0.08	6.68
7500	100A	0.70	0.04	0.03	0.04	5.94
10000	111A	1.14	0.05	0.05	0.06	4.89
20000	101A	0.95	0.04	0.04	0.05	4.97

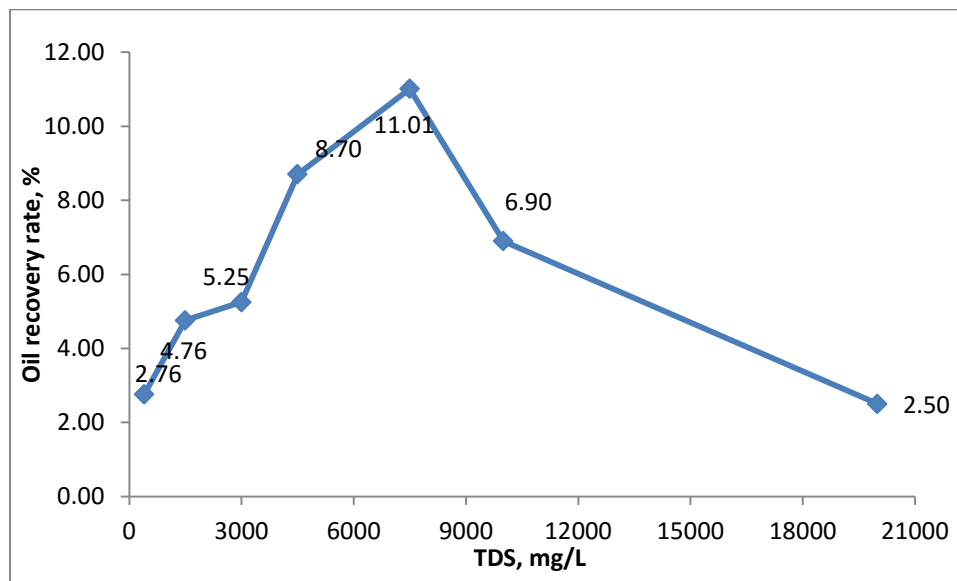


Figure I-11. Average oil recovery rate vs. TDS of imbibition water from cleaned B marl plugs.

**Run #6 – cleaned B chalk cores**

This round of spontaneous imbibition was performed with cleaned core plugs saturated with crude oil from B chalk. The results are summarized in Table I-13, and the oil recovery is

plotted in Figure I-12. From Figure I-12, average oil recovery rate is also peaked at TDS of 3,000 mg/L, and the fresh water (TDS=400 mg/L) comes as the second highest recovery point. The decline at TDS of 1,500 mg/L indicates the uncertainty of this set of results, and further tests will be needed.

Table I-13. Results of the 3<sup>rd</sup> round of spontaneous imbibition with cleaned B chalk core plugs.

TDS mg/L	Plug #	Oil saturated ml	Oil imbibed			Average oil recovery %
			Weight g	Volume ml	Average ml	
400	112A	0.82	0.05	0.07	0.07	8.30
1500	91A	0.67	0.04	0.03	0.04	6.02
3000	95A	0.76	0.07	0.08	0.08	10.91
4500	110A	1.18	0.06	0.08	0.08	6.68
7500	100A	0.70	0.04	0.03	0.04	5.94
10000	111A	1.14	0.05	0.05	0.06	4.89
20000	101A	0.95	0.04	0.04	0.05	4.97

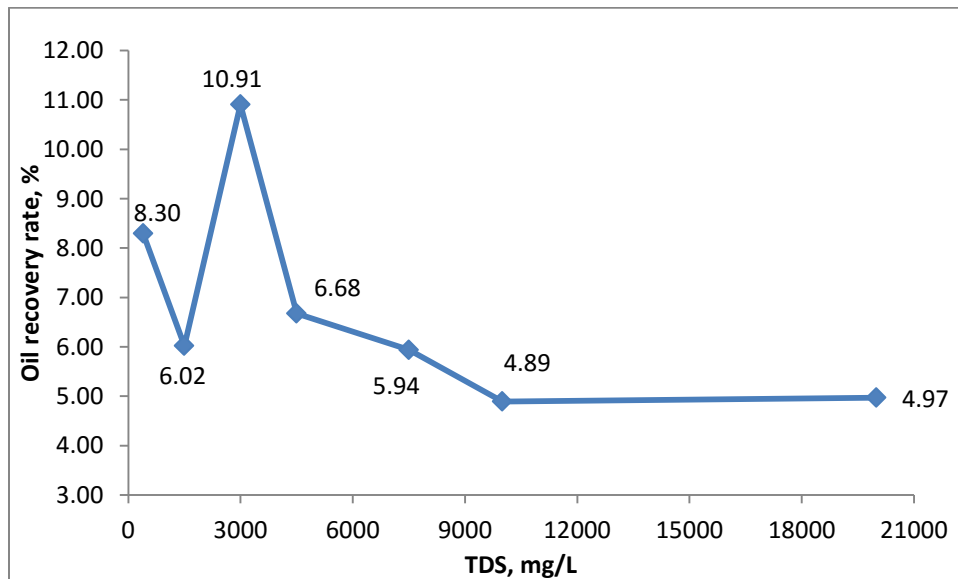


Figure I-12. Average oil recovery rate vs. TDS of imbibition water from cleaned B chalk plugs.

