

PRODUCED WATER QUALITY BASED ON THERMAL RECOVERY
PROCESSES AND AFTER INTERACTION WITH SHALE

A Thesis

by

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ABSTRACT

Management of produced water has always been an issue in the oil and gas industry. As the amount of water injected to produce from unconventional (heavy oil and source rock) resources increases, proper management and treatment of produced water has become increasingly important. The objective is to develop a thorough understanding of the expected quality of produced water originating from different hydrocarbon recovery processes and shale reservoirs to aid the development of plans to manage produced water.

The produced water quality can greatly vary depending on water injection processes employed and rock and fluid composition of the formation injected. Produced water originating from steam flooding (SF), steam assisted gravity drainage (SAGD), expanding solvent-SAGD (ES-SAGD), and hot water injection (HWI) processes were characterized. Furthermore, water-shale interaction was investigated for Eagle Ford, Marcellus, Barnett, and Green River. The anion and cation concentration were analyzed with ion chromatography. Total dissolved solids (TDS), conductivity, pH, total organic carbon (TOC), and average particle sizes of colloids were measured. The colloids were characterized with zeta potential.

The analysis of the ions in the water samples after the shale water interaction indicated a high concentration of sulfate, magnesium and calcium. The concentration of sulfate in the water was discovered to correlate with well with the amount of pyrite and gypsum in the Marcellus, Eagle Ford, and the Green River. However, in the water sample which interacted with the Barnett, there was abundance of sulfate in the water although

the amount of pyrite and gypsum was low. This was attributed to the calcium in water samples which interacted with the Marcellus and Eagle Ford causing a reversible reaction during the dissolution of gypsum. Calcium and Magnesium concentrations in the water were correlated with their respective minerals. Water which interacted with the Green River sample did not have a significant amount of calcium and magnesium even though it contained a high amount of magnesium and calcium minerals. This was attributed to both the low solubility constant of dolomite and the high CEC of the Green River sample. Zeta potential and the ionic strength due to cations correlated well for the water samples after the interaction with the shale. However, a similar correlation for the water samples from the EOR experiments could not be achieved due to variation of pH of the samples as well as the variability of the exposed pressure and temperatures which the produced water was subjected to. The analysis of the produced water originating from the EOR processes indicated the ion concentration decreased as the stage at which the water was collected increased. The produced water from the ISC processes contained the largest amount of impurities due to bitumen cracking and therefore, would require the most treatment. Management options for produced water from shale reservoirs traditionally involves treating the water and reusing it for water injection based methods, however, disposal to Class II injection wells is also a possibility.

DEDICATION

This thesis is dedicated to my parents for their endless love and support.

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NOMENCLATURE

μm	Micro-meter
bb/d	barrel per day
CC	Calcium Concentration
cP	centi poise
DI	Deionized Water
DW	Distilled Water
E&P	Exploration and Production
EOR	Enhanced Oil Recovery
EPA	Environmental Protection Agency
ES-SAGD	Expanding Solvent Steam Assisted Gravity Drainage
HWI	Hot Water Flooding
IC	Ion Chromatography
ISC	In-Situ Combustion
K	Kaolinite
K+I	Kaolinite and Illite
MC	Magnesium Concentration
mg/L	Milligrams per liter
mV	milli Volt
nm	Nano-meter
NPDES	National Pollutant Discharge Elimination System

OS	Ottawa Sand
ppm	Parts per Million
SAGD	Steam Assisted Gravity Drainage
SF	Steam Flooding
TDS	Total Dissolved Solids
TGA	Thermo Gravimetric Analysis
TOC	Total Organic Carbon
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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CHAPTER I

INTRODUCTION

The demand for oil over the next 10 years is expected to rise drastically. The U.S Energy Information Administration (EIA) reported that the demand for oil will rise by approximately 10 MMbbl/d in the year 2024 (BP Statistical Review 2012; IHS 2013). The majority of this demand will be met from the production of unconventional reserves. To produce from unconventional reserves at an economically viable rate, a variety of enhanced oil recovery (EOR) methods will need to be implemented. This increase in EOR processes will lead to an increase in water production (Mukhametshina et al. 2014). If not managed properly, this produced water may have many adverse effects to the general population, the environment, and other living organisms. Therefore, exploration and production (E&P) companies must have thorough understanding of the characteristics of produced water, methods used to treat produced water and ways to manage the produced water.

This thesis will summarize the quality of produced water after the interaction with shale. Furthermore, the quality of produced water from EOR experiments previously conducted at Texas A&M will also be analyzed. Correlations between various characteristics of water will be made to determine the source of the contaminants. Finally, treatment and management options based on the quality of the produced water will be discussed.

CHAPTER II

PRODUCED WATER IN THE UNITED STATES*

2.1 Enhanced Oil Recovery Processes

The potential to produce heavy oil resources and shale oil is enormous. With the demand of oil rising and the production of conventional crude oil remaining stagnant, it is inevitable that E&P companies operating in the United States will need to increase their production from these unconventional resources. Although the majority of the reserves will be unconventional, E&P companies will rely on conventional technologies to extract these hydrocarbons. Some of the most common methods to produce from these unconventional reserves are enhanced oil recovery methods. Therefore, this paper will start by providing a brief description on hot water injection, steam injection, steam assisted gravity drainage (SAGD), and in-situ combustion (ISC).

2.1.1 *Hot Water Injection*

Water injection is one of the most widely used methods due to its simplicity. Water injection involves injecting water into the reservoir to increase the reservoir pressure and to sweep the oil into the wellbore. Willhite (1986) described several factors to consider

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when designing a waterflood field. An accurate evaluation of the reservoir which includes a measurement of the reservoir properties, fluid properties, and the drive mechanisms prior to starting any waterflooding project. Furthermore, appropriate well patterns should be selected. The economics, reservoir characteristics, and the subsurface topology all play an important role as to what type of pattern should be selected. In addition, the determination of optimal injection rates is also an important aspect of a successful waterflooding project. Injection rates are calculated based on rock properties, pressure drop in the wellbore, and the fluid and rock interactions.

Hot water injection is similar to traditional water injection processes in that water is injected into a reservoir to assist in the production of hydrocarbons. However, a primary difference is that hot waterflooding involves injecting water at a higher temperature. Hot waterflooding is particularly useful for reservoirs which contain heavy or extra heavy oil (Morrow et al. 2014). Hot water injection is usually used when the viscosity of the oil in the reservoir ranges from 100 to 1000 cP (Mukhametshina et al. 2014). The hot water enters the formation and therefore, increases the temperature. This increase in temperature decreases the viscosity of oil which results in a decrease in the mobility of the displacing fluid to displaced fluid. Hot water injection is sometimes preferred over SAGD due to the relatively low cost of hot water injection. Furthermore, SAGD requires the use of freshwater and therefore, hot water injection may be preferred in formations which are sensitive to fresh water (Torabi et al. 2012).

2.1.2 Steam Injection Processes

Steam injection is one of the most widely applied thermal EOR methods. One of the primary reasons as to why steam injection is a common technique to produce heavy oil is the relative simplicity of this process when compared to other enhanced oil recovery methods. However, steam flooding may have drawbacks which include a relatively low recovery factor because of the low sweep efficiency normally associated with steam injection (Willhite 1986). Although the recovery factor associated with steam injection is relatively low, the process has proven to be successful in the United States. In fact, 98% of the oil produced due to EOR methods in the United States has been due to steamflooding projects (Manrique et al. 2006). Steam flooding has been used in several places in the United States including the Big Horn Basin and the San Andres. However, due to the ample amount of heavy oil in the San Joaquin Valley, the majority of steam injection processes in the United States has occurred in California.

In the Cyclic Steam Injection (CSI) process, steam is injected into a wellbore in order to reduce the viscosity of oil by the addition of heat into the reservoir and thereby, improving the oil mobility (Alikhalalov and Dindoruk 2011). In fact, the ultimate recovery factor for an average cyclic steam injection process is between 5 to 25% (Alikhalalov and Dindoruk 2011). Cyclic steam injection was first used in California in the 1960's and it continues to be an important aspect of the production of California's heavy oil (Elias and Medizade 2013). Furthermore, almost all of the oil recovered by tertiary methods in California was a result of steam injection (Hong and Use 1995).

Steam Assisted Gravity Drainage (SAGD) is one of the most commonly used processes to effectively recover bitumen resources. The concept of SAGD relies on drilling two horizontal wells where one of the horizontal wells is a few feet above the other. Steam is injected into the upper horizontal well forming a steam chamber that comes into contact with the bitumen and reduces the viscosity. This allows the oil to flow into bottom production well. An advantage that SAGD has over Steam Flooding (SF) is that the temperature inside the chamber is equal to the temperature of the steam and therefore, as the bitumen flows into the production, it remains hot. In a traditional steam flooding process, the bitumen becomes cold as it reaches the production well (Butler 1991). The use of SAGD has been proven to be more effective than traditional steam injection with ultimate recovery rates as high as 70% (Huc 2011).

Expanding solvent SAGD (ES-SAGD) involves the co-injection of steam and a solvent. The solvent selected is one which evaporates and condenses at the same conditions as steam (Nasr et al. 2003). The purpose of the addition of the solvent is to dilute the oil and as a result, further reduce the viscosity of the oil.

The concept of SAGD was first proposed by Dr. Roger Butler in the 1970's (Butler 1991). Although SAGD is not widely used in the United States, it continues to be an important recovery method in Canada. In fact, it is estimated that nearly 74% of the western Canada's oil production will be recovered by the use of SAGD (Das 2005).

2.1.3 *In-situ Combustion*

In-situ combustion involves the injection of an oxidizing gas (normally air) into the reservoir. The air reacts with the fuel in the reservoir and as a result, a combustion reaction occurs. As the burning front moves towards the production well, the lighter portion of the crude condenses and the heavier portion is consumed during the reaction (Ramey 1971).

In-situ combustion projects may have occurred as early as the 1920's as spontaneous ignition would have likely occurred during air injection processes. The first field tests of in-situ combustion occurred in 1952 and as a result, numerous other projects and studies related to in-situ combustion have occurred since then (Ramey 1971).

Although in-situ combustion has the potential to produce a large amount of oil, there are various drawbacks associated to the process. One of these associated problems is the low pH of the produced water. Although a low pH can be observed for produced water from a variety of thermal recovery processes, due to the extremely high temperatures and complex reactions with the bitumen and rock, low pH of produced waters from in-situ combustion processes are especially common (Starshov et al. 2000). In many instances, the production well must be shut off in order to avoid corroding the tubulars due to the acidity of the produced water.

The Mordovo Karmalski field in Russia requires the use of in-situ combustion to produce the bitumen. Field studies of three of the production wells from this field were conducted and it was found that the pH of the water producing from these wells ranged

from 2.8 to 5.1 (Starshov et al. 2000). Various treatment options were proposed, however, the most effective option was the use of alkali based solutions. These alkali based solutions form thick layered oxide films on the surface of the tubulars which protected it from the corrosiveness of the produced water. The pH of the wells treated with these alkali based solutions saw a decrease of pH of the produced water by a value of approximately 3 (Starshov et al. 2000).

2.2 Characteristics of Produced Water

The produced water originating from the thermal recovery processes will contain various inorganic and organic matters which may be either dispersed in the water or dissolved. The formation water usually contains a wide range of cations and anions which is due to dissolution of rock matrix in water. Hence, produced water may contain ions and particles originated from rock-water interaction and organic matter due to oil/kerogen-water interaction. Some of the most common ions dissolved in produced water are shown in Table 1.

Table 1: Ions in Produced Water (EPA 2012a)

Cations	Anions
Sodium, Na ⁺	Chlorine, Cl ⁻
Potassium, K ⁺	Carbonate, CO ₃ ²⁻
Calcium, Ca ²⁺	Sulfate, SO ₄ ²⁻
Magnesium, Mg ²⁺	Nitrate, NO ₃ ⁻

The ions listed in Table 1 will affect the characteristics of water in various ways. The salinity of the water will depend primarily on the concentration of Na⁺ and Cl⁻ ions. Although these ions may occur naturally in produced water, water injection processes may also alter the chemical composition of the subsurface water due to ion exchange, precipitation, and dissolution (Ishkov et al. 2009). This may lead to the formation of scales at different composition and amounts (Wang et al. 2013). The formation of scales can have many detrimental effects during oil production including a reduction in permeability which leads a reduction in the oil flow rate and the corrosion of tubular (Al-Humaidan, A. Y. and Nasr-El-Din 1999).

Metals are a great cause of concern when dealing with produced water. Metals commonly found in produced water such as arsenic and mercury are detrimental to the environment and considered toxic (Frankiewicz 1998). These metals, along with other metals commonly found in produced water such as selenium, barium, cadmium, chromium, and copper, are all regulated by the EPA (EPA 2012a). Furthermore, calcium

and magnesium present in produced water would lead to an increase in the hardness of the water (Bowman et al. 1997). Due to the potential of scaling, water with higher hardness may not be suitable for reinjection. In addition to metals, radium is also another element which may be found in the produced water.

Various inorganic suspended solids may also be present in the produced water. The Total Suspended Solids (TSS) in the produced water generally consist of fine particles, clays, sand, and various corrosion products due to the corrosion of tubular or other completion equipment (Ye et al. 2013). High concentration of silica may also be present in the produced water (Bowman et al. 1997).

In addition to inorganic compounds, produced water may also contain organic compounds as well due to water-oil interaction and for thermal EOR applications more pronounced interaction should be expected. Some of the most common organic compounds found in the produced water are Benzene, Toluene, Ethylbenzene, Xylene (BTEX), Polycyclic Aromatic Hydrocarbons (PAHs), and phenyls.

BTEX is the group of organic compounds that are readily soluble in water. BTEX compounds are regulated by the EPA, because they pose a variety of health risks including kidney damage and nervous system complications (EPA 2012a).

PAHs are compounds which consist of many aromatic rings. Two of the most common polycyclic aromatic hydrocarbons are naphthalene and phenanthrene. A common method in determining the total aromatic hydrocarbon content is to calculate the ratio of naphthalene to phenanthrene. As this ratio increases, the total amount of dissolved aromatic compounds also increases (Smith et al. 1996).

Phenyls are an organic compound which contains a benzene ring and at least one hydroxyl group. Phenyl compounds are considered hazardous to both animals and humans at certain concentrations (Priatna et al. 1994).

2.3 Water Management

Produced water is managed through a variety of methods. According to Arthur et al. (2009), four common ways to manage produced water are as follows injecting produced water underground, discharging produced water to the ocean, reusing produced water for agricultural or industrial use, and reinjection of water for water injection processes.

2.3.1 Underground Injection

Injecting produced water underground is one of the methods used to dispose produced water associated with oil and gas produced. The EPA classifies these injection wells as Class II wells. Class II wells are regulated by the Underground Injection Control division of the EPA and are further classified as either enhanced recovery wells, disposal wells or hydrocarbon storage wells. Approximately, 400 million gallons of water are injected into Class II wells classified as disposal wells (EPA 2014). Class II disposal wells are generally drilled to the injection zone which has a low permeability zone above to prevent the migration of the injected water. Injected zones are typically 1 ½ to 2 miles in depth so that drinking water may not be contaminated (EPA 2014).

2.3.2 *Discharge*

Discharging produced water is a common management strategy. In the United States, the EPA, through the National Pollutant Discharge Elimination System (NPDES), issues permits allowing companies to discharge produced water. One of the most common regulatory requirements contained in these permits is to limit the oil and grease in discharged water. The EPA uses a liquid-liquid extraction where n-hexane is used as the extraction solvent. After the extraction, the hexane is evaporated and the remaining residue of oil and grease is measured. The monthly average limit of the oil and grease in produced water that is being discharged is set to 29 mg/L and a maximum daily limit is set to 42 mg/L (EPA 2012b).

2.3.3 *Reuse for Irrigation, Thermoelectric Power and Public Supply*

Instead of injecting and discharging, produced water may also be reused. In the United States, water is reused in a variety of ways. Figure 1 shows the distribution of water consumption in the United States as reported by the United States Geological Survey (USGS) in 2005.

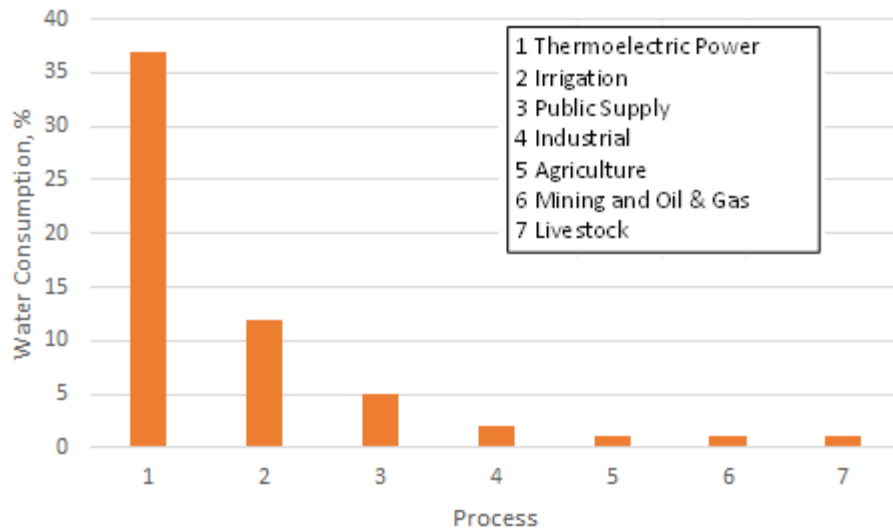


Figure 1: United States Water Consumption (USGS 2005)

As shown in Figure 1, the majority of water consumed in the United States is due to thermoelectric power, irrigation and public use.

Water consumed for irrigation purposes account for nearly 37% of the water consumption in the United States (USGS 2005). Water used for agricultural purposes must be treated and therefore, produced water containing a large amount of impurities may not always be a cost effective solution to meet the demand for water use in the agricultural industry. However, if produced water is of high quality and limited treatment is required, then, using it for agricultural purposes may be economically viable.

The EPA provides guidelines on the use of water in irrigation processes. Table 2 provides the maximum concentration and potential hazards associated with various contaminants found in water injection processes which might be used for irrigation purposes.

Table 2: Agricultural Regulations and Hazards (EPA 2012a; Greenfacts 2014)

Compound	Maximum Concentration (ppm)	Hazards
Aluminum	5	Non-productiveness in acid soils
Cadmium	0.01	Toxic to beans, beets, and turnips
Fluoride	1	Severe inhibition of microbial activity
Lead	5	Detrimental to plant growth
Molybdenum	0.01	Toxic to livestock that may eat the plants
Selenium	0.02	Toxic to plants
TDS	450-2000	Recommended TDS

The majority of water consumed in the United States goes into generating thermoelectric power (USGS 2005). According to the EPA, this water is mainly used for steam generation or to provide work to turn turbines. The EPA provides various limits for water used in boilers. Table 3 lists these limits.

Table 3: Water Concentration Limits for Feed Water in a Boiler System (EPA 2012a)

Parameter	Concentration, ppm
Iron	0.02
Copper	0.015
Total Hardness (CaCO ₃)	0.1
Total Organic Carbon (TOC)	0.5
TDS	0.1

When generating steam from a boiler, a major cause of concern is the damage the impurities in the water may cause in steam generators. Two of the biggest concerns are the buildup of scales and the corrosion of the equipment (EPA 2012a). Therefore, the hardness, magnesium, and calcium concentration need to be controlled before using produced water for steam generation. Furthermore, the concentration of organic compounds needs to be limited in order to avoid foaming in the boilers (EPA 2012a).

According to the USGS, approximately 86% of the people living in the United States obtain their water from a public water supply (USGS 2000). Due to the numerous impurities associated with produced water, it is often uneconomical to treat the produced water so that it meets the regulatory requirements for public supply water (Challenges in Reusing Produced Water, 2011). Nevertheless, technologies do exist that can treat produced water to meet the regulatory requirements (Xu et al. 2007).

In the United States, public supply water is strictly regulated by the EPA. Table 4 shows the maximum concentration allowed and the various hazards in drinking water.

Table 4: Drinking Water Regulations and Hazards (EPA 2009)

Compound	Maximum Drinking Water Concentration (ppm)	Health Hazards
Selenium	0.05	Blood circulation effects
Barium	2	Increase in blood pressure
Cadmium	0.005	Damage to the kidneys
Chromium	0.1	Skin inflammation
Copper	1.3	Liver or kidney damage and Gastrointestinal related problems
Benzene	0.005	Anemia and cancer
Toluene	1	Skin irritation and nervous system damage
Xylene	10	Nervous system damage
Ethylbenzene	0.7	Liver and kidney problems
Lead	0.015	Kidney and blood pressure problems

Other contaminants are also regulated by the EPA, however, Table 4 shows common contaminants found in produced water originating from water injection processes.

Produced water may also be reused for petroleum gas or liquid recovery through hydraulic fracturing, steam injection, SAGD, waterflooding, and hot waterflooding. However, the water treatment processes will vary based on the injection process. The subsequent section will discuss the produced water treatment methods.

2.4 Water Treatment

The treatment of water depends on the type of impurities present in the produced water and their sizes. Impurities can be classified as either dispersed or dissolved and in addition, can be further classified as either organic or inorganic.

2.4.1 Dispersed Organic Matter Removal

There are various technologies which exist that allow for the removal of organic compounds from the water phase. These include biological degradation, gravity separation, induced gas flotation, hydrocyclones, and centrifuges. The biological degradation method is the least used among all, since the separators which incorporate biological degradation processes are usually large and require large space and the amount of time to degrade the oil droplets is long which make the process less popular (Broek and Zande 1998). Because of the negative aspects associated with biological degradation, the following sections will focus only on gravity separators, induced gas flotation, hydrocyclones, and centrifuges.

One of the most common ways to remove organic matter is to use a gravity separator. The standard API Oil Water Separator normally includes a skimming device. When produced water is injected into a separator, oil particles rise up to the surface of the water due to the difference in density. Once the oil is at the surface, a skimmer would be used to remove the oil and the treated water would flow out of the tank. However, not all of the oil droplets may be removed using the conventional API separator. Coalescing plate packs are usually inserted into a separator tank to aid in the removal of oil.

As the velocity of the oil droplet size to reach the surface increases, the time necessary to get to the surface decreases (Shearer and Hudson, 2008). Therefore, the larger the diameter of the oil droplet, the easier it will be to remove the droplet from the water (Plebon et al. 2006).

To increase the diameter of the oil droplet, parallel plate packs are inserted into a separator. As water flows between the plates, the oil droplets will have an upward vertical velocity due to the difference in density. Once the oil droplet reaches the plate, it will coalesce with other oil droplets on the bottom surface of the plates and as a result, the droplets will be easier to remove (Plebon et al. 2006). For a general configuration of a gravity separator with coalesce plates, the smallest sized oil droplet is typically in the range of 20 to 30 microns (Broek and Zande 1998). For emulsions, more complex technologies might be necessary. For the produced water, the emulsions are expected to be in the form of oil in water emulsions. These types of emulsions can be treated by physical or chemical methods. Commonly used chemicals are cationic chemicals which can be added to produce waters by following coagulation and flocculation treatments.

During coagulation, the aim is to break the repulsive forces between oil droplets and in flocculation, the oil droplets should agglomerate. Both organic and inorganic chemicals can be applied (Sarathi and Olsen 1992).

Even with coalesce plates inserted, gravity separators are normally only capable of removing droplets greater than 20 microns. Therefore, after produced water goes through a gravity separator, it usually passes through a gas flotation unit. A gas flotation unit is essentially a unit where gas is injected into the water. The gas bubbles interact with the oil droplets and float up to the surface of the water. There are three types of methods of interaction which may occur between the gas bubble and the oil droplet. The oil may coat the gas bubble which occurs when the contact angle between the gas bubble and oil droplet is low. The second interactions occur when the oil droplet sticks to the gas bubble. This usually occurs at a relatively low contact angle. Finally, the oil droplet may rise and be dragged up as the gas bubble rises. This occurs in a medium or high contact angle (Frankiewicz et al. 2005).

A deoiling hydrocyclone is another piece of equipment that can aid in the removal of dispersed oil droplets. Hydrocyclones work by injecting the produced water in the tangential direction at a high pressure. The cross sectional area of the hydrocyclone unit decreases in the downward direction. Therefore, once the produced water is injected, due to the centrifugal force, the difference in density and decreasing cross sectional area, two vortexes which accelerate in the opposite directions are created. Water, being the denser fluid, will be included in the outer vortex and would accelerate downward in a spiral

motion. The oil would move to the inner vortex and would accelerate upward (Gomez et al. 2002).

There are a few considerations to take note of when designing a hydrocyclone. The centrifugal force generated in the hydrocyclone is a function of the produced water injection rate. A higher injection rate may be required for smaller sized oil droplets. Furthermore, a larger difference between the density of water and oil droplets increases the efficiency of the hydrocyclone. The oil droplet size also has a significant impact on the performance of the hydrocyclone. A typical hydrocyclone will have around a 90% efficiency when the medium droplet size is between 35 to 50 microns. However, the efficiency will decrease to 50% when the droplet size is 15 microns or less (Broek and Zande 1998).

Disk centrifuges work based on the principle of centrifugal force using a stack of disks. The produced water is injected in the middle of the centrifuge. The stacked disks will then start rotating causing the oil droplets to move towards the center and up the stack disks. The oil droplets will then flow upward and out of the centrifuge. A lower flow rate of the water will result in the removal of smaller sized oil droplets. It has been determined that oil droplets with diameters of 8, 6, and 5 microns may be removed with a flow rate of $0.0079 \text{ m}^3/\text{s}$, $0.0045 \text{ m}^3/\text{s}$, and $0.0031 \text{ m}^3/\text{s}$, respectively. Furthermore, the oil droplets with diameters as small as 2 microns can be removed using a typical stacked disk centrifuge. However, the corresponding flow rate required would make this separation unfeasible (Broek and Zande 1998).

2.4.2 Dissolved Organic Compounds Removal

Although gravity separators, induced gas flotation units, hydrocyclones, and centrifuges are effective in removing dispersed oil, they are not capable of removing dissolved oil. Dissolved hydrocarbons, such as PAHs and BTEX, can have a detrimental impact on the environment if they are not removed from water. To remove these dissolved hydrocarbons, techniques based on absorption, adsorption, extraction, and oxidation should be used (Meijer 2007).

One of the most widely used technologies to remove dissolved hydrocarbons is Macro Porous Polymer Extraction (MPPE). The MPPE technology involves porous polymer particles with diameters of approximately 1000 microns. The pores of the bead particles are filled with an organic solvent. The produced water will flow through a pack of beads and as it enters the pore space, the solvent will extract the dissolved hydrocarbons. Based on previous case studies, when the concentration of PAHs and BTEX was between 300 to 800 ppm, approximately 99% of the dissolved hydrocarbons were successfully separated (Meijer 2007).

2.4.3 Inorganic Dispersed Particles Removal

The equipment used to remove suspended inorganic solid particles is similar to those used to remove the dispersed oil droplets. Hydrocyclones, separators, and centrifuges which are similar to the design of those used to remove dispersed oil, can all be used to

remove dispersed inorganic particles. The main difference in design is associated with the density of the solid particles. Unlike dispersed oil droplets which have a density less than water, solid particles have a density greater than water and therefore, will settle at the bottom. As a result, the design of the equipment should take into account this phenomenon. Removing these suspended particles is required before reinjecting produced water during a hydraulic fracturing job. A high concentration of TSS can greatly reduce the permeability of proppant packs. In a study, it was determined that the treatment of produced water for suspended particles can increase the permeability of the proppant pack by 40% (Ye et al. 2013). In addition to hydraulic fracturing, water used for steam generation during SAGD and steam injection processes should be treated for suspended particles. These suspended particles may damage the boilers used in steam generation (Sarathi and Olsen, 1992, EPA 2012a). Furthermore, the removal of suspended particles is essentially recommended for all water injection processes. Suspended particles may settle in the pore spaces in the reservoir and reduce the permeability.

2.4.4 Inorganic Dissolved Particles Removal

Special techniques are needed to remove inorganic dissolved particles in produced water. Two of the most common techniques used are membrane filtration and water softening.

The process of membrane filtration involves the injection of water through membranes from a high pressure vessel to a low pressure vessel. The membrane sheets

include microscopic pore sizes which allow only water and a limited number of molecules to pass through. The size of these pores determines which molecules may pass through (Myers 2000). Membranes are divided into four categories. These classifications along with their respective pore sizes are listed in Table 5.

Table 5: Membrane Classification (Myers 2000)

Membrane Classification	Pore Size (microns)
Microfiltration	0.05-1
Ultrafiltration	0.005-0.1
Nanofiltration	0.001-0.005
Reverse Osmosis	0.0001-0.001

Among these membranes, microfiltration and ultrafiltration are not be able to remove any of the dissolved ions. Therefore, nanofiltration is required to remove divalent ions but may fail to remove monovalent ions. However, reverse osmosis membranes are capable of removing almost all ions in a produced water stream (Myers 2000). In fact, it has been determined that reverse osmosis membranes are capable of removing more than 95% TDS of produced water (Barrufet et al. 2005).

Another common technique used to remove dissolved particles is water softening. Water softening is mainly used during steam injection to protect steam generators from scaling (Sarathi & Olsen 1992). Water softening involves the exchange of ions. During

ion exchange, a resin or polymer typically containing sodium ions will be exchanged with calcium or magnesium ions. Calcium and magnesium increase the hardness of water and to generate steam, the water must have a limited amount of hardness which is in the order of 1 ppm (Sarathi and Olsen 1992). Therefore, water softening is an essential step before heating up water to use steam or hot water injection purposes (Bowman et al. 1997). In addition, water softening can lead to the removal of boron. In fracturing fluids, boron may lead to over cross linking and therefore, the ability of the fluid to carry proppant may seriously be hampered (Fedorov et al. 2014). As a result, water softening may also be used during hydraulic fracturing operations. Furthermore, if the pH of injected water decreases, calcium and magnesium can precipitate out and reduce the permeability. As a result, water softening may also be applied during waterflooding operations (Fedorov et al. 2014).

Before implementation of any water treatment options, a thorough characterization of produced water must be obtained. Characteristics such as the total dissolved solids (TDS), pH, particle size, zeta potential, and organic content of the water provide valuable information on the quality of the water and consequently, on the selection of the right treatment and management technique.

CHAPTER III

MATERIALS AND METHODS: CHARACTERIZATION OF PRODUCED WATER

3.1 Materials and Methods

Steam flooding (SF), hot water injection (HWI), in situ combustion (ISC), steam assisted gravity drainage (SAGD), and ES-SAGD (with varying solvents) experiments were previously conducted in the Petroleum Engineering Department at Texas A&M University (Mukhametshina et al. 2014; Mukhametshina and Hascakir 2014). The rock samples were prepared using 20 to 40 mesh size Ottawa Sand and mixing it with 15 weight percent clay containing 10 to 20% illite and 80 to 90% kaolinite (Bayliss and Levinson 1976). The pore spaces of the sample were saturated with 14 volume percent distilled water and 86 volume percent Peace River Bitumen (8.8° API) (Hamm and Ong 1995). In the scope of this thesis, produced water samples collected from all experiments were subjected to characterization studies.

In addition to produced water characterization from thermal recovery processes, static experiments were conducted on four different shale samples to determine the resulting contaminants due to water-rock interactions. Outcrop rock samples from Green River, Eagle Ford, Barnett, and Marcellus formations were crushed and sieved to 1 micron for the static experiments which were conducted at a reservoir temperature of 150°F. A reservoir temperature of 150 °F is commonly encountered in the Eagle Ford, Marcellus, Green River, and Barnett reservoirs (Morsy et al. 2013; Yu et al. 2014; Prats and O'Brien

1975; Yevhen et al. 2011). Approximately 10 grams of each of the crushed shale samples was mixed with 50 mL of deionized water. These water samples were stored in an oven at constant temperature (150 °F) for a period of 3 weeks. The water samples were then analyzed.

A thorough water analysis was achieved on both the produced water from thermal recovery experiments and from the static experiments to determine the degree of shale-water interaction. The total dissolved solids (TDS), pH, conductivity, ion concentration, inorganic and organic matters, zeta potential, average particle size, total organic carbon (TOC), and total organic content were determined for all of experimentally obtained samples. In addition, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) analysis, and thermogravimetric analysis (TGA) were conducted for the shale rock samples, Ottawa Sand, and two clay samples (Clay1: Kaolinite, and Clay2: Kaolinite+Illite) which was used as reservoir rock to conduct the thermal EOR experiments.

3.2 TDS and pH Measurements

The TDS of water is one of the most fundamental parameter gives idea on the quality of the produced water (Bowman et al. 1997). The TDS can provide an indication of the total amount of ions that may be present in produced water (Bowman et al. 1997). As discussed in Chapter 2, the EPA regulates the maximum value of TDS based on the various purposes (EPA 2012).

TDS, conductivity, and pH of the water samples were measured. An Oakton Conductivity Probe was used to measure the TDS and conductivity. Conductivity measurements is directly correlated with TDS. As the ions in water increase, the water becomes more conductive and as a result, TDS can be correlated with the conductivity (Alhumoud et al. 2009). The Oakton TDS probe measures TDS of up to 100,000 ppm and conductivity up to 170,000 $\mu\text{S}/\text{cm}$ with an error range $\pm 1\%$ (Oakton, 2007). The pH of the samples was measured using the pH 5+ Oakton pH meter. The range of the pH meter is from 0 to 14 with an error percentage of $\pm 1\%$ (Oakton, 2000).

3.3 Ion Chromatography

The concentration of various anions and cations was measured using the Thermo Fisher Ion Chromatography 900 Unit. Figure 2 shows a schematic of the unit.

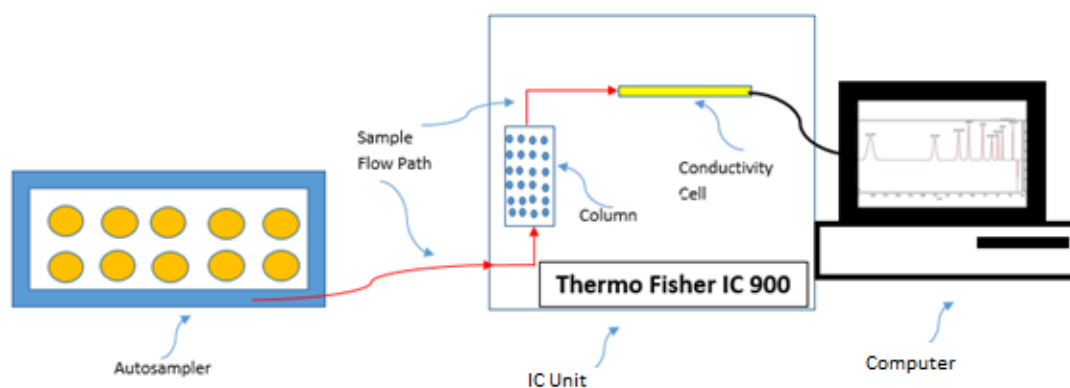


Figure 2: Thermo Fisher Ion Chromatography 900

The Ion Chromatography (IC) unit works on the principle of ion exchange (Thermo Fisher Scientific, 2012). The sample is injected into the loop, where it enters and binds to the column. The eluent is used to push the sample onto the column. Furthermore, the eluent contains exchangeable counter ions which, based on the affinity of the ions, exchange with the ions of the sample on the column. Once the exchange takes place and the counter ions take the place of the ions of the sample, the individual sample ions are passed through the conductivity cell where the conductivity of the ions are measured. The conductivity detected will be a function of the concentration of the individual ions. An ion chromatograph of the sample will then be displayed.

Anions and cations were both analyzed during the detection of the ions. The maximum detection limit of an ion is 20,000 ppm. Therefore, to ensure correct concentrations could be detected, each of the samples were diluted by a factor of 10. Standards were prepared for common ions found in produced water. The standards are listed in Table 6.

Table 6: Standard Solutions for Anions and Cations

Anions	Cations
Sulfate, SO_4^{2-}	Sodium, Na^+
Chloride, Cl^-	Magnesium, Mg^{++}
Nitrate, NO_3^- and Nitrite, NO_2^-	Potassium, K^+
Phosphate, PO_4^{3-}	Lithium, Li^+
Bromide, Br^-	Ammonium, NH_4^+
Fluoride, F^-	Calcium, Ca^{++}

A chromatograph was constructed using the Ion Chromatography Unit 900 for each sample. Anion concentrations were measured once, however, cation chromatographs were constructed two times for each sample. Chromatographs for each of the samples can be found in (Appendix A).

3.4 Zeta Potential

One of the most important characteristic of a water sample containing impurities is its zeta potential value (Vincent, 2009). Figure 3 shows a visualization of the zeta potential concept.

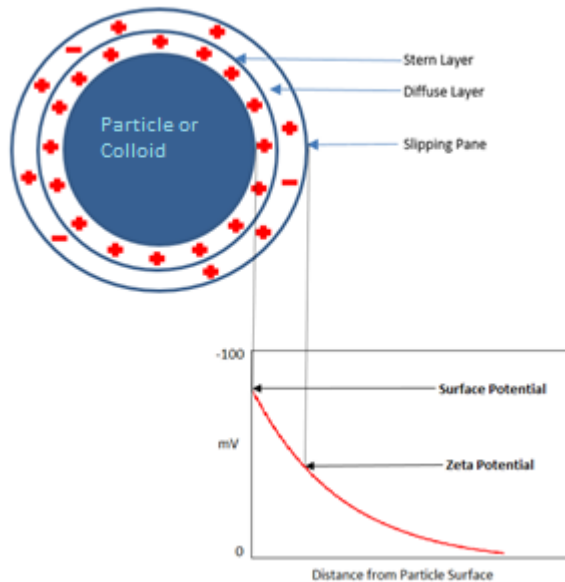


Figure 3: Zeta Potential (Adapted from Vincent, 2009)

The slipping plane is an imaginary boundary in which the particle, the stern layer and the diffuse layer act as a single entity. Zeta potential is essentially the potential at the slipping plane with respect to a point in the bulk solution (water). The zeta potential of a water sample can provide an indication of the stability of the particles in the water (Kaya et al. 2003). The repulsive forces between two particles is a function of zeta potential. As the absolute value of the zeta potential increases, the repulsive forces increases as well. Since high repulsive forces prevent particles from agglomeration, water samples with high absolute values of zeta potential will contain colloids that will have a lower tendency to settle (Kaya et al. 2003). Generally, zeta potential values between -20 mV to 20 mV indicate good aggregation characteristics (Johnson et al. 2010).

Kaya et al. (2003) studied how the pH level affected the zeta potential for water samples containing kaolinite. They showed that when the pH of the solution was low, the particles settled in a dispersed form. In addition, there was a correlation between zeta potential and settling characteristics as higher absolute values of zeta potential indicated dispersed settling whereas samples which had lower absolute values of zeta potential showed characteristics of flocculation.

In this study, the zeta potential measurements were carried out with a ZetaPALS zeta potential analyzer by Brookhaven Instruments Corporation. To achieve accurate repeatability results, the zeta potential measurements were repeated 10 times for each sample. The ZetaPALS has a range of -150 mV to 150 mV with an error of about 1% (Brookhaven, 1999).

3.5 Particle Size Measurements

Determining the average particle size is vital when discussing treatment options of produced water (Myers 2000). Particles can be classified as either suspensions or colloids. Particles whose diameters are between 1 nm to 1000 nm can be classified as colloids whereas particles whose diameter is greater than 1000 nm would be classified as suspensions (Petrucci et al. 2006).

The particle size was measured using the 90Plus Particle Size analyzer by Brookhaven Instruments Corporation. To ensure repeatability, the particle size was determined six times for each sample. Distribution curves the particle size was also

determined using the 90Plus. The 90Plus particle size analyzer has a range of 1 nm to 3000 μm with an error of between 1 to 2% (Brookhaven, 1994). The list of the particle sizes can be found in Appendix A.

3.6 Total Organic Carbon (TOC)

The determination of TOC of water samples is essential for effective water management. Specific treatments are needed in order to effectively remove the organic contaminants in the water and therefore, the total organic carbon of the water samples was also be determined.

3.7 Thermogravimetric Analysis (TGA)

TGA is a common technique used to determine the various chemical and physical properties of the shale samples (Foldvari 2011).

TGA was done using the STA 449 by Netzsch. Shale samples were analyzed using TGA. Shale samples were heated till 900°C under constant air injection to determine the amount of organics in the shale sample as well to qualitatively determine the inorganic minerals in the shale sample.

3.8 XRD

Qualitative XRD analysis is one of the most widely used methods to determine the mineral composition of rock samples (Ruessink and Harville 1992). During an XRD analysis, a beam of electrons is emitted on the crushed rock samples. The beam will diffract different minerals at different angles and as a result, based on the intensity of the beam and the angle created, the mineral composition of the rock sample can be determined (Ruessink and Harville 1992).

XRD analysis was conducted off campus at Ellington and Associates. The shale samples before and after water rock interaction were analyzed. The results of the XRD analysis can be found in (Appendix A).

3.9 XPS

The principle behind XPS is low energy x-rays are emitted on the surface of the rock. Based on the binding energy of the electrons, as the x-rays pass through the electrons, the electrons will be removed as a photoelectron. Since the electrons of different atoms have different binding energies, the element composition can be determined. XPS can detect all of the elements except for hydrogen (Yamashita and Hayes 2007).

XPS was performed in the Materials Characterization Facility at Texas A&M University. To determine the elemental composition of the shale and Ottawa Sand

samples, XPS analysis was conducted. The operator has stated that the error for XPS is generally less than 10%. The results of XPS can be found in Chapter 4.

CHAPTER IV

DISCUSSION AND RESULTS

The produced water quality can vary greatly depending on the EOR processes employed and rock and fluid composition of the formation injected. Produced water originating from steam flooding (SF), steam assisted gravity drainage (SAGD), expanding solvent SAGD (ES-SAGD), and hot water injection (HWI) processes are characterized in this chapter. The water shale interaction is investigated with static experiments over three weeks period of time on Green River, Marcellus, Eagle Ford, and Barnett. For all the samples, the anions and cations were analyzed with ion chromatography. Total dissolved solids (TDS), conductivity, pH, average particle sizes, and TOC of the water were measured. The stability of the colloids were characterized with zeta potential. Analysis of the rock samples was carried out using XRD, TGA, and XPS.

4.1 Shale Analysis

One of the most fundamental steps regarding rock analysis is to determine the mineral composition of the rock. XRD analysis was conducted to obtain the mineral composition of the shale samples. The figure below shows the results of the XRD analysis.

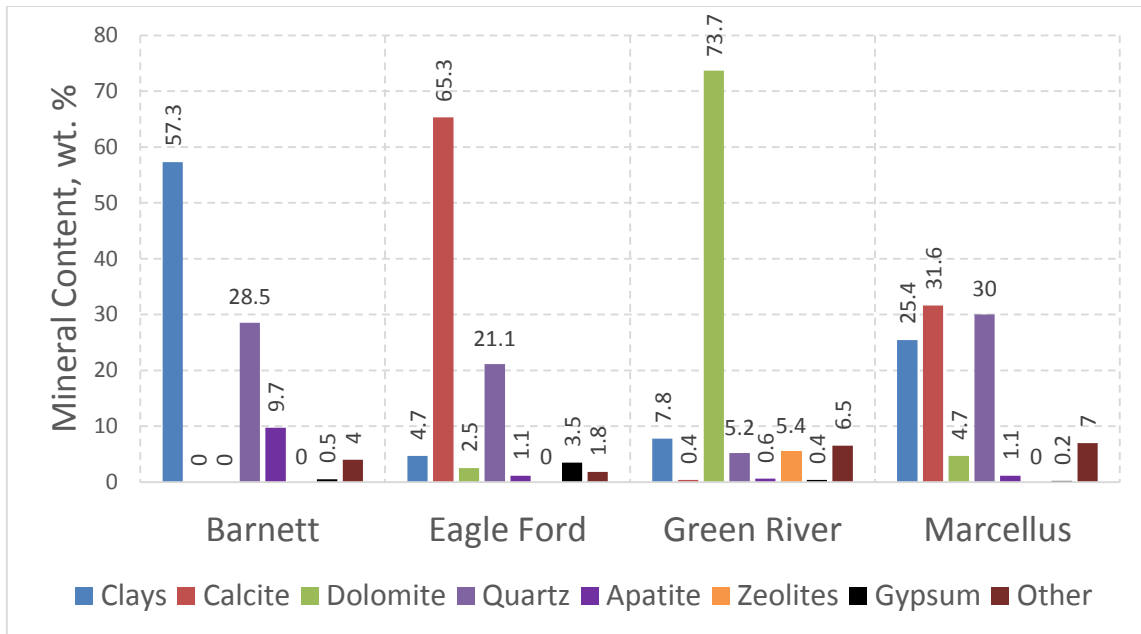


Figure 4: Mineral Composition of Original Rock Samples Determined by XRD

From the XRD results, it is apparent that all of the samples do contain quartz. However, Barnett consists mainly of clay; Eagle Ford consists mainly of calcite; Green River consists mainly of dolomite; and Marcellus contains a mixture of calcite, quartz, and clay. The clays measured were illite (mica), smectite, kaolinite, and illite with smectite layers. The other minerals consist of feldspar, plagioclase, and pyrite. The reaction with water of the various minerals

Table 7: Hydrolysis Reaction of Minerals Present in Shale Samples

Mineral	Reaction of Mineral with Water	Solubility Constant
Calcite	$\text{CaCO}_{3(s)} \rightleftharpoons \text{Ca}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)}$	$3.8 * 10^{-9}$ (Arrigo, 2006)
Dolomite	$\text{CaMg}(\text{CO}_3)_{2(s)} \rightleftharpoons \text{Ca}^{2+}_{(aq)} + 2\text{CO}_3^{2-}_{(aq)} + \text{Mg}^{2+}_{(aq)}$	10^{-17} (Arrigo, 2006)
Quartz	$\text{SiO}_{2(s)} \rightarrow \text{H}_2\text{SiO}_3^-(\text{aq}) + \text{H}^+$	$10^{-9.9}$ to $10^{-11.7}$ (Krauskopf and Bird, 1995)
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})_{(s)} \rightleftharpoons 10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2(\text{F}^-, \text{OH}^-)$	$10^{-11.8}$ (Somasundaran et al. 1985)
Gypsum	$\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)}$	$2.6 * 10^{-5}$ (Arrigo, 2006)
Illite	$(\text{K}, \text{H}_3\text{O}, \text{Na})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})] \rightleftharpoons \text{K}^+ + \text{Na}^+ + \text{Mg}^{2+} + 2-68\text{Al}(\text{OH})^- + \text{H}_4\text{SiO}_4^+ + 4(\text{OH})^-$	$10^{-45.8}$ to 10^{-73} (Reesman, 1973)
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightleftharpoons 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	$10^{-37} - 10^{-40}$ (Reesman and Keller, 1968)
K-Feldspar	$3\text{KAlSi}_3\text{O}_8 \rightleftharpoons \text{KAl}_2(\text{AlSiO}_{10})(\text{OH})_2 + 6\text{SiO}_2 + 2\text{K}^+$	$1.1 * 10^{-20.04}$ (Arrigo, 2006)
Plagioclase	$5\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) + \text{CaAl}_4\text{Si}_2\text{O}_{10}(\text{OH})_2 + 2\text{SiO}_2$	$1.08 * 10^{-15}$ to $2.5 * 10^{-15}$ (Casey et al. 1991)
Pyrite	$4\text{FeS}_{2(s)} + 4\text{H}_2\text{O}_{(l)} \rightarrow 4\text{Fe}^{2+}_{(aq)} + 7\text{S}^{2-} + \text{SO}_4^{2-}_{(aq)} + 8\text{H}^+$	$10^{-15.2}$ to $10^{-17.6}$ (Davison, 1991)
Zeolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \rightleftharpoons \text{Na}^+_{(aq)} + \text{Al}(\text{OH})^-_{4(aq)} + 2\text{Si}(\text{OH})_{4(aq)}$	$10^{-16.1}$ to $10^{-26.5}$ (Wilkin and Barnes, 1998)

The Barnett was reported to be rich in clay (Nieto et al. 2009), Eagle Ford rich in calcite (Carman and Lant 2010), and Marcellus rich in clay and calcite (Morsy et al. 2014).

The quantitative results from XRD were verified qualitatively using TGA and XPS analyses. TGA analysis of the rock samples was conducted to verify the mineral composition of the shale samples (Figure 4). The dehydroxylation, dehydration, and decomposition temperature of the minerals and organic matter is compiled from the literature and summarized in Table 8.

Table 8: Temperature Ranges for Mass Loss of Minerals and Matter

Mineral / Matter	Temperature Range of Mass Loss	Chemical Process
Kerogen	325– 475 °C (Aboulkas and Harfi 2008)	Decomposition of kerogen
Calcite	700 – 900 °C (Foldvari 2011)	Decomposition to form carbon dioxide
Quartz	900 – 1500 °C (Zhou et al. 2007)	Decomposition of quartz to form oxygen.
Dolomite	750 – 800 °C (Foldvari 2011)	Decomposition of dolomite
Gypsum	1200 °C (Foldvari 2011)	Decomposition to steam
Illite	550 – 900 °C (Foldvari 2011)	Dehydroxylation of hydroxyl group

TGA experimental results are evaluated according to the temperature ranges provided in Table 8 for the thermal decomposition of each mineral and kerogen. As a result, the weight percent of each mineral and kerogen in the rock can be estimated. However, obtaining a quantitative analysis using TGA analysis for samples containing a variety of minerals is extremely difficult. This is because, as shown in Table 8, there are temperature ranges at which various reactions overlap and therefore, accurate quantitative analysis based on stoichiometric equations cannot be achieved (Foldvari 2011). However, qualitative analysis is still helpful to characterize rock samples by TGA.

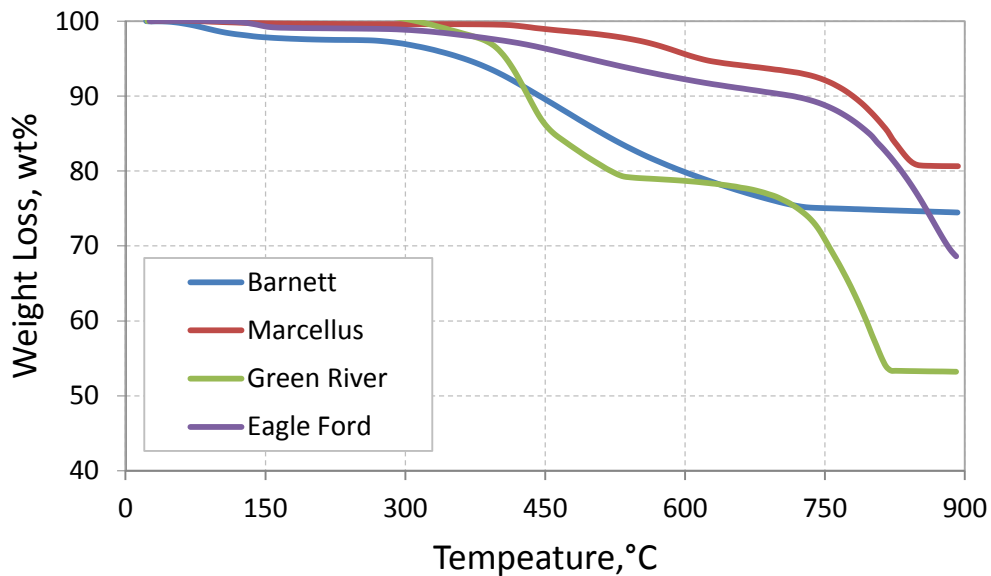


Figure 5: TGA Analysis of Shale Samples

In Figure 5, the mass loss of the Eagle Ford sample from approximately 740 °C to 900 °C indicates the presence of calcite (Foldvari 2011). Furthermore, the mass loss between from 400 °C to 500 °C indicates the presence of organic content (Aboulkas and Harfi 2008). For the Marcellus sample, a mass loss between 375 °C to 500 °C and from 700 °C to 875 °C indicates the presence of kerogen and calcite, respectively (Aboulkas and Harfi 2008; Foldvari 2011). For the Green River sample, the mass loss between 400 °C to 475 °C indicated the presence of kerogen and the mass loss between 700 °C to 815 °C indicated the presence of dolomite (Aboulkas and Harfi 2008; Foldvari 2011). Finally, for the Barnett sample, the mass loss between 350 °C to 500 °C and 550 °C to 600 °C indicated the presence of kerogen and illite, respectively (Aboulkas and Harfi 2008; Foldvari 2011). The mass loss for the kerogen temperature range can provide semi quantitative analysis of the total organic content present in the shale samples. The table below shows the total organic content of the shale samples based on the decomposition of the kerogen from Figure 5.