### I.3 Imbibition Test Part III – Modeled Water without Organic Compounds

This round of spontaneous imbibition was performed to examine the theory with modeled lab water without organic compounds. Lab water was modeled based on the inorganic composition of field water used for previous spontaneous imbibition tests. The inorganic composition of modeled water is shown in Table I-14.

Table I-14. Inorganic composition of modeled water used for spontaneous imbibition

Modeled water	mg/L	mg/L											TDS
		Ca	Na	K	Fe	Mg	Mn	Br	Sr	Cl	SO4		
CaCl2	522.6	190.0364	6896.563	92.768	0.276543	24.75789	0.218543	130.4854	36.30908	12197.49	0.381457		19569
KCl	178.4												
FeCl3	0.8												
MgCl2	98												
MnSO4	0.6												
BrNa	168												
SrCl2	110												
NaCl	17800												

Spontaneous imbibition tests with modeled water were conducted with both B chalk and B marl core plugs, and for each formation bench, two rounds of imbibition tests were performed. No statistical analysis was performed due to the limited number of core plugs. Results of all spontaneous imbibition tests with modeled water are shown in Table I-15 and Figure I-13.

Table I-15. Oil recovery rate from spontaneous imbibition with modeled water

Brine TDS (mg/L)	Niobrara B chalk		Niobrara B marl	
	Round 1	Round 2 (reused)	Round 1	Round 2 (reused)
400	5.6	4.28	4.38	7.11
1,500	12.16	3.02	8.58	6.42
3,000	23.91	8.99	22.7	9.63
4,500	18.39	5.39	20.82	27.96
7,500	9.11	7.95	24.75	28.78
10,000	7.72	7.23	20.92	12.16
20,000	7.37	7.16	5.54	8.6

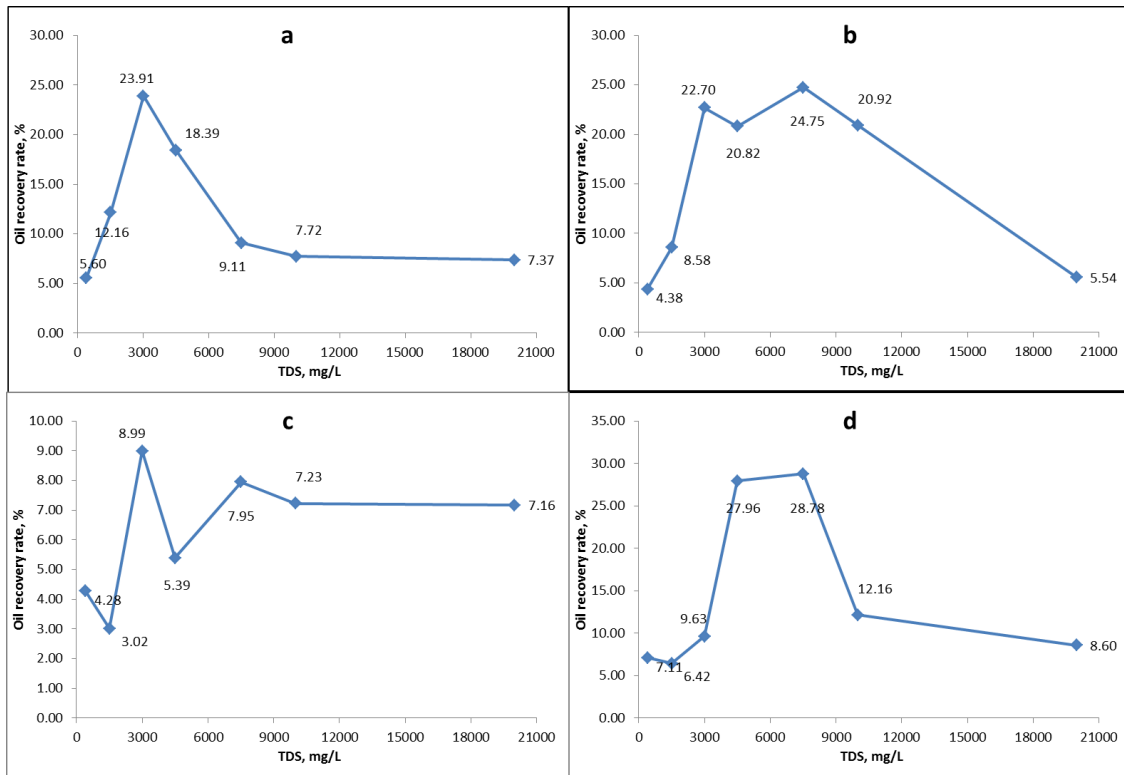


Figure I-13. Oil recovery rate of four rounds of spontaneous imbibition with modeled water. (a and c: Nio B chalk plugs, b and d: Nio B marl plugs)