Table 9: Temperature Range of Mass Loss of Shale Sample Minerals and Organic Matter

Shale Sample	Temperature Range of Mass Loss	Chemical Process
Barnett	350 °C to 500 °C	Decomposition of kerogen
	550 °C to 650 °C	Dehydroxylation of Illite
Marcellus	375 °C to 500 °C	Decomposition of kerogen
	700 °C to 875 °C	Decomposition of calcite to carbon dioxide
Green River	400 °C to 475 °C	Decomposition of kerogen
	750 °C to 800 °C	Decomposition of dolomite to carbon dioxide
Eagle Ford	400 °C to 500 °C	Decomposition of kerogen
	740 °C to 900 °C	Decomposition of calcite to carbon dioxide

The presence of the minerals quantified by XRD analysis is verified by analyzing the TGA. A comparison of the mass loss in Figure 5 with the chemical process temperature ranges in Table 8 can provide qualitative analysis of the presence of various minerals in the shale samples. The table below provides this comparison.

Table 10: Total Organic Content of Rock Samples Determined by TGA

Shale Rock	Total Organic Content, wt%
Eagle Ford	3.4%
Barnett	8%
Marcellus	1.2%
Green River	17.1%

As shown in Table 10, Green River has the highest organic content at 17.1% whereas the Marcellus sample has the least amount of organic present.

XPS analysis was also conducted to semi quantitatively validate the results from XRD and TGA. Figure 6 shows the relative atomic ratios of the shale samples from XPS analysis.

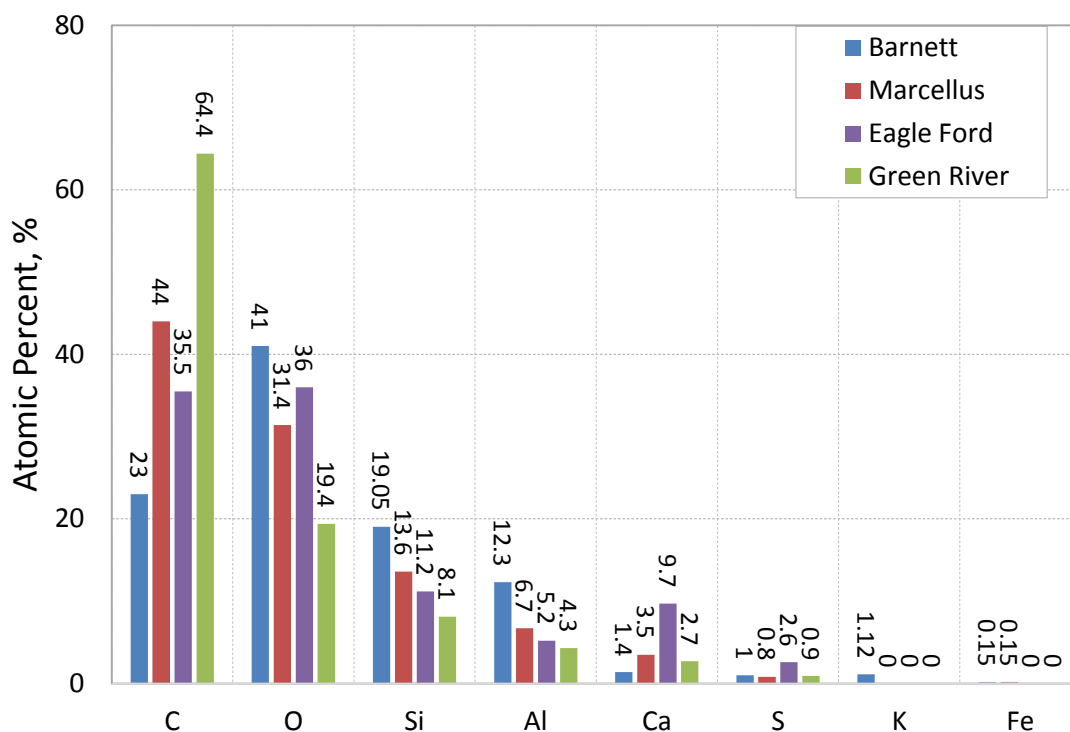


Figure 6: Relative Atomic Ratios of Shale Samples Determined by XPS

In Figure 6, the majority of the shale samples consist of minerals containing either oxygen, calcium, carbon, silicon, or aluminum. The relative ratios of the atoms can be used to verify the results from XRD analysis. Barnett and Marcellus contain the greatest amount of quartz and as a result, the atomic ratios of silica in these two shale samples is higher compared to Green River and Eagle Ford. From the XRD results, Eagle Ford had the highest amount of calcite at 63.9% (Figure 4) and consequently, the highest calcium atomic ratio was detected in Eagle Ford samples (Figure 6). Furthermore, Barnett contained the greatest amount of clays and therefore, the amount of aluminum and silicon

in Barnett was greater than the other shale samples. Finally, from TGA, it was determined that Green River contained the maximum organic material at 17.1% and as a result, the relatively high amount of carbon in Green River sample can be attributed to the high organic content and high dolomite content in the sample.

4.2 Water-Rock Interactions for Shale Samples

After the characterization of shale samples in terms of their mineralogy, static experiments were conducted on crushed shale samples to observe and interpret the water-rock interaction. Shale samples were crushed and sieved to 1 micron. Afterwards, 10 grams of each of the samples was added to 40 mL of deionized water and put in an oven at 150 °F for a period of three weeks. The TDS, pH, anions, cations, zeta potential, particle size, and TOC were measured after each static experiment.

4.2.1 Ion Concentrations of Water Samples Exposed to Shale Sample

The TDS of the water samples after the rock water interaction was measured and is summarized in the table below.

Table 11: TDS of Water Samples after Interaction with Shale

	Barnett	Marcellus	Eagle Ford	Green River
TDS (ppm)	2094.3	1382.7	2422.7	389.7

The water samples after the interaction with the Eagle Ford and Barnett had the largest amount of TDS at 2422.7 ppm, and 2094.3, respectively. The water after the interaction with the Marcellus samples had an intermediate TDS value of 1382.7 ppm and the Green River had the lowest at 389.7 ppm. The values of the TDS are based on the specific ions in the water sample.

The most common ions found in oil field waters are sodium, chloride, calcium, magnesium, sulfate, potassium and strontium (Collins and Wright 1982). Therefore, the concentration of these ions along with other ions was measured using Ion Chromatography. The cation concentration in the water samples is shown in the figure below.

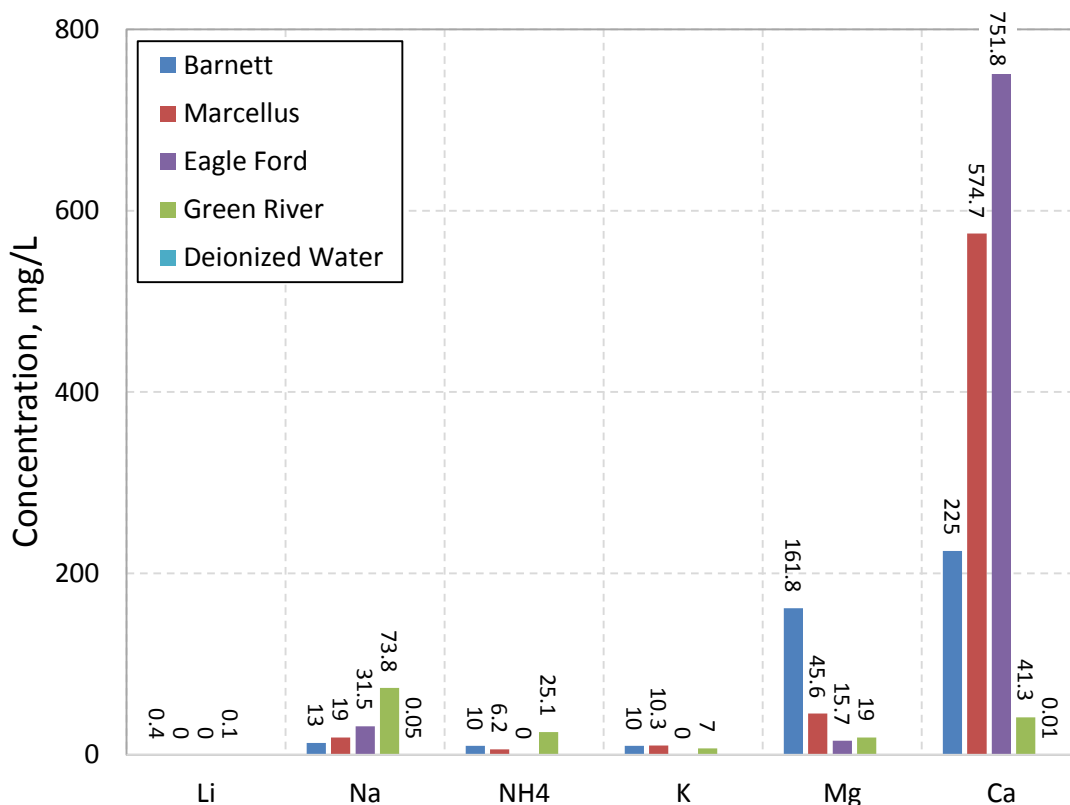


Figure 7: Cation Concentration for Water Samples after Interaction with Shale Samples

In Figure 7, the concentration of lithium, potassium, and ammonium ranges between 0 mg/L to 26 mg/L. Sodium concentration range is from 13 mg/L to 75.8 mg/L. Sodium ions may be attributed to zeolite, mica, and smectite. The magnesium and calcium concentrations were discovered to be the highest. Magnesium concentrations ranges from 19 mg/L to 162 mg/ and calcium concentration in the water samples ranges from 41 mg/L to 752 mg/L.

Figure 7 also shows a high concentration of calcium ions. The source of these calcium ions should be due to high amount of calcium containing minerals in the shale

samples (Figure 4). Hence, to determine the calcium source of water samples exposed to the shale samples, the calcium concentration in the water is plotted against the calcium containing minerals.

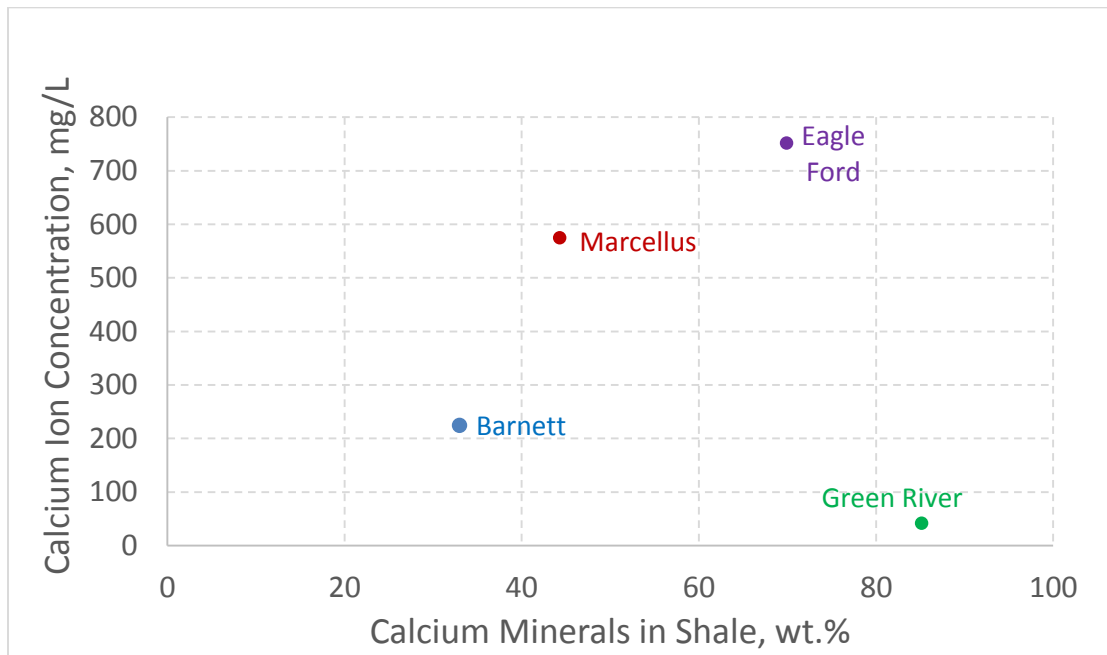


Figure 8: Relationship between Calcium Ions of Water Samples and Calcium Mineral Content of Shale Samples

The calcium containing minerals in the shale samples are: smectite, calcite, dolomite, plagioclase, apatite, and gypsum. Barnett has relatively low amount of these minerals and as a result, the water rock interaction resulted in low calcium ion concentration. Although Green River rock sample has the highest amount of calcium containing minerals, the water rock interaction yields low calcium ion concentrations. This

can be attributed to two reasons. The first is that the main source of calcium in the Green River sample is dolomite and the second is the high amount of minerals and matter contributing to the cation exchange capacity (CEC) of the rock.

Dissolution of rocks after the interaction with water can be best described by the equilibrium constant of the reversible chemical reaction during the dissolution process (Krauskopf and Bird, 1995). During the dissolution process, the solid form of the rock disassociates into ions. The equilibrium constant provides an indication of the amount of disassociation that takes place. If the equilibrium constant is high, the reaction moves towards the right (substantial dissolution occurs). If the equilibrium constant is low, then, the reaction moves towards the left (the solid rock does not dissociate). The reason as to why water sample originated from Green River-water interaction does not have a substantial amount of magnesium can be attributed to the equilibrium constant of dolomite. The equilibrium constant of the dolomite dissolution reaction is extremely low and ranges from 10^{-17} to 10^{-19} whereas the equilibrium constant for the calcite dissolution reaction is relatively high and is usually around 10^{-9} (Krauskopf and Bird, 1995; Fauer, 1998). This low of a dissolution rate of dolomite essentially means that the reaction occurs to the left and the solid form of the mineral remains intact.

The fact that dolomite's solubility in water is low when compared to calcite is also evident when the before and after water-rock interaction XRD analyses are observed. The table below shows the mineral composition percent changes for both calcite and dolomite after the water shale interaction.

Table 12: XRD Before and After Water Rock Interaction

	Barnett	Eagle Ford	Green River	Marcellus
Calcite (wt. %)	0.1	-1.4	-0.2	0.2
Dolomite (wt. %)	0	1.1	2.3	-0.2

As shown in Table 12, the relative percentage of dolomite increased or only slightly decreased after the interaction with shale whereas the relative percentage of calcite decreased or only slightly increased after the interaction with water. This further bolsters the fact that dolomite is insoluble in water when compared to calcite as the relative percentage of calcite decreased whereas the relative percentage of dolomite decreased.

Another reason as to why there is a low amount of calcium in the water sample after the interaction with Green River is due to the organic content and the amount of zeolite present in the Green River sample. Analysis of the organic content and the presence of zeolite is important because they contribute significantly to the cation exchange capacity (CEC) of a particular rock (Ketterings et al. 2007). The CEC indicates the ability of the rock to retain cations; the larger the value of CEC, the more cations the rock can hold (Ketterings et al. 2007). Clays, zeolite, and organic matter all contribute to the CEC as they have negatively charged surfaces and therefore, can attract cations. The table below lists the CEC of the minerals and organic content.

Table 13: CEC of Minerals and Matter

Mineral / Organic Content	CEC (meq/100g)
Quartz	<2 (Ketterings et al. 2007)
Kaolinite	10 (Ketterings et al. 2007)
Illite	25 – 100 (Ketterings et al. 2007)
Smectite	25 – 100 (Ketterings et al. 2007)
Zeolite	380 – 460 (Essington, 2004)
Organic Matter	250 – 450 (Ketterings et al. 2007)

The CEC of organic matter and zeolites is relatively high compared with clay minerals. The Green River shale sample contains the largest amount of TOC (17.1%) and zeolite (5.4%) (Table 10 and Figure 4). Therefore, it can be inferred that the Green River shale sample has a large CEC when compared with the other shale samples. As a result, the amount of calcium in the water sample after the interaction with Green River is low even though a large amount of calcium containing minerals are present in the Green River. The same reasoning can be applied to the amount of magnesium present in the water samples after the interaction with the rock.

The source of the magnesium ions is attributed to the amount of magnesium containing minerals in the shale samples determined by the XRD analysis. Figure 9 shows the relationship between the magnesium content of the water samples (Figure 7) and the magnesium containing minerals (Figure 4).

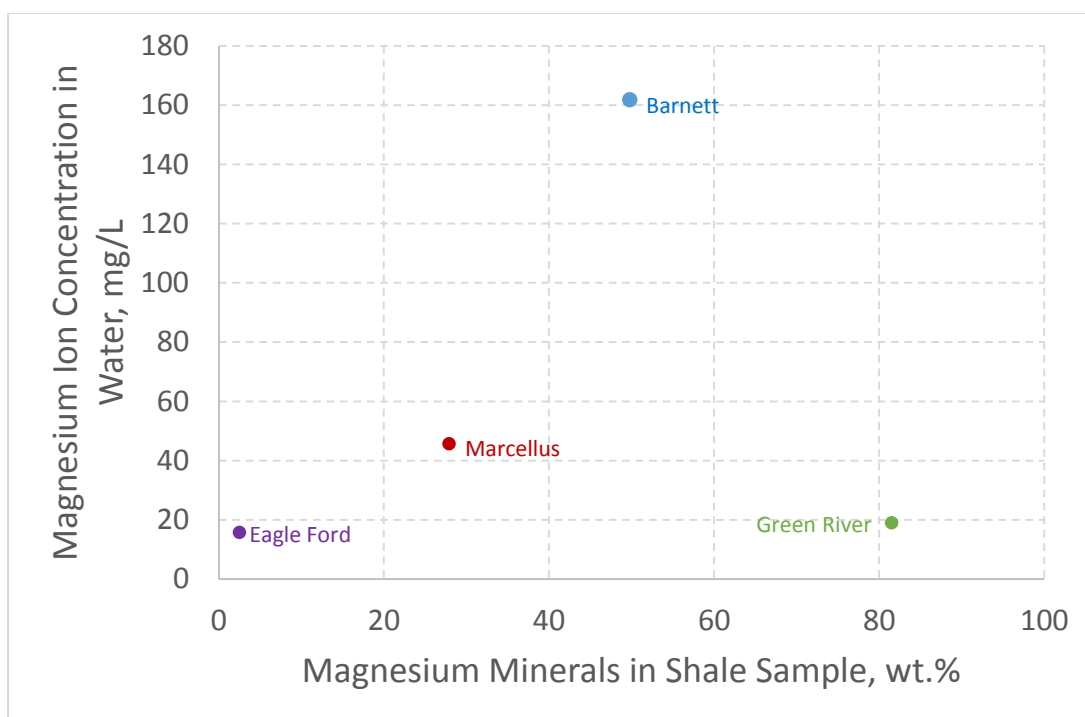


Figure 9: Relationship between Magnesium Ions of Water Samples and Magnesium Minerals in Shale Samples

Illite, smectite, and dolomite, which are Mg containing minerals, were plotted against the magnesium concentration of the water. From Figure 9, Eagle Ford, Marcellus, and Barnett follow a similar trend; as the amount of illite, smectite, and dolomite increases, the amount of magnesium in the water increases. However, Green River does not follow this trend. Even though 82.4% of Green River sample consists of minerals containing magnesium, the amount of magnesium in the water sample is only 19 mg/L. The reason for this phenomenon can again be attributed to the high amount of organic content and zeolite in the Green River shale sample (Figure 4).

The presence of zeolite in the Green River shale sample can also be the reason as to why there is a large amount of sodium present in the water sample after the interaction with Green River (Figure 7). Various forms of zeolite contain sodium atoms and due to the affinity of sodium and the high CEC of the Green River shale sample, sodium from the zeolite is exchanging with the calcium and magnesium ions and as a result, the concentration of sodium in the water sample after interacting with the Green River is relatively high (Essington, 2004).

The concentration of anions was also measured and is shown in the figure below.

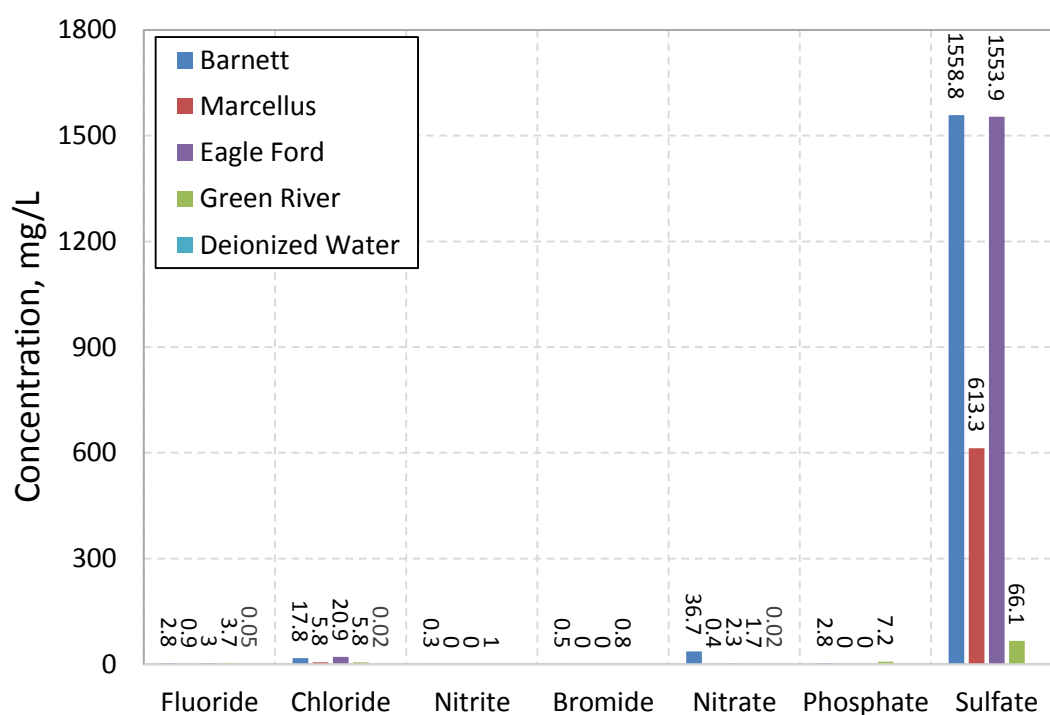


Figure 10: Anion Concentration of Water Samples after Interaction with Shale Rocks

As shown in Figure 10, the concentrations of chloride, nitrite, bromide, nitrate, and phosphate are relatively low and range from 0 ppm to 37 ppm when compared to sulfate. The shale samples were outcrops and therefore, nitrate and nitrite may be originated by people and animal activities. The concentration of sulfate in the water samples after shale interaction is shown below.

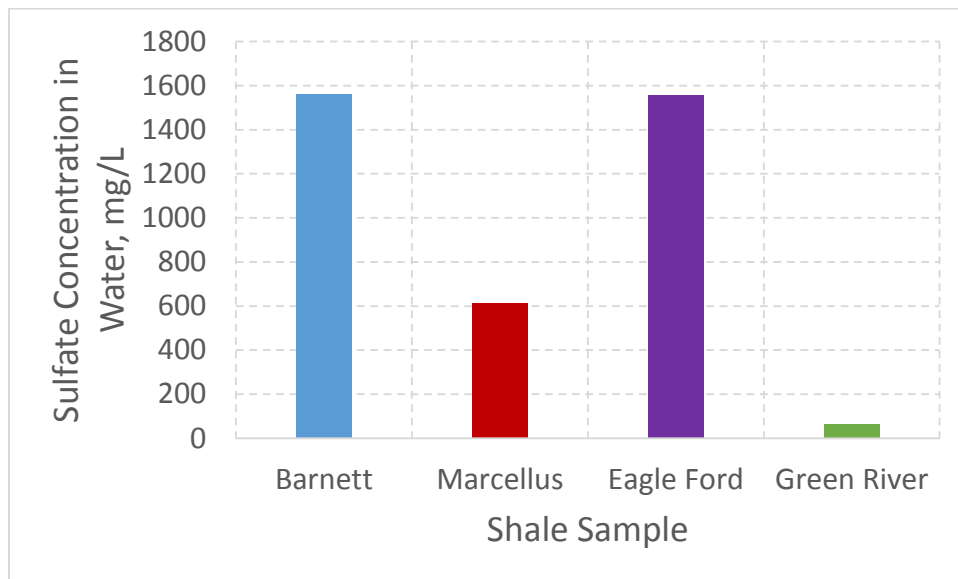


Figure 11: Sulfate Concentration in Water

The Eagle Ford shale sample had a relatively large amount of gypsum (Figure 4) and as a result, the amount of sulfate in the water was relatively high. The Marcellus and Green River had a low amount of gypsum and therefore, the amount of sulfate in the water sample was low. However, the Barnett also had a low amount of gypsum, however, the amount of sulfate present in the water after the interaction was similar to that of the water

sample which interacted with the Eagle Ford. This can be attributed to the amount calcium present in the water Eagle Ford and Marcellus water samples (Figure 10). According to Le Chatelier's Principle, if there is a common ion present in the water sample, then the solubility reaction will shift towards the left (Petrucci et al. 2006). In other words, due to the amount of calcium containing minerals present in the Eagle Ford and Marcellus, there is an ample amount of calcium ion in the water sample after the rock water interaction and as a result, there is a high amount of calcium. Therefore, the solubility of gypsum will decrease and consequently, the amount of sulfate that could be present in the water will decrease. In the case of the Barnett, there is a relatively low amount of calcium minerals present (Figure 8) and therefore, a low amount of calcium ions (Figure 10). Therefore, gypsum in the Barnett water sample will be more soluble and consequently, more sulfate will dissociate.

The hardness of the water can also be calculated from the concentration of the calcium and magnesium ions (Skipton and Dvorak, 2009). The total hardness of the water can be calculated using the following equation:

$$TH = 2.5 * CC + 4.12 * MC \quad \text{Equation 1}$$

where: TH is the total hardness expressed in mg/L as CaCO₃

CC is the calcium concentration expressed in mg/L

MC is the magnesium concentration expressed in mg/L

The table below shows the hardness of the water of all the water samples after the interaction with shale.

Table 14: Total Hardness as CaCO₃ in mg/L of Water after Interaction with Shale

Deionized Water	Barnett	Marcellus	Eagle Ford	Green River
0.025	1229.1	1624.6	1944.2	181.5

The total hardness of the water which interacted with the shale samples ranged from 181.5 mg/L to 1944.2 mg/L. The water after the interaction with Barnett, Marcellus, and Eagle Ford samples is expected to be harder than the water which interacted with Green River sample due to the higher concentration of calcium and magnesium ions. Therefore, to reuse the water, softening treatments would have to be applied for the water interacting with Barnett, Marcellus, and Eagle Ford.

4.2.2 Water Characterization after Exposure to Shale Samples

Water samples, after three-week exposure to shale samples, are characterized by determining the TDS, pH, zeta potential, and particle size. All of these measurements are important to determine the treatment and/or handling recipes of the produced water. Small particle sizes will warrant the need of additional treatment options before successful management strategies can be implemented. The table below summarizes the average particle size of the water samples.

Table 15: Particle Size of Water Samples after Exposure to Rock for Three Weeks

	Barnett	Marcellus	Eagle Ford	Green River
Average Particle Size (nm)	1394	1397	1522	1376.3

Table 15 shows the particle size and of the water samples. The lower the values for particle size, the more difficult it will be to treat and manage the water. It is apparent that produced water with small diameters will have a lower settling velocity. As a result, the time it takes for particles to settle will be longer for low settling velocities.

Produced water which has a high zeta potential value indicates that particles in the water will have a tendency to stabilize and as a result, does not settle with only gravity effect (Kaya et al. 2003). The zeta potential of a solution can also be correlated to the ionic strength due to the cations of the solution. The formula to calculate the ionic strength of a solution is shown below.

$$I = 0.5 * \sum_{i=1}^n c_i * z_i^2 \quad \text{Equation 2}$$

where I is the ionic strength, c is molar concentration of the cation (mol/L) and z is the valence charge of the ion (Chieh 2015). The molar concentration of the ion can simply be determined by the concentration of the cations given in Figure 7 and as a result, the ionic strength due to the presence of cations can be calculated.

The zeta potential of a solution is dependent on whether the electrostatic repulsion or Van-der waals attraction dominate the net energy of the solution (Trefalt and Borkovec, 2014.). Figure 12 shows a typical net force diagram.

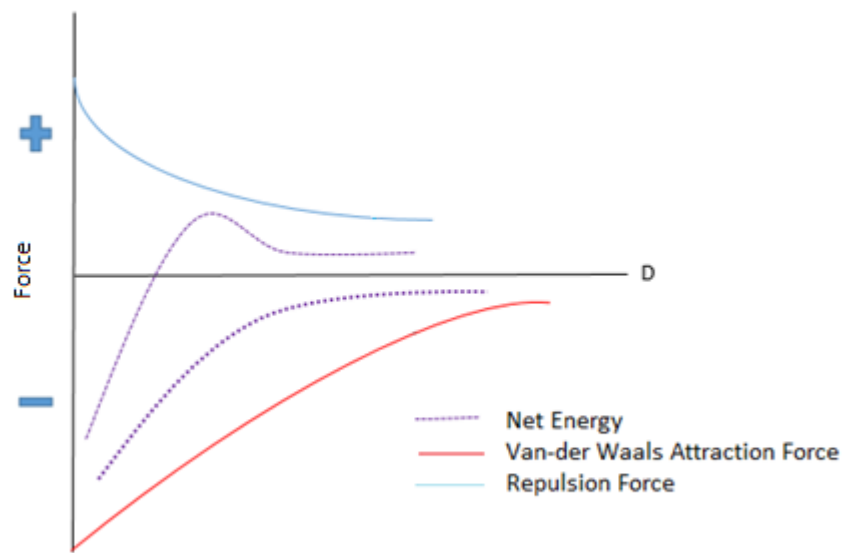


Figure 12: Net Energy Diagram of Colloids in the Water Samples. Adapted from (Trefalt and Borkovec, 2014)

In Figure 12, the electrostatic repulsion force (positive) of a double layer is plotted with Van-der waals attraction force (negative). If the particles have a high repulsion force, then, the net force will be positive. This indicates that the repulsion force is dominant and as a result, particles will tend to repel and therefore, the particles

will become stabilized. This would result in a high absolute zeta potential value. However, if the particles have a high attraction force, then, the net force will be negative. This indicates that the attractive force is dominant and therefore, flocculation and coagulation can occur (Trefalt and Borkovec, 2014). As the ionic strength due to cations of the samples increases, the repulsion force decreases and as a result, the net energy becomes lower until Van-der Waals forces begin to dominate (Shehata and Nasr-el-din, 2015). Figure 13 shows the ionic strength due to cations (calculated from Equation 2) versus the zeta potential for the water shale samples given in Figure 13.

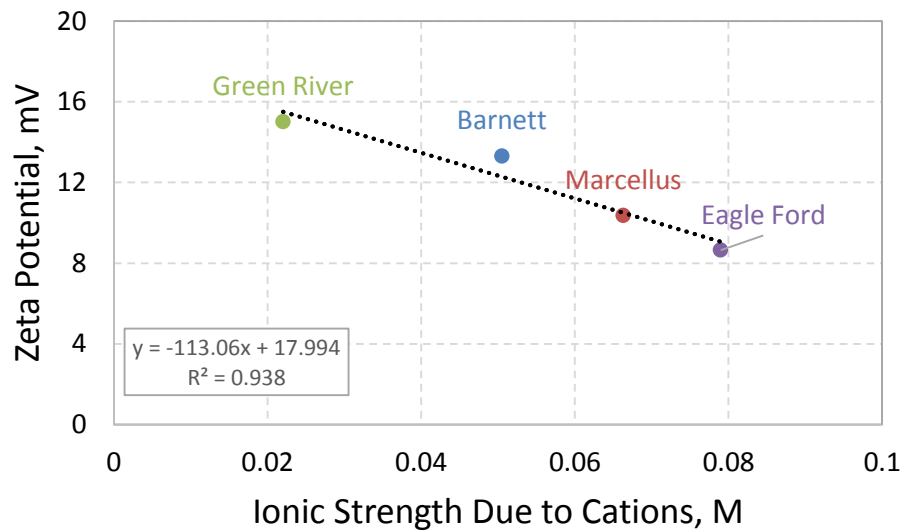


Figure 13: Ionic Strength versus Zeta Potential

From Figure 13, it is evident that high ionic strength values due to cations correspond to low absolute zeta potential values. The Barnett and the Eagle Ford water

samples contain a high amount of calcium and magnesium which are divalent cations (Figure 7). As Equation 2 indicates, divalent cations will increase the ionic strength four times as much as monovalent cations and as a result, the zeta potential for the Eagle Ford and Marcellus water samples will be relatively low. The water samples which interacted with the Green River and Barnett have a small amount of magnesium and calcium and therefore, have low ionic strengths. This results in zeta potential values of 15.01 mV and 13.33 mV for the water samples after the interaction with Green River and Barnett, respectively. Although this value is high compared to the other shale samples, the particles still may have a tendency to flocculate as particles begin to stabilize at an absolute zeta potential value greater than 20 mV (Johnson et al. 2010). Several studies have also showed the same correlation of water samples with high amounts of divalent cations yielding low zeta potential values (Shehata and Nasr-el-din 2015; Nasralla and Nasr el Din, 2011; Kaya et al. 2003).

The pH of the samples was also measured. The pH for the samples is relatively neutral ranging from 6.9 for Eagle Ford, 7.1 for Barnett, 7.6 for Marcellus and 8.3 for Green River. The reason as to why Eagle Ford and Barnett water samples are more acidic than Marcellus and Green River water samples is most likely due to the amount of sulfate present in the samples. As shown in Figure 11, Eagle Ford and Barnett water samples have sulfate concentrations greater than 1550 mg/L whereas Marcellus and Green River water samples have sulfate concentrations of 613 mg/L and 66 mg/L, respectively (Figure 11). Higher sulfate concentration results in a lower pH and therefore, it is expected that Green

River water samples have a high pH whereas Eagle Ford and Barnett water sample have a low pH value (Petrucci et al. 2006).

The total organic carbon (TOC) of the water samples was also measured to have a better understanding of the organics in the water. The table below lists the TOC for each water sample.

Table 16: TOC of Water Samples after Shale Interaction

	Barnett	Marcellus	Eagle Ford	Green River
TOC (mg/L)	34.6	18.2	178	122

The lowest value of TOC was obtained after Marcellus-water interaction. This can be attributed to the low amount of organic content in Marcellus shale sample as determined through TGA analysis (Figure 5 and Table 10). The water samples which interacted with Barnett, Eagle Ford, and Green River had higher TOC than the water sample which interacted with Marcellus due to their relatively higher organic content (Table 10).

4.2.3 Proposed Treatment Methods for Water after Shale Interaction

The most appropriate treatment methods can be proposed by considering the quality of the water and the geographical location of the reservoir. As mentioned earlier,

there are various treatment options that may be used to remove ions, solid particles, and lower the zeta potential value. After water is interacted with Eagle Ford and Barnett samples, a relatively high amount of ions were detected (Figures 7 and 10). Furthermore, a high concentration of sulfate was detected for both samples (Figure 11). Sulfate may interact with bacteria and produce H_2S and as a result, corrosion and problems related to toxicity may occur (Wang et al. 2013). In addition, water after the interaction with Barnett, Marcellus, and Eagle Ford samples had a high amount of total hardness and this can lead to possible precipitation and scaling problems (Table 14). Therefore, it is recommended that before reuse, the ions in these water samples should be removed. As explained earlier, one of the most common ways to remove ions is by membrane filtration (reverse osmosis) (Barrufet et al. 2005).

The particle size and TOC are also important characteristics when treating water. The particle size of these water samples ranged from 1376 nm to 1528 nm and the TOC ranged from 18.2 mg/L to 178 mg/L. Therefore, it is recommended that gravity separators, hydrocyclones, centrifuges, or induced gas flotations be used to remove these particles. These equipment can be configured to remove both inorganic suspended particles and the organic particles to lower the TOC.

The absolute value of the zeta potential for the water samples ranged from 8.65 to 15.01 mV. To reduce the zeta potential, chemical treatment is necessary. Coagulants, which have a charge opposite to that of the particle charge in the produced water (positively charged coagulants should be used since the zeta potential was negative) neutralize the charges of the particles. The coagulant is rapidly mixed into the produced

water for approximately 1 to 2 minutes. Once the charges are neutralized, the particles will come together. Following the coagulation, the flocculation process is implemented and the samples are gently mixed for a period of 15 minutes to one hour (Edzwald 1993). The particles then begin to form flocs which have a larger diameter than the original particles. Due to the larger diameter, the particles will settle and then can be removed by using conventional equipment such as hydrocyclones or centrifuges (Edzwald 1993).

Once treated, the water may be either disposed, reused for commercial purposes, or reinjected during water injection operations (Arthur et al. 2009). To determine whether the water is discharged or reused, the geographical location and onsite treatment equipment available needs to be taken into account.

As explained in Chapter 2, a convenient method to dispose water during onshore operations is by injecting it in Class II disposal wells. However, in Marcellus formation, there are only 8 disposal wells in the state of Pennsylvania (Gaudlip and Paugh 2008). Each of these injection wells can only inject at an average of 8000 bbl/day and as result, alternate management techniques such as obtaining a NPDES permit to discharge the water to surface waters or treating the water for reuse. It is estimated that around 90% of the produced water from Marcellus formation is reused for water injection processes (Mantel 2011). Generally, the produced water is treated onsite through stored in tanks at nearby locations. Afterwards, the water may be reused at the same well or transported to other wells for water injection purposes (Mantell 2011). The most common treatment options in the Marcellus field are thermal evaporation and reverse osmosis (Gaudlip and Paugh 2008).

Similar to the Marcellus reservoir, the majority of the produced water from the Eagle Ford and Barnett is being reused for water injection purposes. Produced water with low TDS is reused immediately whereas produced water with medium or high TDS is sent to treatment facilities which include processes such as thermal distillation and reverse osmosis to treat the water. However, unlike the Marcellus, where strict regulations from the state of Pennsylvania make it difficult to drill Class II disposal wells, Texas has over 12,000 disposal wells and as a result, it may be economical for some companies producing from Barnett and Eagle Ford to inject the water in these disposal wells (McCurdy, 2012).

Green River formation contains the largest amount of shale oil in the United States (Guerra et al. 2011). Therefore, the majority of produced water from Green River formation is used for hydraulic fracturing jobs (Guerra et al. 2011). Similar to the produced water from the other shale formations, treated water may also be discharged to surface waters or in Class II disposal wells.

4.3 Produced Water from EOR Processes

4.3.1 Analysis of Produced Water Originating from EOR Processes

The analysis conducted to observe on water-rock interaction area also achieved on the produced water samples originated from several thermal EOR processes to extract bitumen. The bitumen was characterized in previous experiments by its API, viscosity, and elemental composition. All experiments were conducted on the rock samples prepared

by mixing 85 wt. % 20-40 mesh size Ottawa Sand and 15 wt. % clay (Mukhametshina et al. 2014). Produced water samples from HWI, SAGD, ES-SAGD, SF, and ISC were all analyzed for TDS, anion and cation concentrations, zeta potential, particle size, pH, and TOC. Three samples were collected at different stages of each experiment. Sample 1 is the produced water collected at the early stages of the experiment, Sample 2 is the water collected at the intermediate time of each experiment, and Sample 3 is the very last produced water samples.

The table below summarizes the experimental parameters for all of the EOR experiments.

All experiments were conducted with reservoir rock prepared by mixing 85 wt% Ottawa sand and 15 wt% clay (Mukhametshina et al. 2014; Hamm and Ong 1995). However, in E1, E2, and E3, only kaolinite was used as clay and for the rest of the experiments illite-kaolinite mixture was used. The pore space of the rock was filled with 84% bitumen and 16% water. The highest temperature, 1000 °C, was observed in E9 (in-situ combustion). In hot water injection, E3, 155 °C; in steam flooding, E1, 135 °C; in SAGD, E2 and E4, 165 °C temperature values were achieved to obtain either steam or hot water at designated pressure value given in Table 13. ES-SAGD experiments were conducted with three different combinations of solvents: n-hexane and toluene, n-hexane and cyclohexane, and only n-hexane. Both co-injection and cyclic injection experiments were conducted for the ES-SAGD process which included n-hexane and toluene as the solvents.

Table 17: Experiment Parameters for EOR Experiments (Mukhametshina and Hascakir, 2014; Mukhametshina et al. 2014)

Experiment Number	EOR Type	Clay Type	Solvent Type	Comments
E1	Steam Flooding	Kaolinite	-	Max temperature 135 °C & pressure 0 psig
E2	Steam Assisted Gravity Drainage	Kaolinite	-	Max temperature 165 °C & pressure 75 psig
E3	Hot Water Injection	Kaolinite	-	Max temperature 155 °C & pressure 75 psig
E4	Steam Assisted Gravity Drainage	Kaolinite + Illite	-	Max temperature 165 °C & pressure 75 psig
E5	Expanding Solvent SAGD	Kaolinite + Illite	n-hexane	Max temperature 165 °C & pressure 75 psig
E6	Expanding Solvent SAGD	Kaolinite + Illite	n-hexane + toluene	Solvents co-injected + Max temperature 165 °C & pressure 75 psig
E7	Expanding Solvent SAGD	Kaolinite + Illite	Cyclohexane + n-hexane	Max temperature 165 °C & pressure 75 psig
E8	Expanding Solvent SAGD	Kaolinite + Illite	n-hexane + toluene	Cyclic injection of solvents & Max temperature 165 °C & pressure 75 psig
E9	In-situ Combustion	Kaolinite + Illite	-	Max temperature 1000 °C & pressure 100 psig
DW	-	-	-	Distilled Water

The TDS was determined for all of the EOR processes and is shown below.

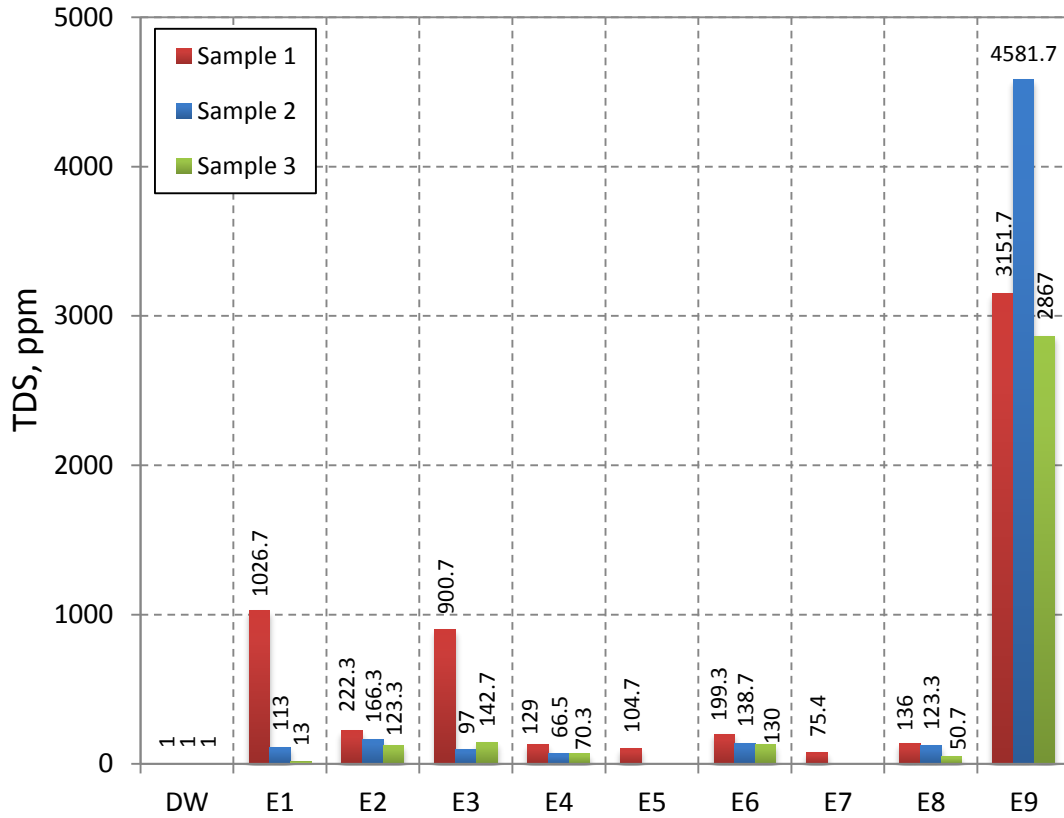


Figure 14: TDS of Produced Water Samples Originated from Thermal EOR Processes Summarized in Table 17

The TDS of all three produced water samples from ISC yield the greatest value. The TDS of steam flooding and hot water injection from the first sample is also relatively high; 1027 ppm and 901 ppm, respectively. The TDS of the other EOR processes range from 13 ppm to 222 ppm. The general trend of the TDS concentration yields the highest concentration for the earliest collected sample (Sample 1). This can be attributed to the

wettability of the rock. Quartz is water-wet and therefore, there is a significant amount of water-rock interaction occurring at the initial stage of the water injection processes (Abdallah et al. 2011). As the water is injection, a film layer of water is formed on the surface of the rock which inhibits the interaction of the rock and water at the later stages.

The reason for the relatively large amount of TDS in the ISC (E9) produced water samples can be attributed to the bitumen cracking which occurs at elevated temperatures (Fukuyama and Nakamura 2010). To determine the specific ions contribution to the TDS, cations and anions were analyzed for all produced water samples. The concentrations of the cations for the Sample 1 are shown in the figure below and the concentration of the cations for Sample’s 2 and 3 can be found in (Appendix A).

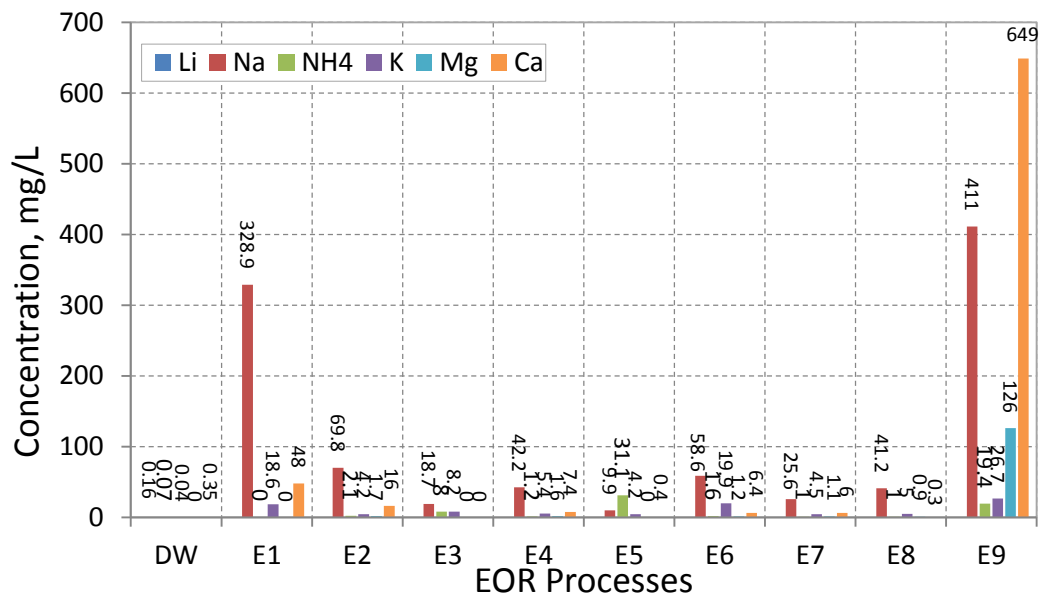


Figure 15: The Cation Concentration of Sample 1 Originated from All Thermal EOR Processes

Two of the most abundant cations are calcium and sodium from the first samples of all of the EOR processes. Calcium concentrations are detected to be up to 649 mg/L (for ISC Sample 1) and sodium concentration were detected to be up to 411 mg/L (for ISC Sample 1). The concentrations for the other cations ranged from 0 mg/L to 31 mg/L. In their study, they (Morrow et al. 2014) analyzed the original bitumen that was used in the EOR processes and showed that the original bitumen contained a large amount of sodium and calcium ions and therefore, the source of sodium and calcium is most likely the bitumen sample. The ISC process (E9) had the largest amount of calcium present. Calcium is relatively stable at low pH levels and as a result, the low pH of produced water from ISC (3.1) may have caused the calcium ion to stabilize (Hayes and Severin 2012). The calcium source may also be due to the quartz present in the rock samples. Hence, after removing residual oil samples from the spent rock samples, rock samples were analyzed with XPS and for reference purposes, the XPS analysis of initial Ottawa Sand and two clays were achieved (Figure 17).

Evidence of the produced water samples being contaminated after the interaction with the rock can be seen in the figure below.

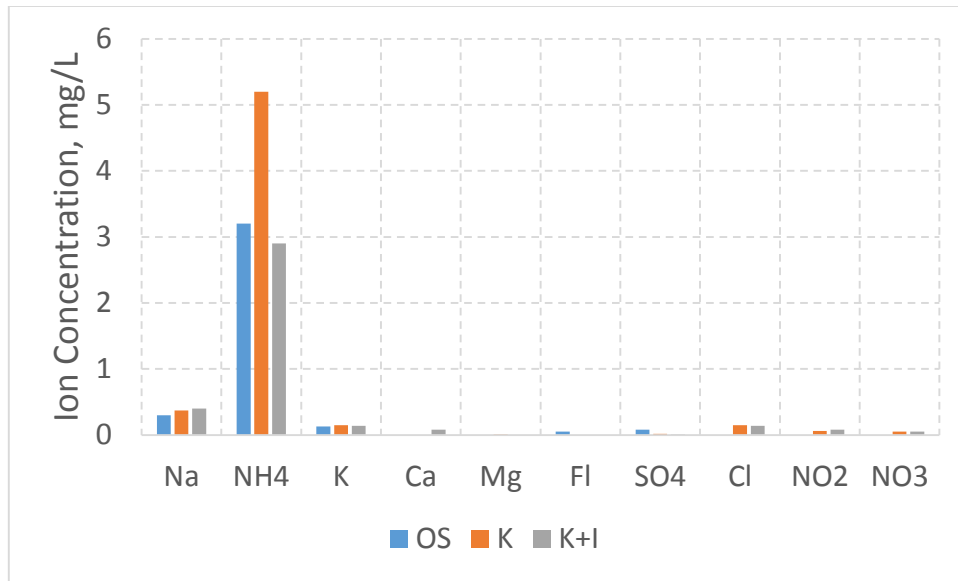


Figure 16: Ions in the water after interaction with Original Ottawa Sand (OS), Kaolinite (K), Kaolinite and Illite (K+I)

From Figure 16, it is apparent that the source of ions in the water can be attributed to the rock samples. Ottawa Sand (OS), Kaolinite (K), and Kaolinite and Illite (K+I) mixtures were mixed with deionized water and the concentration of ions was measured. There was a relatively large amount of sodium, ammonium, potassium, sulfate, chloride, nitrite, and nitrate present in the water samples which indicates that the interaction of the produced water with the rock samples did cause an addition of contaminants. Further evidence of the source of contaminants in the produced water can be seen from XPS analysis. The amount of calcium from the XPS analysis of the spent rock samples for all of the EOR processes has decreased when compared to the original Ottawa Sand (Figure 17). In addition, while the amount of iron in the rock samples is observed to decrease, even though the iron concentration could not be measured in the water samples due to the

limitation of the Ion Chromatography unit, it is reasonably inferred that some amount of iron would be present in the water samples.

The concentration of cations for Samples 2 and 3 follow similar trends where the concentration of calcium and sodium is elevated. These concentrations can be found in (Appendix A).

The concentration of anions was also measured for the EOR processes. Figures 17 shows the concentration of the anions.

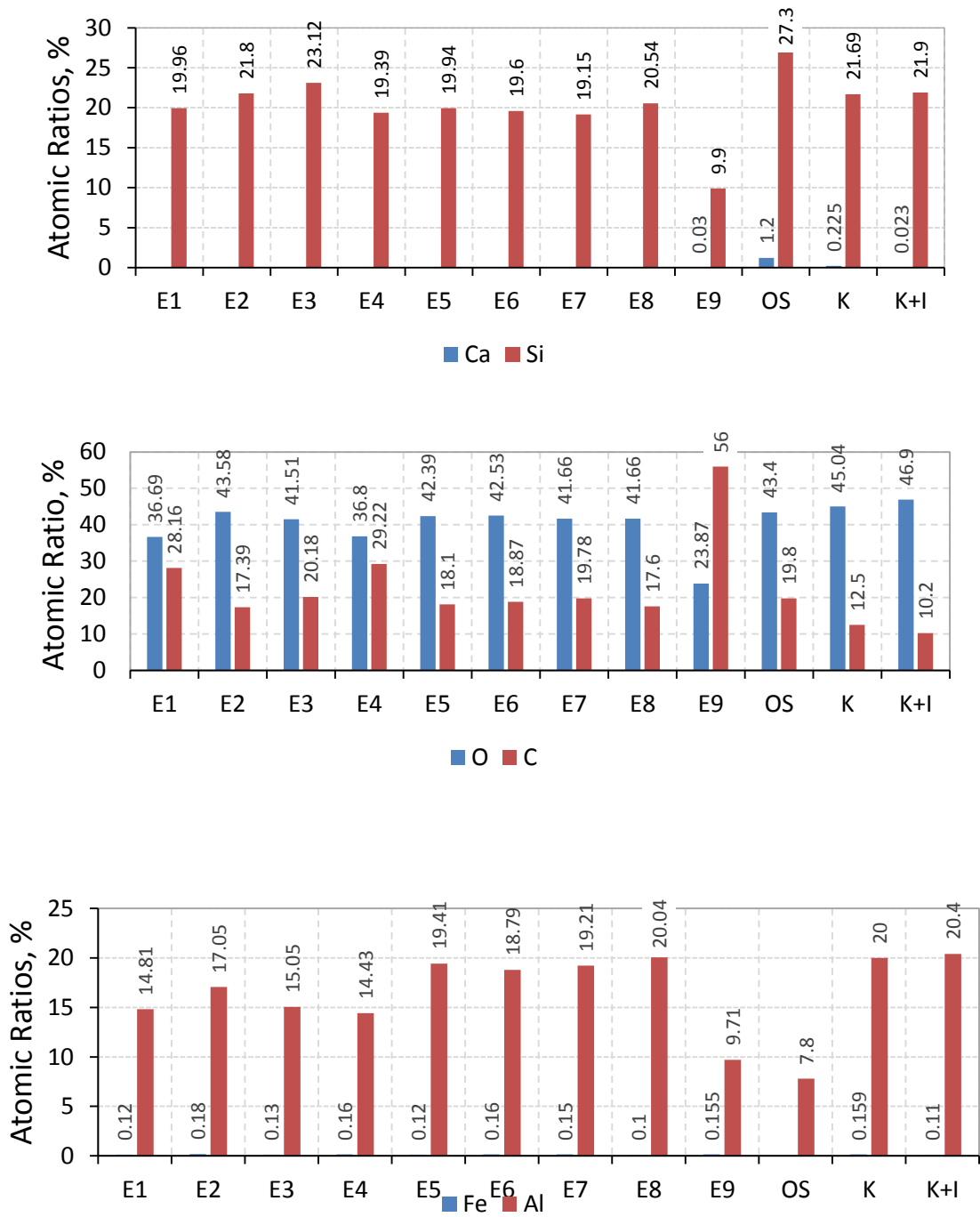


Figure 17: Elemental Atomic Ratios of Spent Rock Samples after Removing the Residual Oil Originated from all Thermal EOR Processes (OS: Ottawa Sand, K: Kaolinite, K+I: Kaolinite+Illite)

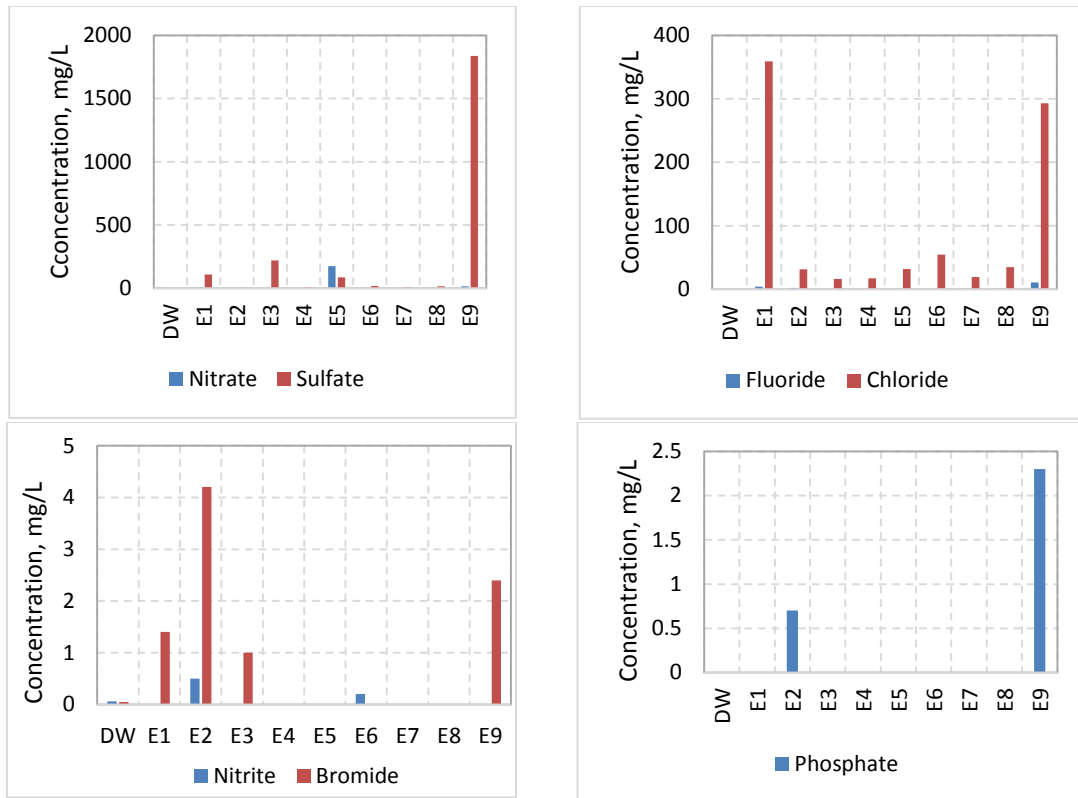


Figure 18: Concentration of Anions in Produced Water from EOR Processes

The ISC processes has the greatest concentration of anions. This is expected due to the bitumen cracking at elevated temperatures (Fukuyama and Nakamura 2010). The concentration of anions for the other EOR processes range from 0 mg/L to 359 mg/L and the concentration of anions from Samples 2 and 3 can be found in (Appendix A).

The zeta potential of the produced water from EOR processes was also measured and is plotted against the ionic strength of the produced water due to the cations.

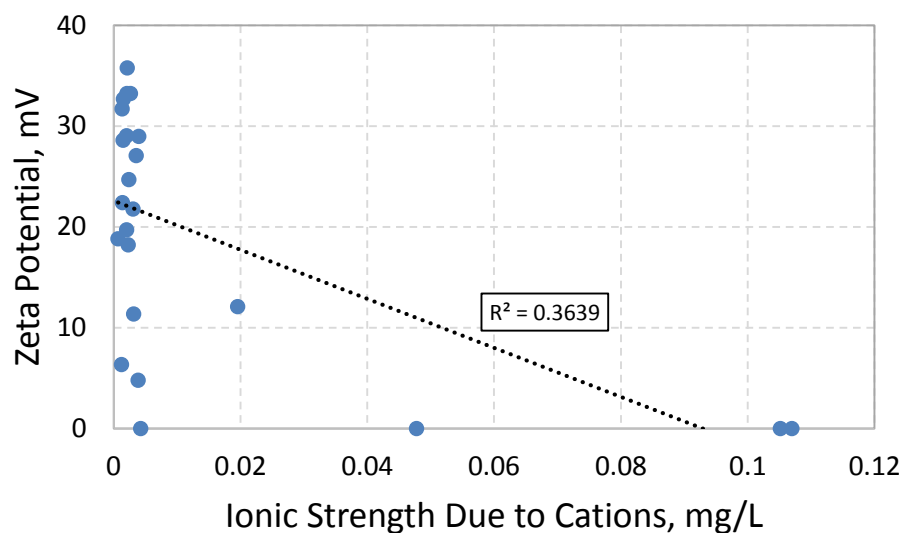


Figure 19: Zeta Potential of Produced Water vs. Ionic Strength due to Cations

For the water which interacted with the shale samples, it was found that the ionic strength of the water due to cations was inversely proportional to the zeta potential of the water. However, as shown in the figure above, the correlation between zeta potential and ionic strength due to cations in the produced water originating from EOR processes is extremely poor. The reason as to why there was a correlation for the waters which interacted with the shale and there was not a correlation for the produced water originating from EOR processes is due to the pH of the water samples as well as the experimental conditions of both experiments.

The pH of the water samples after the interaction with shale rocks was between 6.9 to 8.3 whereas the pH of the water samples from EOR processes was between 3.1 to 8.1 (Appendix A). Even a slight increase in acidity can decrease the zeta potential of the

water significantly and therefore, since there was a wide range of pH values for the produced water from EOR processes, a correlation between ionic strength and zeta potential could not be established (Salgin et al. 2012). In addition to the pH, the temperature and pressure can also have an effect on the zeta potential (Salgin et al. 2012). The water rock interaction for all of the shale samples was carried out at a constant temperature and pressure of 150°F and 14.7 psig, respectively. However, the maximum temperature and pressure that was encountered during the EOR experiments ranged from 135°C to 1000°C and from 0 psig to 100 psig, respectively (Table 17). The variability in temperature and pressure is a further reason as to why a correlation between zeta potential and ionic strength due to cations was established for the water interaction with shale and not for the produced water from EOR processes.

The hardness of the water for produced water from EOR processes was also calculated by applying Equation 1. Figure 20 shows the hardness of the produced water from all of the EOR processes.

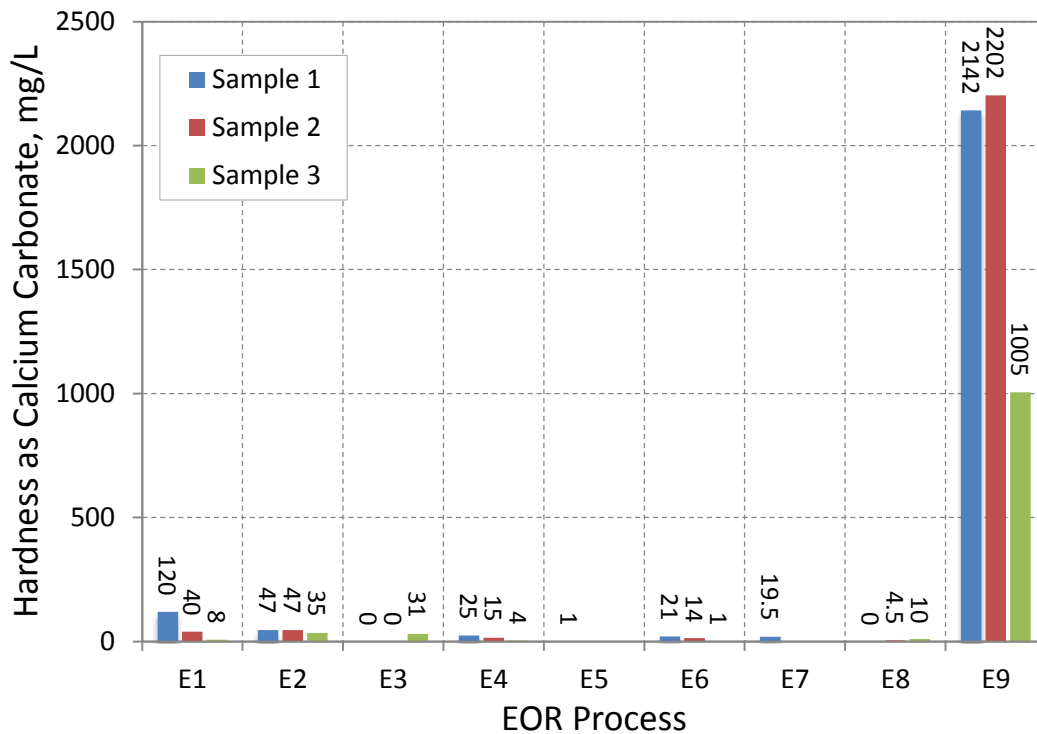


Figure 20: Hardness of Produced Water Samples Originated from all Thermal EOR Processes

It is apparent that produced water from ISC processes have the highest concentration of hardness as calcium carbonate. Produced ISC water samples 1, 2, and 3 have hardness levels of 2142 mg/L, 2202 mg/L, and 1005 mg/L, respectively. The hardness range of the water samples from the other EOR processes range from 0 to 120 mg/L. Both TDS and water hardness are a fundamental characteristic when deciding the reuse of produced water. As explained earlier, water may be reused for reinjection purposes, public supply, the generation of thermoelectric power, and for agricultural purposes (USGS 2005).

The total organic carbon (TOC) was also measured and is shown in the figure below.

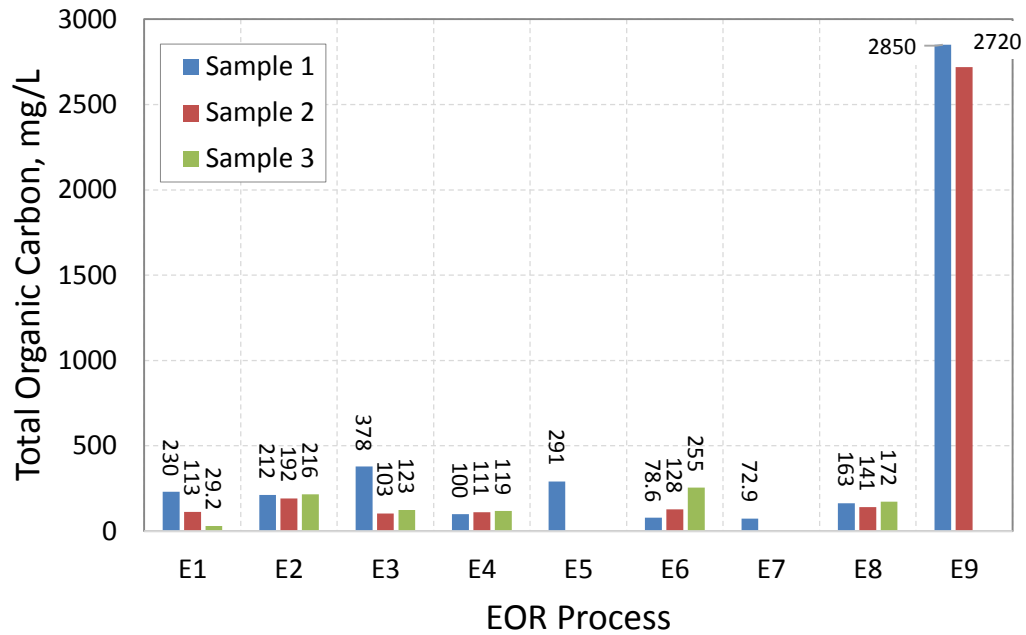


Figure 21: Total Organic Carbon of Produced Water Samples from EOR Processes

The TOC of the produced water from the ISC processes was the greatest with values ranging from 2720 mg/L to 2850 mg/L. The TOC for all of the other produced water samples was below 400 mg/L. During the in-situ combustion experiment (E9), the temperature reached 1000 °C (Mukhametshina et al. 2014) that high of a temperature, the bitumen goes through a pyrolysis reaction. During pyrolysis, volatile hydrocarbons, such as saturates, are formed (Barbour et al. 1976). These volatile hydrocarbons can readily mix with the water and as a result, produced water from ISC processes will have a high

amount of organics. Comparatively, the temperature during the SF, HWI, SAGD, and ES-SAGD experiments only reached a maximum of 165 °C (135 °C for SF and 155 °C for HWI) (Mukhametshina et al. 2014). At that low temperature values, the bitumen will not be upgraded and as a result, low molecular weight hydrocarbons will not form. Therefore, the produced water from SF, HWI, SAGD, and ES-SAGD have low TOC. Furthermore, the amount of carbon on the spent rock from the ISC process (E9) more than doubled when compared to the original Ottawa Sand (Figure 17). This may indicate that although the residual oil was removed, due to the large amount of oil which would have interacted with the rock during the ISC process, some residual oil might have been left behind.

The particle size of the produced water was also measured and ranged from 474 nm to 2078 nm (Appendix A). The particle size is an important characteristics when considering treatment options. The following section will discuss how the zeta potential, particle size, and other characteristics of water will affect the treatment process.

4.3.2 Water Treatment for Produced Water Originating from EOR Processes

The limits for the hardness and TDS for the reinjection processes is shown below.

Table 18: TDS and Hardness Limits for EOR Processes (Royce et al. 1985)

EOR Process	TDS Limit (mg/L)	Total Hardness Limit (mg/L)
Reusing Water for Steam Injection Processes	10,000	1
Reusing Water for ISC	50,000	500

By comparing Figures 14 and 20 with Table 14, it is apparent that the majority of the produced water from the EOR processes cannot be used for steam generation purpose. Figures 14 and 20 show that SAGD and steam injection processes have the least amount of TDS and hardness. This is because the water used to generate the steam during steam injection processes is distilled water which is a higher quality than the water used for water based injection processes. This can also be seen in Table 14 where the hardness of water for ISC processes can be 500 times greater than that for water used in steam injection operations. From Figures 14 and 20, it is apparent that produced water from ISC processes will require the most significant treatment whereas produced water originating from steam injection processes will require the least amount of treatment.

Produced water may also be used for commercial purposes. However, similar to reinjection processes, there are limits and guidelines for the TDS and total hardness for each reusable process.

Table 19: TDS and Total Hardness Limits for Commercial Purposes (EPA 2012)

	TDS Limit (mg/L)	Hardness Limit (mg/L)
Thermoelectric Power	0.1	0.1
Agricultural Use	450-2000	N/A
Public Supply	500	100

As shown in Table 19, there are strict regulations regarding the TDS and hardness for water reuse for thermoelectric power, agricultural use and public supply. Water used for thermoelectric power must be of high quality because hard water may damage the steam generator by scaling and causing corrosion (EPA 2012). Water with a high TDS and hardness count may have an unpleasant taste and therefore, the TDS and hardness of water for public use is regulated (EPA 2012). In addition, a high TDS in the produced water may damage plants and therefore, the TDS of water used for agricultural purposes is regulated (EPA 2012).

Due to the strict regulations for water reuse for commercial purposes and the quality of water that has to be achieved for EOR processes, the produced water from the EOR processes must be treated. Traditional water treating methods such as hydrocyclones, induced gas flotations and centrifuges are common methods to remove contaminants in water (Frankiewicz et al. 2005; Broek and Zande 1998). However, the average particle size of the contaminants must also be taken into account before these treatments are implemented.

The average particle size for all of the EOR processes is less than 2.5 μm . Hydrocyclones, centrifuges, and induced gas flotation can only remove particles that are 5 μm or greater (Frankiewicz et al. 2005; Broek and Zande 1998). Therefore, treatment processes such as membrane filtration and water softening must be used to remove particles less than 2 μm . (Myers 2000; Fedorov et al. 2014). Furthermore, chelating agents may also be used to chelate the calcium and magnesium ions. Ethylene-diamine-tetra-acetic (EDTA) is a common chelating agent that is capable of removing 1 ppm of hardness for every 10 ppm of EDTA (Walker 1965).

The stability of the particles in the produced water is also an important characteristic for treating produced water. Tabulated values of zeta

In terms of treating water based on the TDS, hardness, ion and particle size measurements, the water produced during the ISC process will be the most difficult to treat. However, produced water from ISC has a low zeta potential value when compared to the other EOR processes. The zeta potential for the produced water from the ISC processes have a maximum value of only 4.7 mV whereas the zeta potential for the other EOR processes are up to 35.8 mV. This indicates that chemical treatment for produced water from ISC processes will not be needed.

The absolute value of the zeta potential for SF, SAGD and ES-SAGD processes range from 4.8 mV to 35.8 mV. To reduce the zeta potential, chemical treatments will be necessary. As explained earlier, coagulants may be used so that coagulation and flocculation may occur. Once these two processes occur and the size of the colloids increase, centrifuges, hydrocyclones and gravity separators may be used.

CHAPTER V

CONCLUSION

The produced water from various EOR processes as well as water after the interaction with shale samples were analyzed. The shale samples were first characterized to gain a thorough understanding of the mineralogy and organics present in the samples. Water-shale interaction was investigated for Eagle Ford, Green River, Barnett, and Marcellus shale samples. Furthermore, produced water originating from steam flooding (SF), steam assisted gravity drainage (SAGD), expanding solvent-SAGD (ES-SAGD), and hot water injection (HWI) processes were characterized. Total dissolved solids (TDS), conductivity, pH, total organic carbon (TOC), zeta potential, and average particle sizes of colloids were measured.

The analysis of the ions in the water samples after the shale water interaction indicated a high concentration of sulfate, magnesium, and calcium. The amount of minerals containing these elements was plotted against their respective ion concentration. It was determined that in all three correlations, there was always one sample that was an outlier. In terms of the magnesium and calcium concentration, the water which interacted with the Green River sample had a very low amount of calcium and magnesium even though it had a large amount of dolomite. The low solubility of dolomite along with the high CEC due to abundance of zeolites and organic matter contributed to the low amount of calcium and magnesium in the water sample after the interaction with the shale sample. In the case of sulfate concentration, the Barnett had a low amount of gypsum and pyrite

when compared to the Eagle Ford and Marcellus, however, the amount of sulfate in the water sample after the interaction with water was as high as the water which interacted with the Eagle Ford sample. This was attributed to the large amount of calcium ions in the water samples which interacted with the Eagle Ford and Marcellus. The large amount of calcium ions caused a reverse reaction resulting in a lower amount of gypsum being dissolved.

Zeta potential measurements were also carried out and it was determined that water with low zeta potential values had a ionic strength due to cations. A similar correlation for the produced water from EOR processes could not be achieved due to different pH values of the water samples as well as the different temperature and pressure the produced water was exposed to. The analysis of the produced water originating from the EOR processes indicated the ion concentration decreased as the time at which the water was collected increased. This was attributed to the water at the initial stage adsorbing to the rock surface and thereby, limiting the reaction of the water from the latter stages with the surface of the rock.

The produced water from the ISC processes contained the largest amount of ions and therefore, would require the most treatment to remove the impurities. However, the zeta potential of the produced water from the ISC process was low compared to the other EOR processes. This indicates that chemical treatment for the other EOR processes may be required to decrease the stability of the colloids.

Management options for produced water from shale reservoirs traditionally involves treating the water and reusing it for water injection based methods. Produced

water from the Green River, Eagle Ford, and Barnett may also be disposed of in Class II injection wells, however, due to regulations, disposing produced water from the Marcellus reservoir in Class II injection wells is usually economically unfeasible.

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APPENDIX A

Table 20: Tabulated Values of TDS and pH of Water Samples

		TDS (ppm)				pH			
		Trial 1	Trial 2	Trial 3	Average	Trial 1	Trial 2	Trial 3	Average
E1 – SF	Sample 1	1030	1030	1020	1026.7	8.1	8	8.05	8.05
	Sample 2	113	113	113	113	8.03	8.05	8.05	8.04
	Sample 3	13.7	12.6	12.6	13	8.1	8.08	8.08	8.09
E2 – SAGD with Kaolinite	Sample 1	223	222	222	222.3	7.7	7.7	7.7	7.7
	Sample 2	167	166	166	166.3	7.76	7.72	7.73	7.74
	Sample 3	124	123	123	123.3	7.6	7.6	7.65	7.62
E3 - HWI	Sample 1	899	901	902	900.7	3.2	3.1	3.2	3.17
	Sample 2	90.9	100	100	97	7.08	7.09	7.08	7.08
	Sample 3	142	143	143	142.7	5.95	5.92	5.93	5.93
E4 – SAGD with Kaolinite + Illite	Sample 1	129	129	129	129	7.16	7.11	7.15	7.14
	Sample 2	66.9	66.9	65.6	66.5	6.85	6.88	6.89	6.87
	Sample 3	68.4	71.2	71.4	70.3	6.48	6.42	6.44	6.45
E5-ES-SAGD (n-hexane)	Sample 1	105	104	105	104.7	5.29	5.28	5.29	5.29
E6 – ES-SAGD (n-hexane + toluene)	Sample 1	199	199	200	199.3	6.99	7	6.95	6.98
	Sample 2	140	138	138	138.7	6.72	6.77	6.76	6.75
	Sample 3	129	131	130	130	5.5	5.5	5.46	5.5
E7 – ES-SAGD (cyclohexane + n-hexane)	Sample 1	75.1	75.5	75.5	75.4	6.62	6.6	6.61	6.61
E8 – ES-SAGD (n-hexane + toluene cyclic)	Sample 1	137	135	136	136	6.63	6.66	6.68	6.65
	Sample 2	125	124	121	123.3	6.74	6.77	6.72	6.66
	Sample 3	50.1	51.1	50.8	50.7	5.5	5.5	5.5	5.5
E9 - ISC	Sample 1	3150	3152	3153	3151.7	5.05	5.02	5	5.03
	Sample 2	4580	4581	4584	4581.7	3.13	3.1	3.16	3.13
	Sample 3	2870	2866	2865	2867	3.24	3.19	3.2	3.21
Distilled Water	x	1	1	1	1	7	7	7	7
Deionized Water	x	<1	<1	<1	<1	7	7	7	7
Barnett	x	2095	2094	2094	2094.3	7.1	7.1	7.1	7.1
Marcellus	x	1383	1383	1382	1382.7	7.6	7.5	7.7	7.6
Eagle Ford	x	2418	2425	2425	2422.7	6.9	6.9	6.9	6.9

Table 21: Anion Concentration of Produced Water (mg/L)

		Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate
E1 – SF	Sample 1	4.3	359	0	1.4	4.8	0	108
	Sample 2	2.6	30.9	0	0	0.2	0	0.2
	Sample 3	0.4	1.5	0	0	1.2	0	0.8
E2 – SAGD with Kaolinite	Sample 1	2	31.5	0.5	4.2	1.5	0.7	5.9
	Sample 2	1.2	39.9	0	0	1.1	0	10.8
	Sample 3	2.6	63.2	0.2	0.5	1.5	0	17.3
E3 - HWI	Sample 1	0	36.3	0	0	0.7	0	13.7
	Sample 2	0.6	23.6	0	0	1	0	7.8
	Sample 3	0.4	16	0	1	1.5	0	219.8
E4 – SAGD with Kaolinite + Illite	Sample 1	0.8	31.8	0	0.3	0.3	0	12.1
	Sample 2	0.6	14.6	0	0	0	0	5.6
	Sample 3	0.2	17.2	0	0	0	0	7.5
E5-ES-SAGD (n-hexane)	Sample 1	0.6	32.1	0	0	175	0	86.3
E6 – ES-SAGD (n-hexane + toluene)	Sample 1	0.4	54.4	0.2	0	0.2	0	18.3
	Sample 2	0.9	36.5	0	0	0	0	15
	Sample 3	0.4	31.6	0	0	0	0	16.1
E7 – ES-SAGD (cyclohexane + n-hexane)	Sample 1	1	19	0	0	0	0	7.9
E8 – ES-SAGD (n-hexane + toluene cyclic)	Sample 1	0.9	34.7	0	0	0	0	14.1
	Sample 2	0.1	15.9	0	0	0	0	12.6
	Sample 3	0.2	10.8	0	0	0.8	0	36.8
E9 - ISC	Sample 1	10.6	292.8	0	2.4	14.2	2.3	1836.1
	Sample 2	39.9	259.8	1.68	4.6	11.9	5.4	0
	Sample 3	3.6	3.5	0	0	0	0	68.5
Distilled Water	x	0.06	0.08	0.06	0.05	0.04	0	0
Deionized Water	x	0.05	0.02	0	0	0.02	0	0
Barnett	x	2.8	17.8	0.3	0.5	36.7	2.8	1558.8
Marcellus	x	0.9	5.8	0	0	0	0	613.3
Eagle Ford	x	3	20.9	0	0	2.3	0	1553.9
Green River	x	3.7	5.8	1	0.8	1.7	7.2	66.1

Table 22: Average Concentration of Cations (mg/L)

		Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
E1 – SF	Sample 1	0	328.9	0	18.6	0	48
	Sample 2	0.3	38.5	2.7	4.6	1.7	13.1
	Sample 3	0	5.9	1.7	0.9	0	3.2
E2 – SAGD with Kaolinite	Sample 1	0	6.9.8	2.1	4.2	1.7	16
	Sample 2	0	50.2	2.1	4.2	1.7	16
	Sample 3	0	40.7	2.1	4.2	1.7	16
E3 - HWI	Sample 1	0	39.9	2.2	3.3	1.2	10.3
	Sample 2	0	28.3	0	3.1	0	0
	Sample 3	0	18.7	8	8.2	0	0
E4 – SAGD with Kaolinite + Illite	Sample 1	0	42.2	1.2	5.4	1.6	7.4
	Sample 2	0	20.8	0.1	0.1	1	4.4
	Sample 3	0	23.9	1.8	4.4	0.9	0
E5-ES-SAGD (n-hexane)	Sample 1	0	9.9	31.1	4.2	0	0.4
E6 – ES-SAGD (n- hexane + toluene)	Sample 1	0	58.6	1.6	19.9	1.2	6.4
	Sample 2	0	43.9	1.3	4.8	0.7	4.4
	Sample 3	0	25.6	1	4.5	1.1	6
E7 – ES-SAGD (cyclohexane + n-hexane)	Sample 1	0	25.6	1	4.5	1.1	6
E8 – ES-SAGD (n- hexane + toluene cyclic)	Sample 1	0	44.4	0	5.4	0	0
	Sample 2	0	41.2	1	5	0.9	0.3
	Sample 3	0.1	12.9	3.6	1.3	0.1	3.9
E9 - ISC	Sample 1	0	411	19.4	26.7	126	649
	Sample 2	1	368.8	27.4	51.7	153.5	628
	Sample 3	1.1	126	20.5	34	59.6	304
Deionized Water	x	0	0.05	0	0	0	0.01
Distilled Water	x	0.01	0.05	0.03	0.035	0.09	0.19
Barnett	x	0.4	13	10	10	161.8	225
Marcellus	x	0	19	6.2	10.3	45.6	574.5
Eagle Ford	x	0	38	0	0	15.7	751.8
Green River	x	0.1	73.8	25.1	7	19	41.3

Table 23: Cation Concentration for Trial 1 (mg/L)

		Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
E1 – SF	Sample 1	0	40.6	0	19.9	0	49.5
	Sample 2	0.2	40.6	2.9	3.2	2	12.5
	Sample 3	0	5.1	1	1	0	4
E2 – SAGD with Kaolinite	Sample 1	0	73.5	4.2	4.9	1.4	15.5
	Sample 2	0	50.9	2	1.6	1.5	18.2
	Sample 3	0	41.8	39.6	1.5	2.7	1.9
E3 - HWI	Sample 1	0	40.8	4	3	2	10.5
	Sample 2	0	29.5	0	1.2	0	0
	Sample 3	0	20.1	7.7	12.7	0	0
E4 – SAGD with Kaolinite + Illite)	Sample 1	0	41.1	0.5	5.8	2.5	7
	Sample 2	0	21	0.1	0.1	0.7	4.3
	Sample 3	0	10	33.7	4.2	0	0.1
E5-ES-SAGD (n-hexane)	Sample 1	0	10	33.7	4.2	0	0.1
E6 – ES-SAGD (n-hexane + toluene co-inj.)	Sample 1	0	60	1.5	20.8	1.1	6.8
	Sample 2	0	45.4	1.8	4.9	0.4	2.5
	Sample 3	0	39.5	0	4	0.1	0.1
E8 – ES-SAGD (n-hexane + toluene cyclic	Sample 1	0	40.9	0	5.1	0	0
	Sample 2	0	41.7	1	6.8	1.5	0.5
	Sample 3	0.2	13.6	3.1	0.8	0.1	4.8
E9 - ISC	Sample 1	0	420.7	20.7	26.5	139	661
	Sample 2	1.2	362.1	25.3	51.3	159.6	625
	Sample 3	1	125.8	21	34.9	64.5	288
Distilled Water	x	0.03	0.05	0	0.3	0.18	0.03
Deionized Water	x	0	0.035	0	0	0	0.02
Barnett	x	0.6	15.6	11.2	10.5	165.7	228.3
Marcellus	x	0	23.2	8.8	11.9	44.3	577.1
Eagle Ford	x	0	33.5	0	0	15.2	754.2
Green River	x	0.1	75.4	25	5.6	19	40.1

Table 24: Cation Concentration for Trial 2 (mg/L)

		Lithium	Sodium	Ammonium	Potassium	Magnesium	Calcium
E1 – SF	Sample 1	0	318.7	0	17.3	0	46.5
	Sample 2	0.4	36.4	2.5	6	1.4	13.7
	Sample 3	0	6.7	2.4	0.8	0	2.4
E2 – SAGD with Kaolinite	Sample 1	0	66.1	0	3.5	2	16.5
	Sample 2	0	49.5	2.2	6.8	1.9	13.8
	Sample 3	0	39.6	2.5	2.5	1.3	11.8
E3 - HWI	Sample 1	0	39	0.4	3.6	0.4	10.1
	Sample 2	0	27.1	0	5	0	0
	Sample 3	0	17.3	8.3	3.7	0	0
E4 – SAGD with Kaolinite + Illite	Sample 1	0	43.3	1.9	5	0.7	7.8
	Sample 2	0	20.6	0.1	0.1	1.3	4.5
	Sample 3	0	22.2	2.2	4.8	1	0
E5-ES-SAGD (n-hexane)	Sample 1	0	9.8	28.5	4.2	0	0.7
E6 – ES-SAGD (n-hexane + toluene)	Sample 1	0	57.2	1.7	19	1.3	6
	Sample 2	0	42.4	0.8	4.7	1	6.3
	Sample 3	0	38.5	0	4.2	0.3	0.1
E7 – ES-SAGD (cyclohexane + n-hexane)	Sample 1	0	28.9	0.9	3.7	1.2	6.7
E8 – ES-SAGD (n-hexane + toluene cyclic)	Sample 1	0	47.9	0	5.7	0	0
	Sample 2	0	40.7	1	3.2	0.3	0.1
	Sample 3	0	12.2	4.1	1.8	0.1	3
E9 - ISC	Sample 1	0	401.3	18.1	26.9	113	637
	Sample 2	0.8	375.5	29.5	52.1	147.4	631
	Sample 3	1.2	126.2	20	33.1	54.7	320.1
Distilled Water	x	0	0.16	0.07	0.04	0	0.35
Deionized Water	x	0	0.07	0	0	0	0
Barnett	x	0.2	10.4	8.8	9.5	157.9	221.7
Marcellus	x	0	14.8	3.6	8.7	46.9	571.9
Eagle Ford	x	0	42.5	0	0	16.2	749.5
Green River	x	0.1	72.2	25.2	8.4	19	42.5

Table 25: Tabulated Values for Particle Size Measurements

		Trial 1	Trial 2	Trial 3	Average
E1 – SF	Sample 1	844.5	973.4	1038.8	952.2
	Sample 2	736.5	757.6	769.3	754.5
	Sample 3	498.3	520.7	537.5	518.8
E2 – SAGD with Kaolinite	Sample 1	796.4	859.6	870	842
	Sample 2	539.9	871.7	1060	823.9
	Sample 3	656.9	1323.8	1537.6	1172.8
E3 - HWI	Sample 1	-	1702.2	1756.7	1729.5
	Sample 2	778.2	1031.5	1092.6	967.4
	Sample 3	1188.1	-	911	1049.6
E4 – SAGD with Kaolinite + Illite	Sample 1	1166.6	1279.4	1266.8	1237.6
	Sample 2	465.6	503.9	534.7	501.4
	Sample 3	1027.3	1372.7	1368.8	1256.3
E5-ES-SAGD (n-hexane)	Sample 1	425.8	933.8	1332	897.2
E6 – ES-SAGD (n-hexane + toluene)	Sample 1	480.9	562.9	582	541.9
	Sample 2	405.7	802.9	1006.5	738.4
	Sample 3	1949.5	1795.9	1897.5	1881
E7 – ES-SAGD (cyclohexane + n-hexane)	Sample 1	454.5	481	487.6	474.4
E8 – ES-SAGD (n-hexane + toluene cyclic)	Sample 1	661	111.4	1295.1	1022.5
	Sample 2	711.4	911.5	1002.1	875
	Sample 3	403.3	596.2	683.3	560.9
E9 - ISC	Sample 1	1883.8	1999.6	2350.1	2077.8
	Sample 2	674.8	1316	1006.2	999
	Sample 3	684.4	976.2	1156.2	938.9
Barnett	x	648.4	1463	2477.7	1394.3
Marcellus	x	970.7	1310.7	1909.4	1396.9
Eagle Ford	x	-	1143.4	1899.9	1521.7
Green River	x	1155.4	1646.9	1326.6	1376.3

* (-) indicates an error in the measurement and therefore, value was not recorded

Table 26: Tabulated Values for Zeta Potential (mV)

		Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average
E1 – SF	Sample 1	-10.07	-13.21	-13.78	-11.89	-11.61	-12.11
	Sample 2	-26.58	-27.15	-26.3	-28.15	-27.18	-27.07
	Sample 3	-18.52	-18.67	-18.35	-19.25	-19.4	-18.84
E2 – SAGD with Kaolinite	Sample 1	-23.39	-23.55	-25.80	-25.43	-25.35	-24.7
	Sample 2	-24	-31.57	-35.81	-30.35	-32.73	-30.89
	Sample 3	-3.49	-7.06	-4.54	-	-4.09	-4.8
E3 - HWI	Sample 1	-10.65	-12.44	-11.77	-10.1	-11.83	-11.36
	Sample 2	-26.07	-24.54	-33.82	-35.43	-38.68	-31.71
	Sample 3	-27.59	-28.67	-28.63	-26.62	-31.54	-28.61
E4 – SAGD with Kaolinite + Illite	Sample 1	-20.7	-20.4	-24.35	-19.98	-23.52	-21.78
	Sample 2	-29.26	-34.1	-31.86	-35.04	-33.22	-32.7
	Sample 3	-	-22.34	-21.3	-21.32	-24.75	-22.4
E5-ES-SAGD (n- hexane)	Sample 1	-18.24	-17.95	-18.62	-17.16	-	-18.21
E6 – ES-SAGD (n- hexane + toluene)	Sample 1	-25.35	-30.62	-29.34	-29.84	-29.69	-28.97
	Sample 2	-30.5	-36.11	-31.94	-37.23	-30.34	-33.23
	Sample 3	-21.11	-20.47	-19.38	-20.74	-16.84	-19.71
E7 – ES-SAGD (cyclohexane + n- hexane)	Sample 1	-28.15	-27.62	-31.88	-30.42	-27.13	-29.04
E8 – ES-SAGD (n- hexane + toluene cyclic)	Sample 1	-33.81	-31.8	-31.63	-38.49	-30.37	-33.22
	Sample 2	-39.11	-37.85	-31.29	-36.73	-33.92	-35.78
	Sample 3	-6.77	-7.16	-6.54	-81.5	-3.18	-6.36
E9 - ISC	Sample 1	-4.59	-4.54	-4.52	-4.63	-5.16	-4.69
	Sample 2	-	-0.1	-0.16	-0.24	-0.25	-0.21
	Sample 3	-5.58	-3.93	-5.46	-2.88	-4.84	-4.54
Barnett	x	-10.67	-13.55	-15.06	-13.33	-13.85	-13.33
Marcellus	x	-11.73	-6.48	-11.15	-12.38	-10.06	-10.36
Eagle Ford	x	-7.18	-9.37	-10.26	-9.21	-7.23	-8.65
Green River	x	-16.64	-15.65	-14.2	-13.5	-15.21	-15.01

* (-) indicates an error in the measurement and therefore, value was not used

Table 27: Cation Chromographs for Trial 1

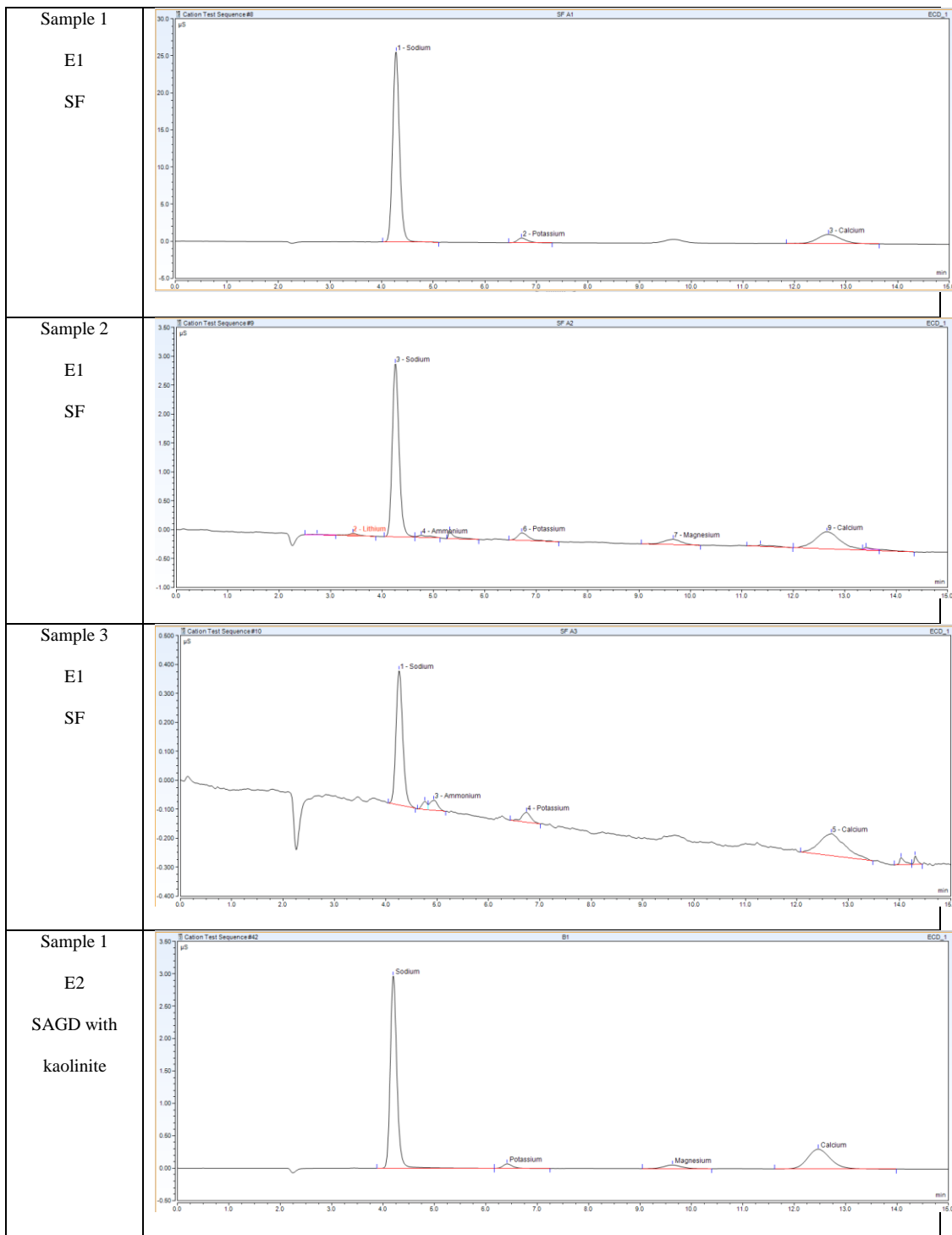


Table 27: Cation Chromatographs for Trial 1 continued

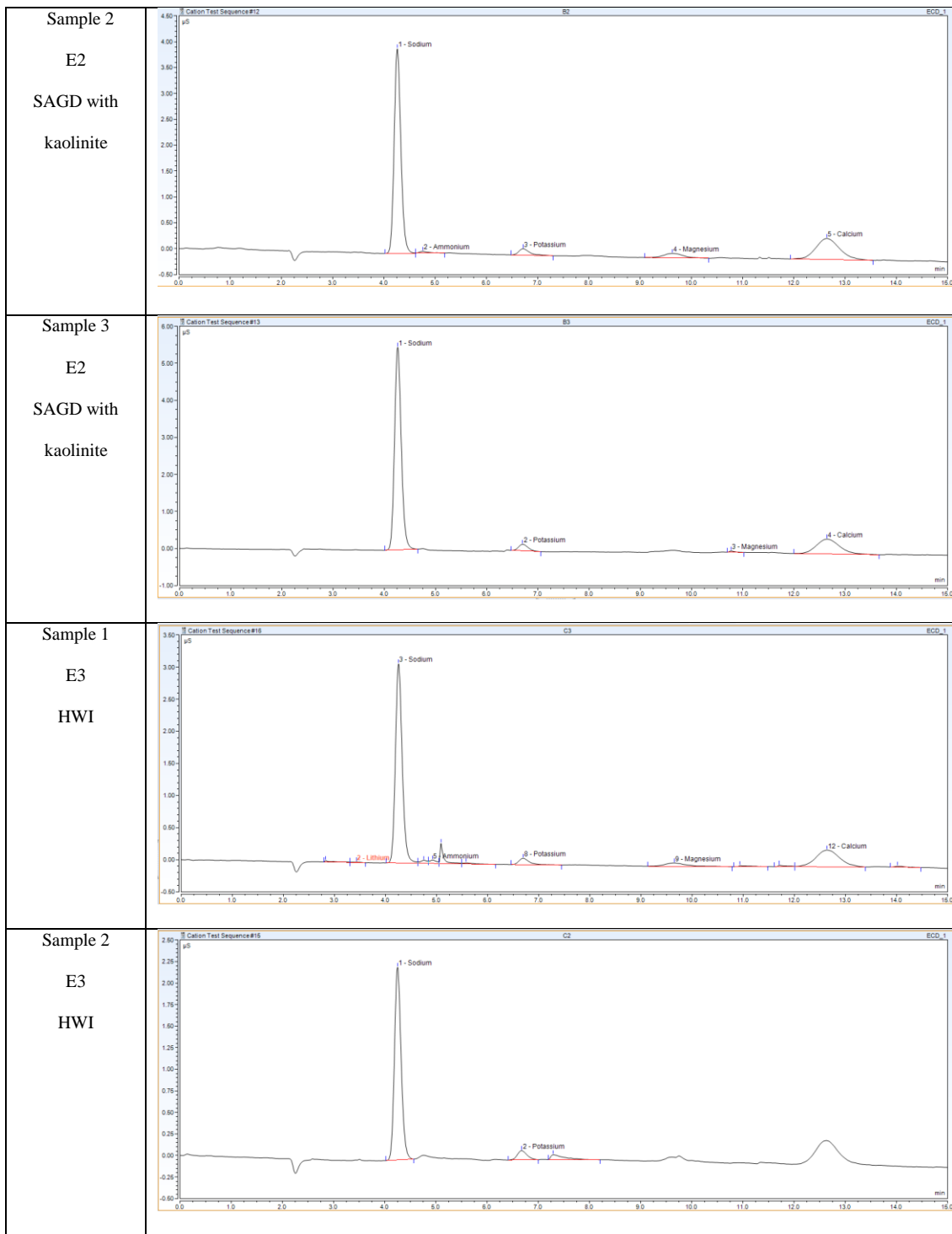


Table 27: Cation Chromatographs for Trial 1 continued

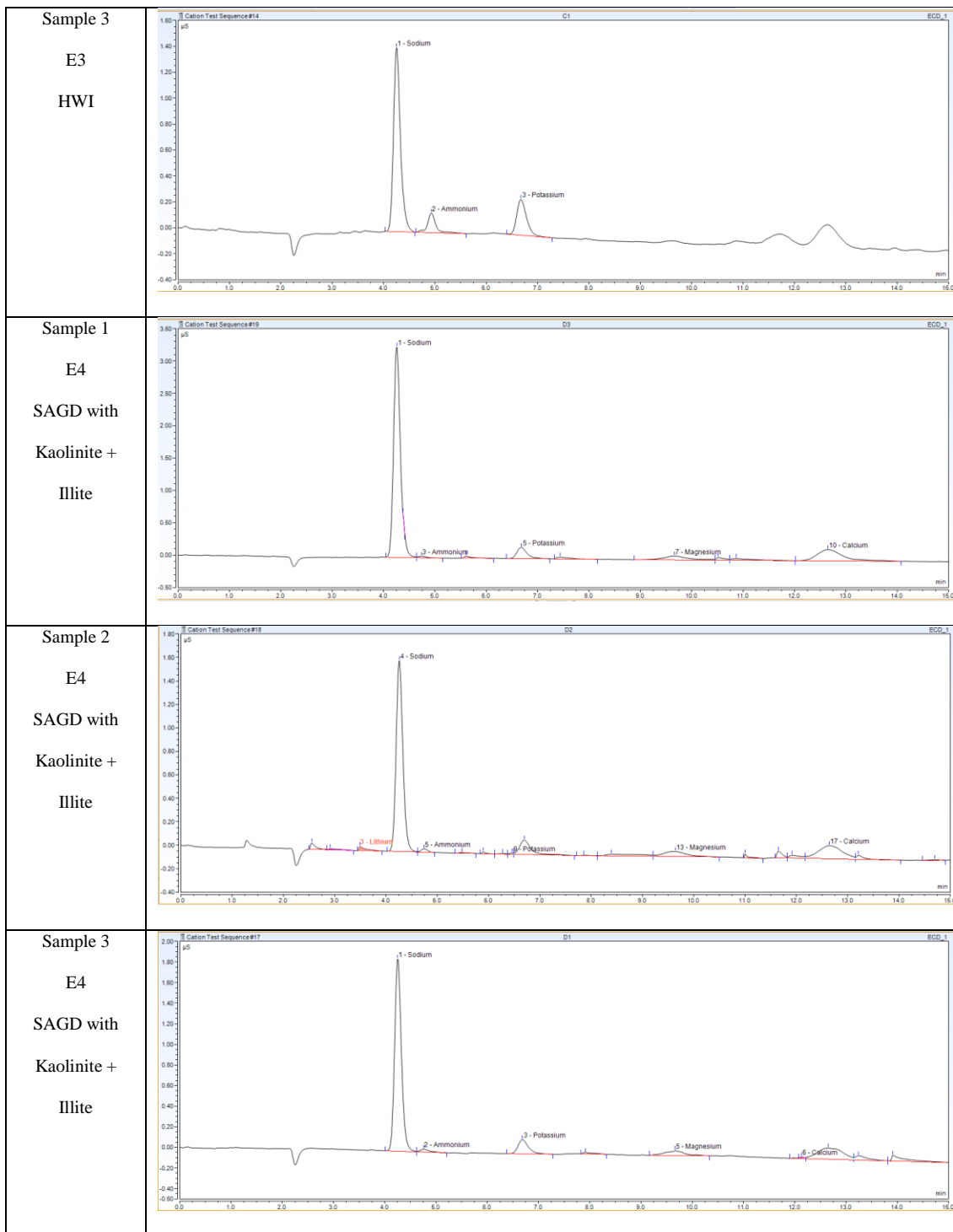


Table 27: Cation Chromatographs for Trial 1 continued

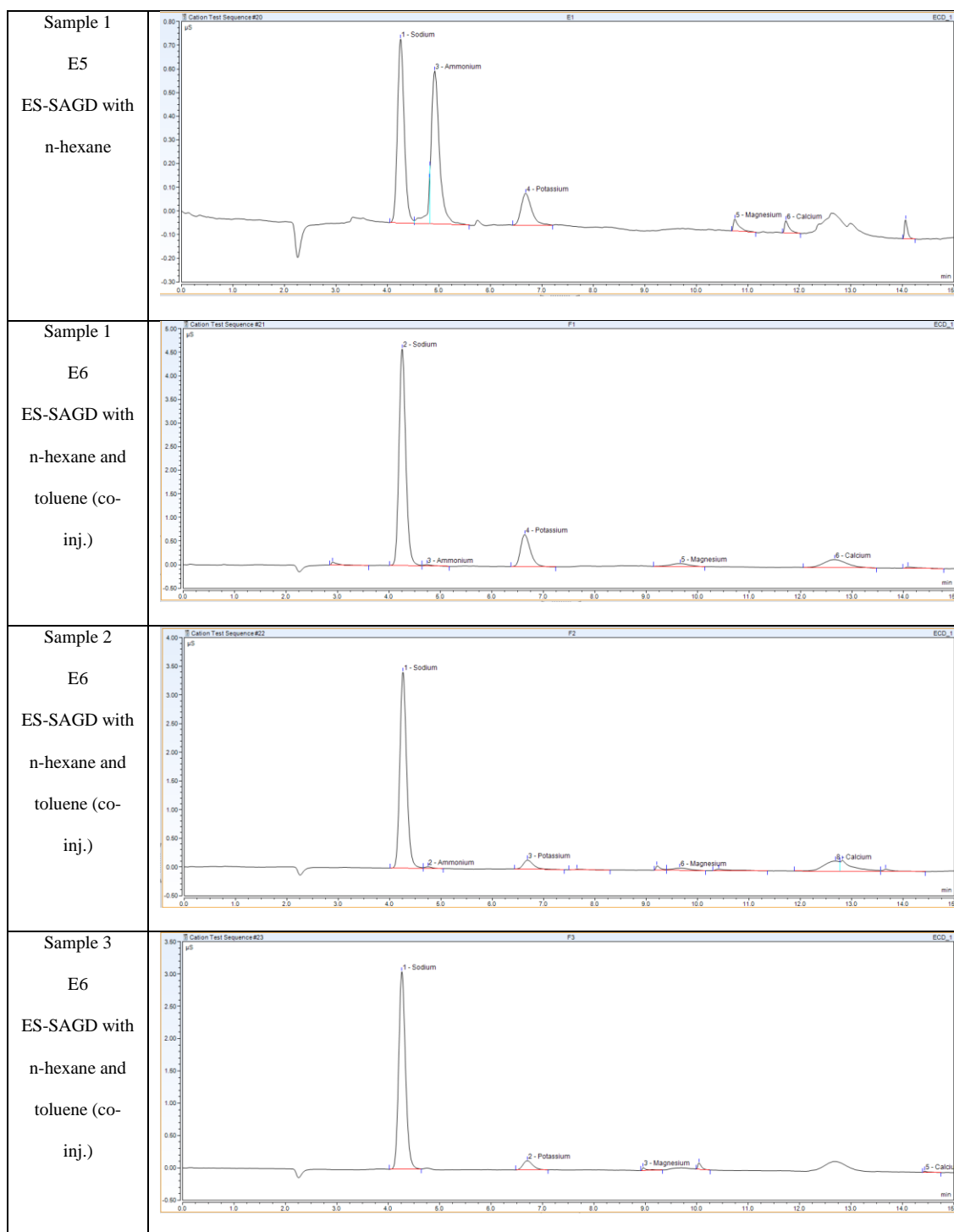


Table 27: Cation Chromographs for Trial 1 continued

<p>Sample 1 E7 ES-SAGD with cyclohexane and n-hexane</p>	
<p>Sample 1 E8 ES-SAGD with n-hexane and toluene (cyclic)</p>	
<p>Sample 2 E8 ES-SAGD with n-hexane and toluene (cyclic)</p>	
<p>Sample 3 E8 ES-SAGD with n-hexane and toluene (cyclic)</p>	

Table 27: Cation Chromographs for Trial 1 continued

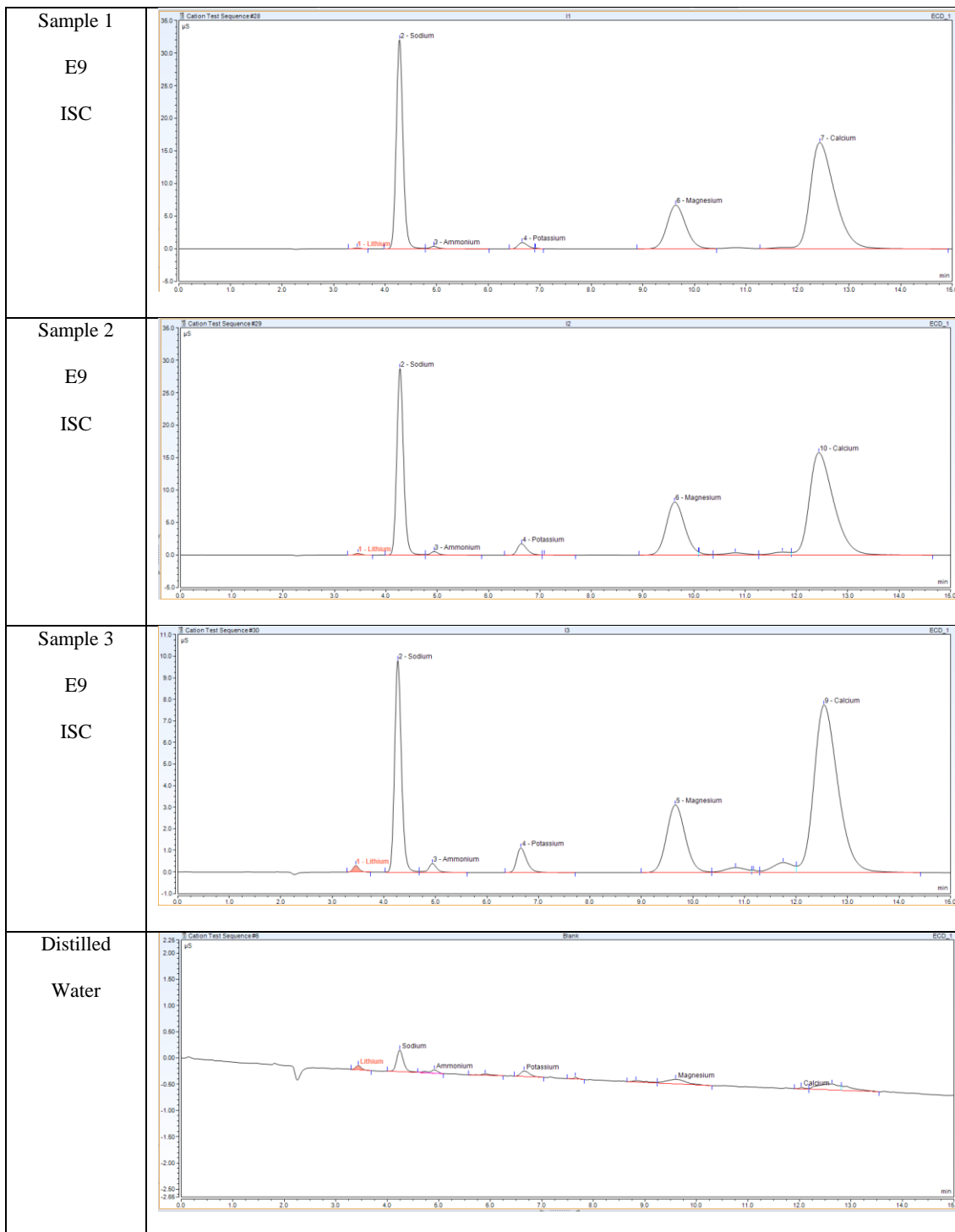


Table 27: Cation Chromographs for Trial 1 continued

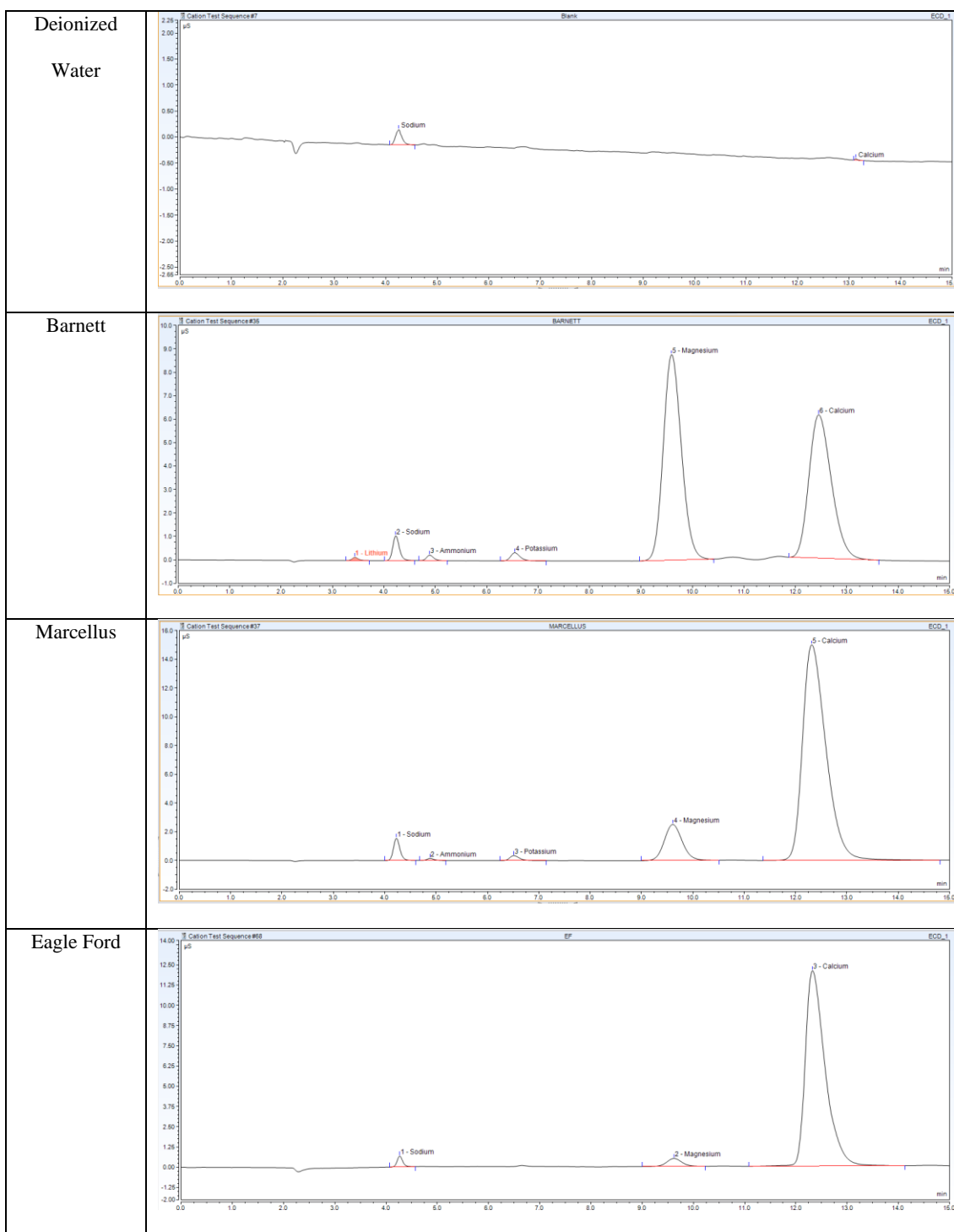


Table 27: Cation Chromographs for Trial 1 continued

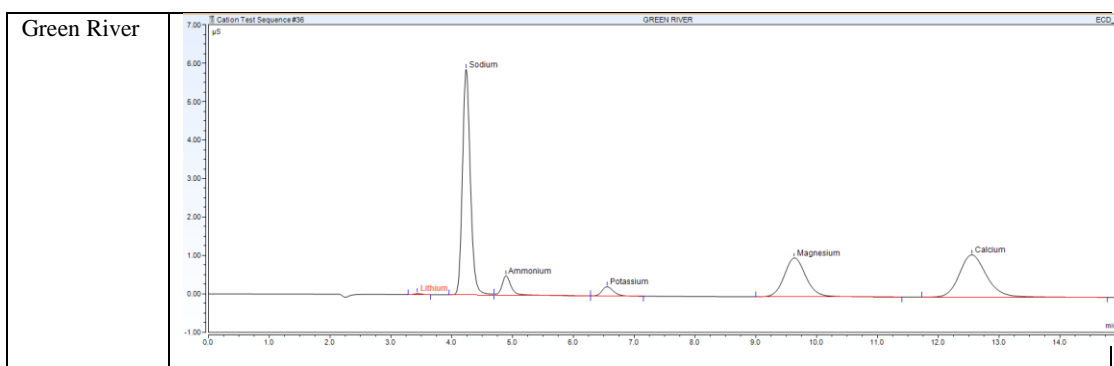


Table 28: Cation Chromographs for Trial 2

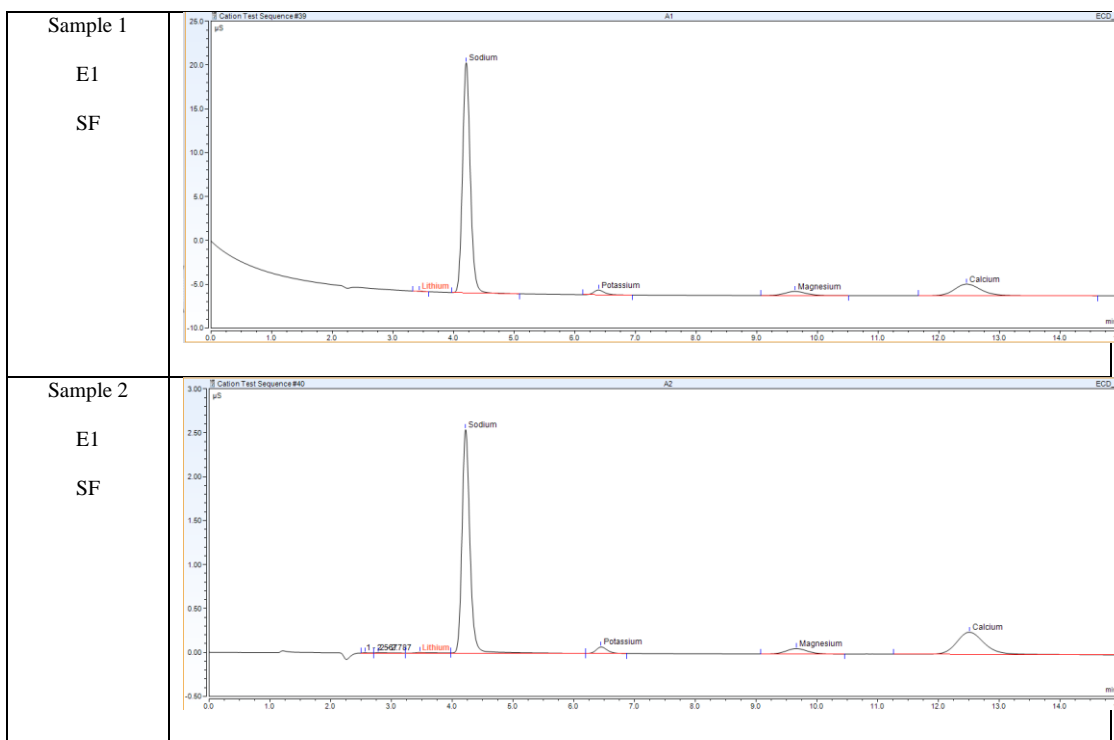


Table 28: Cation Chromatographs for Trial 2 continued

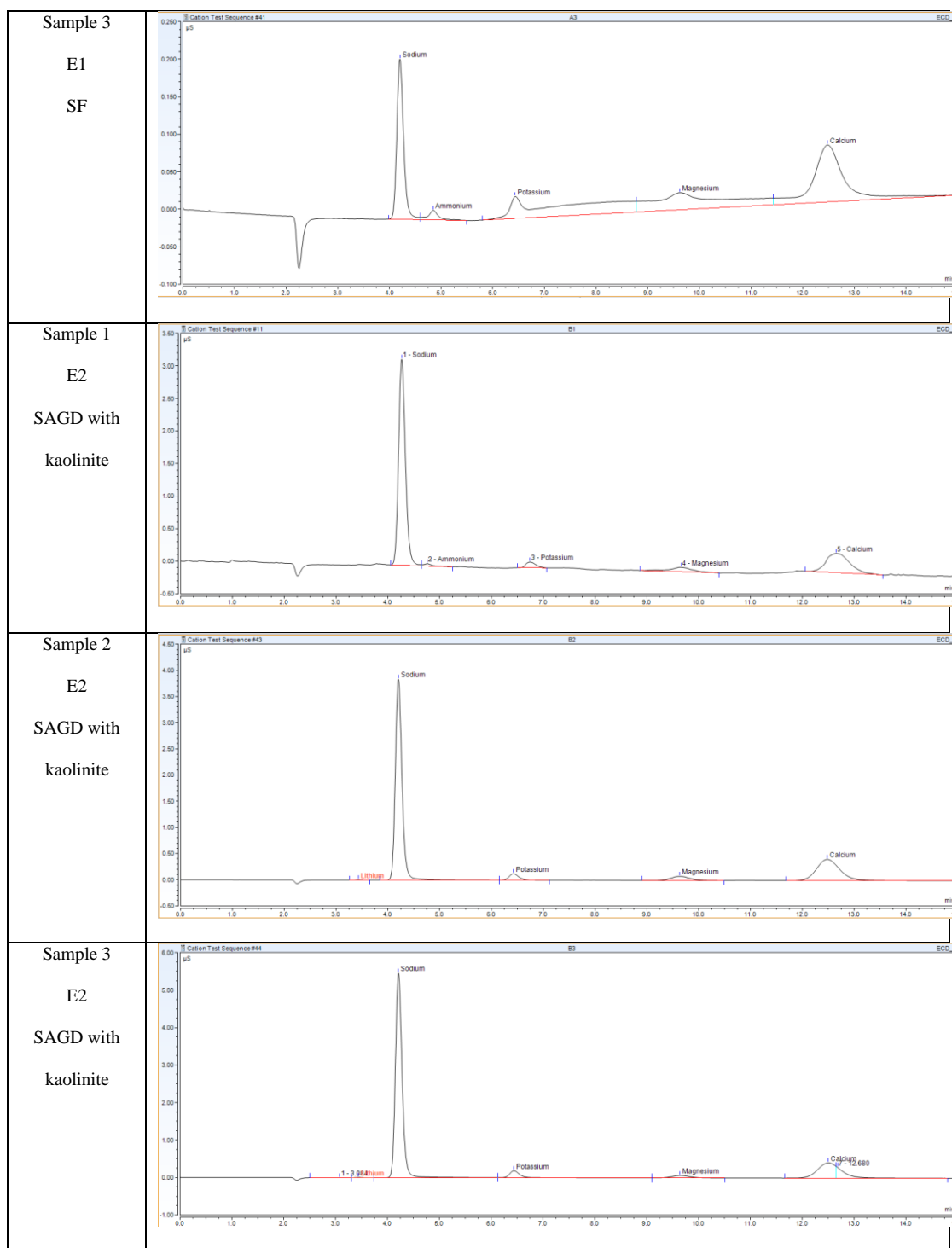


Table 28: Cation Chromatographs for Trial 2 continued

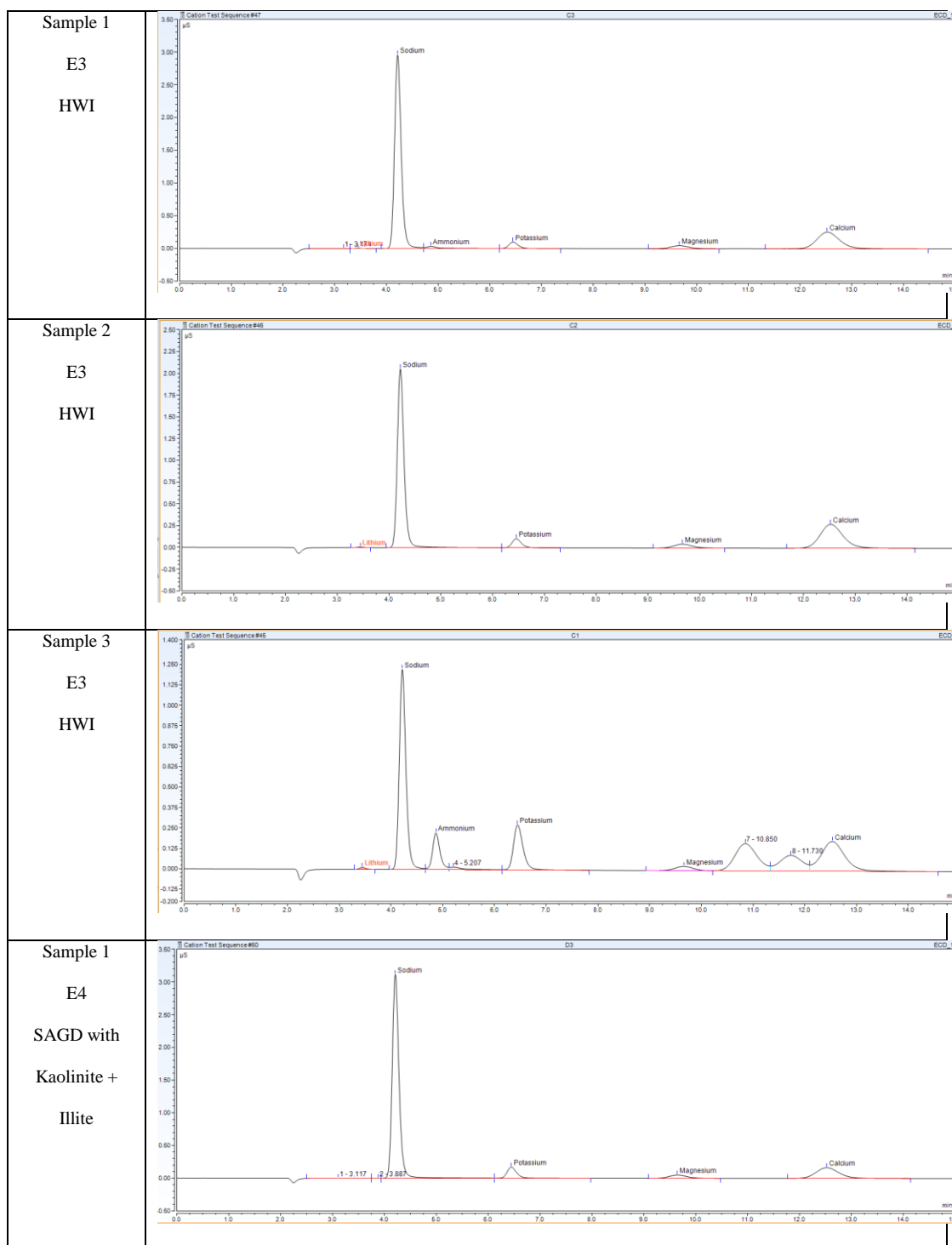


Table 28: Cation Chromatographs for Trial 2 continued

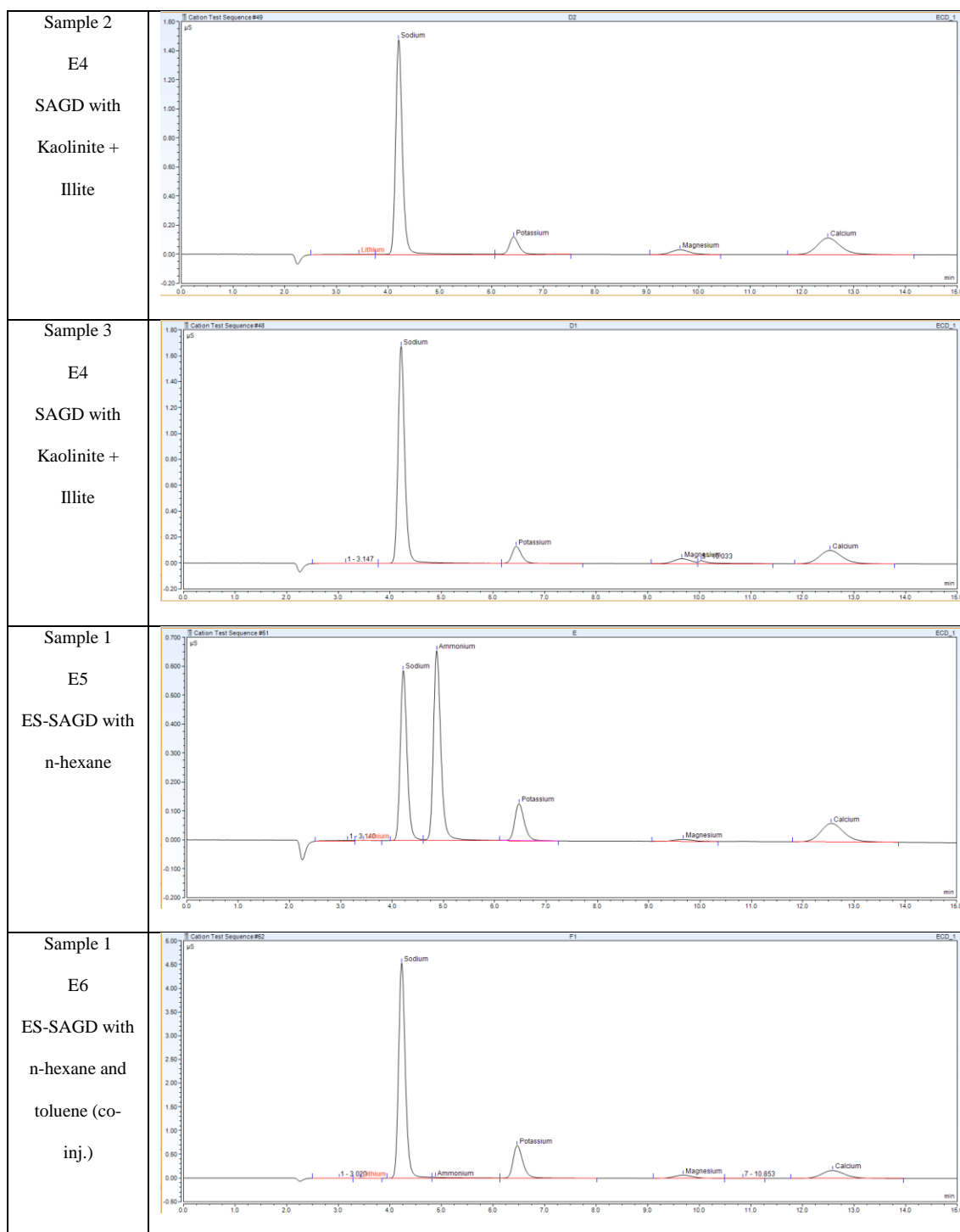


Table 28: Cation Chromatographs for Trial 2 continued

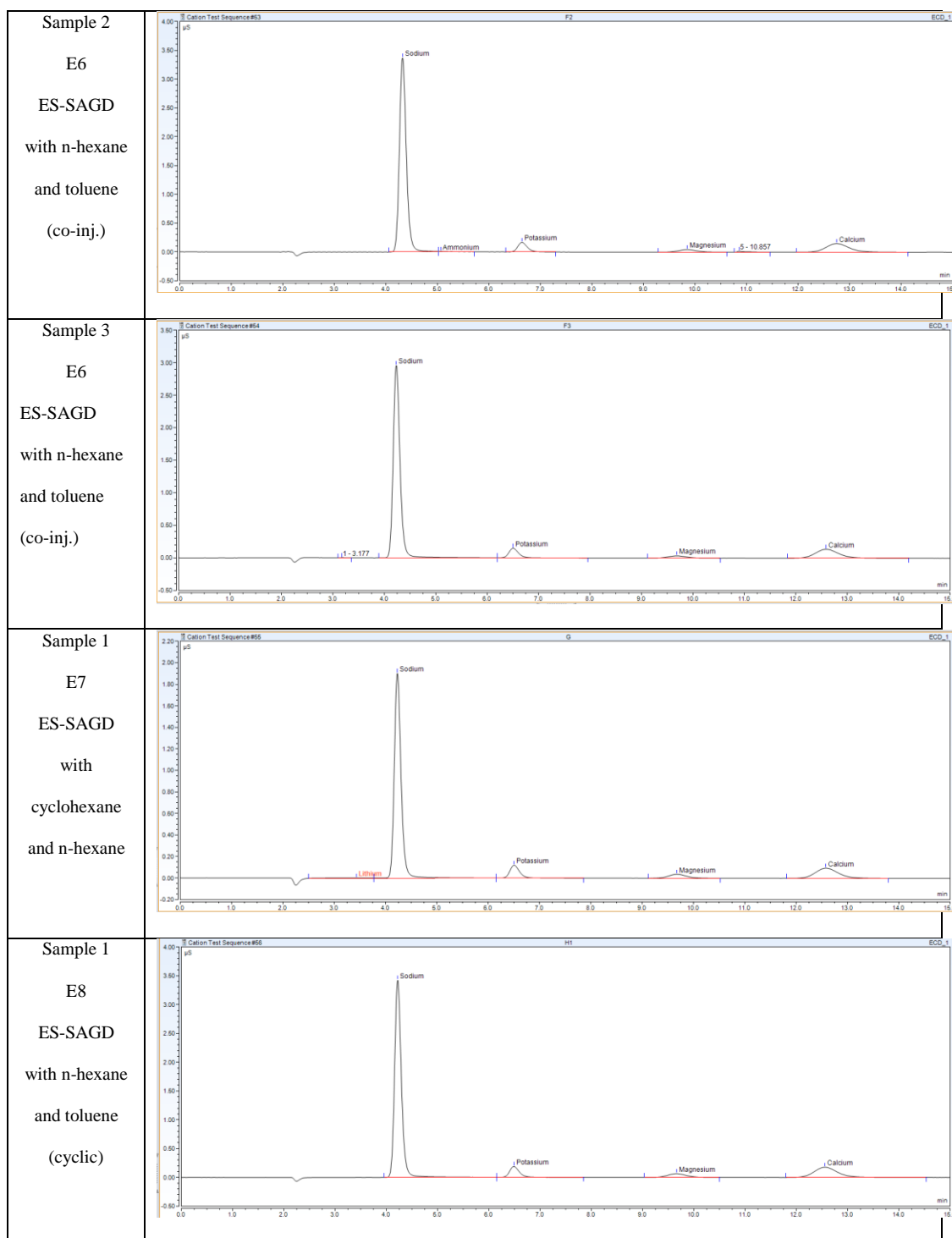


Table 28: Cation Chromatographs for Trial 2 continued

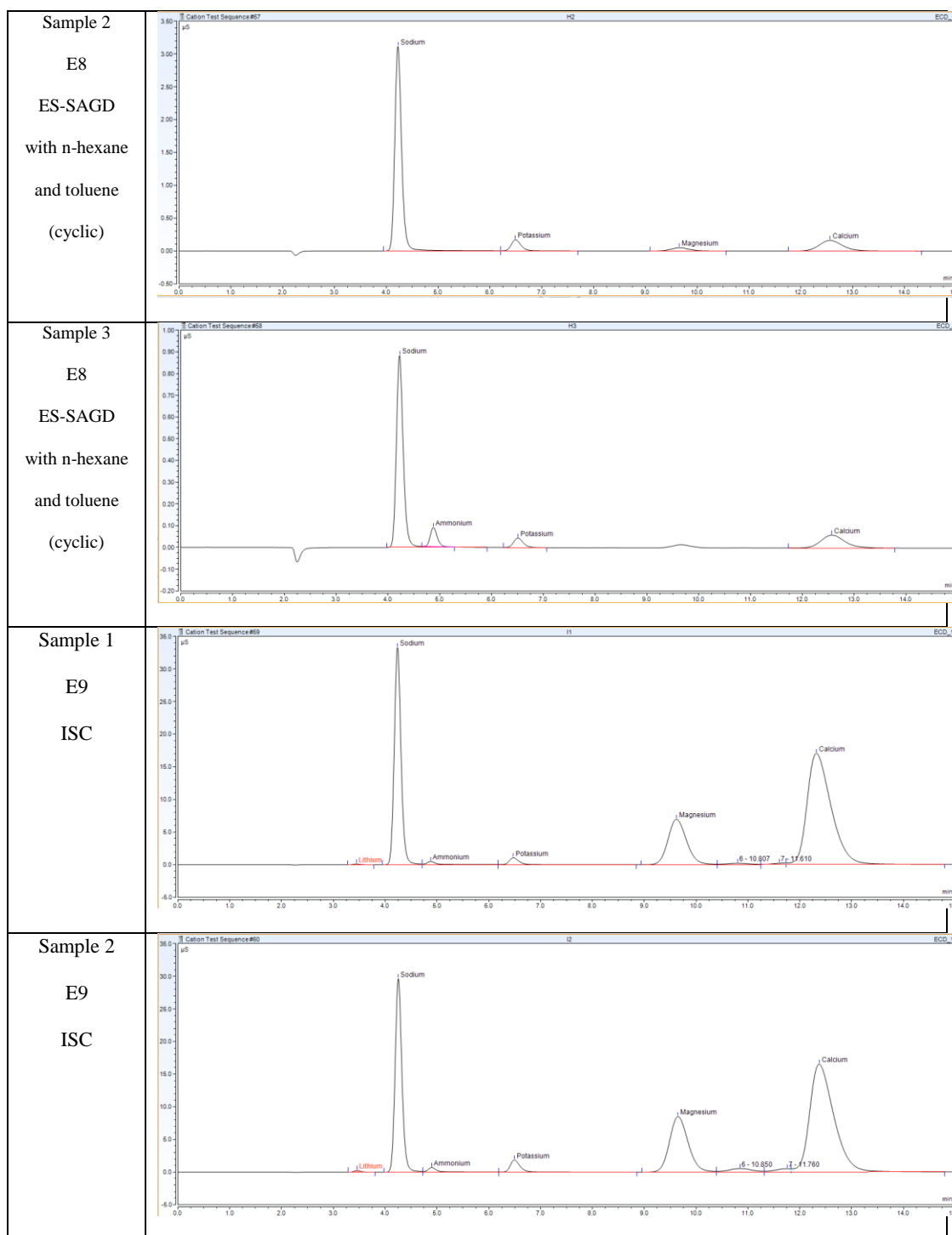


Table 28: Cation Chromatographs for Trial 2 continued

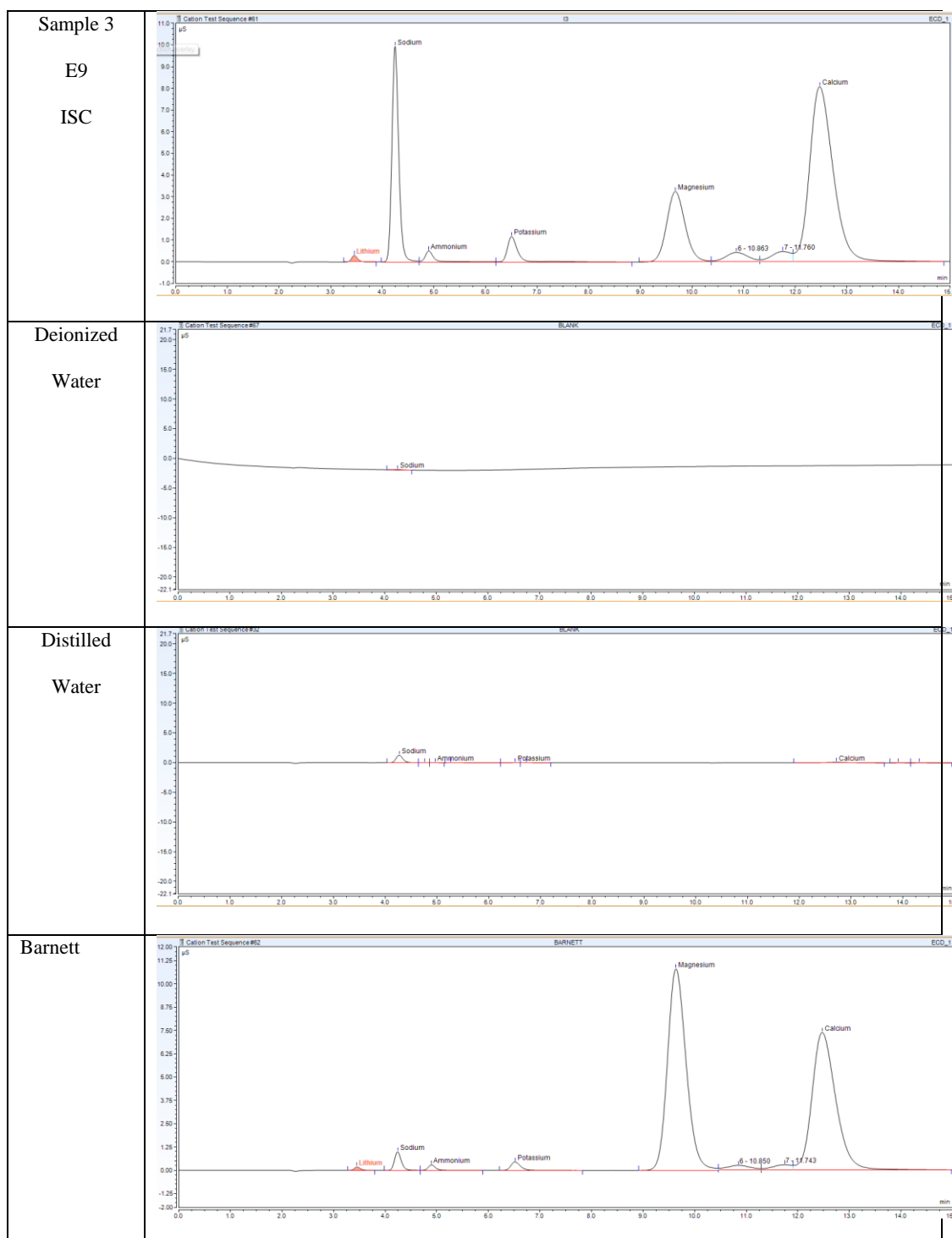


Table 28: Cation Chromatographs for Trial 2 continued

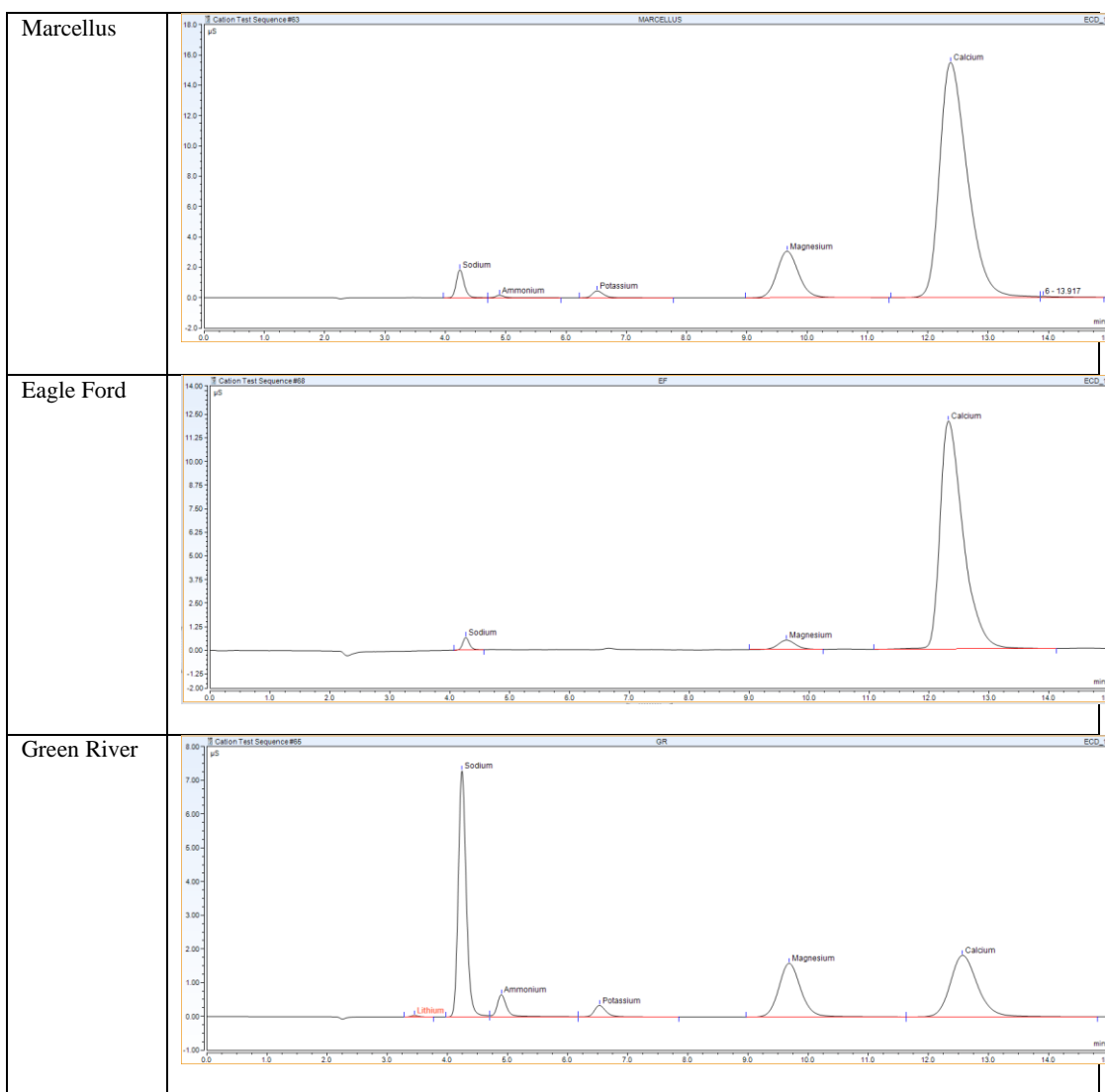


Table 29: Anion Chromatographs

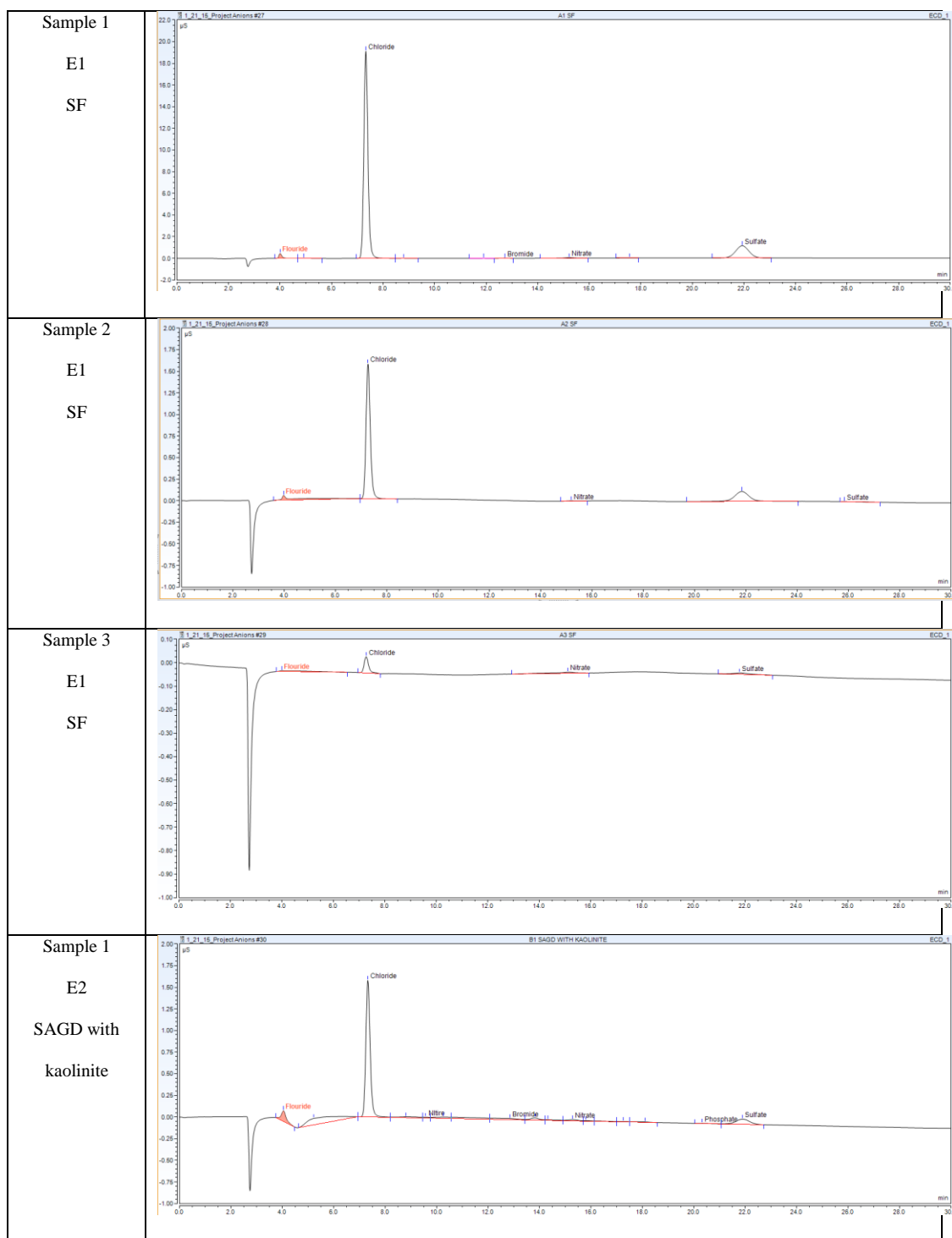


Table 29: Anion Chromatographs continued

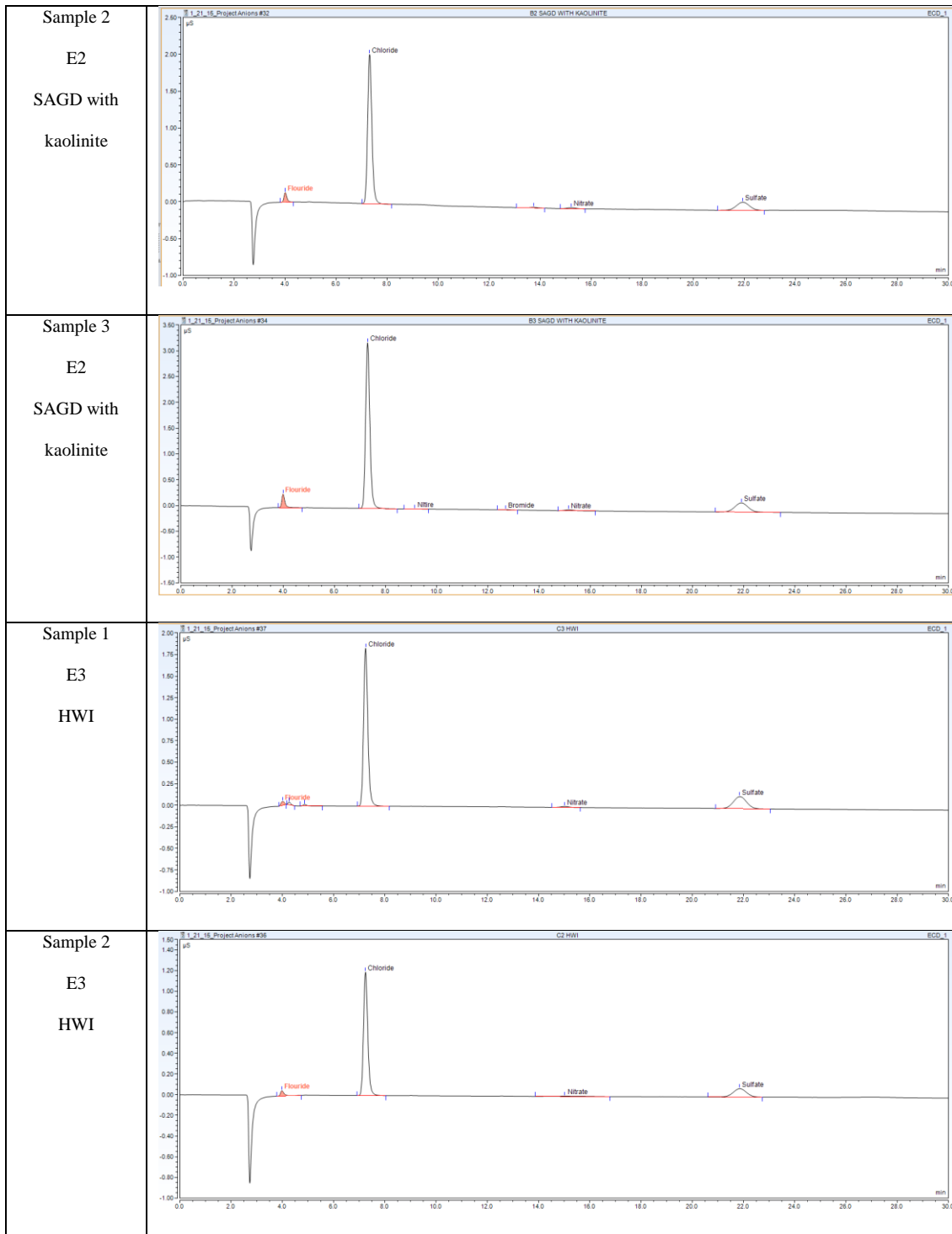


Table 29: Anion Chromatographs continued

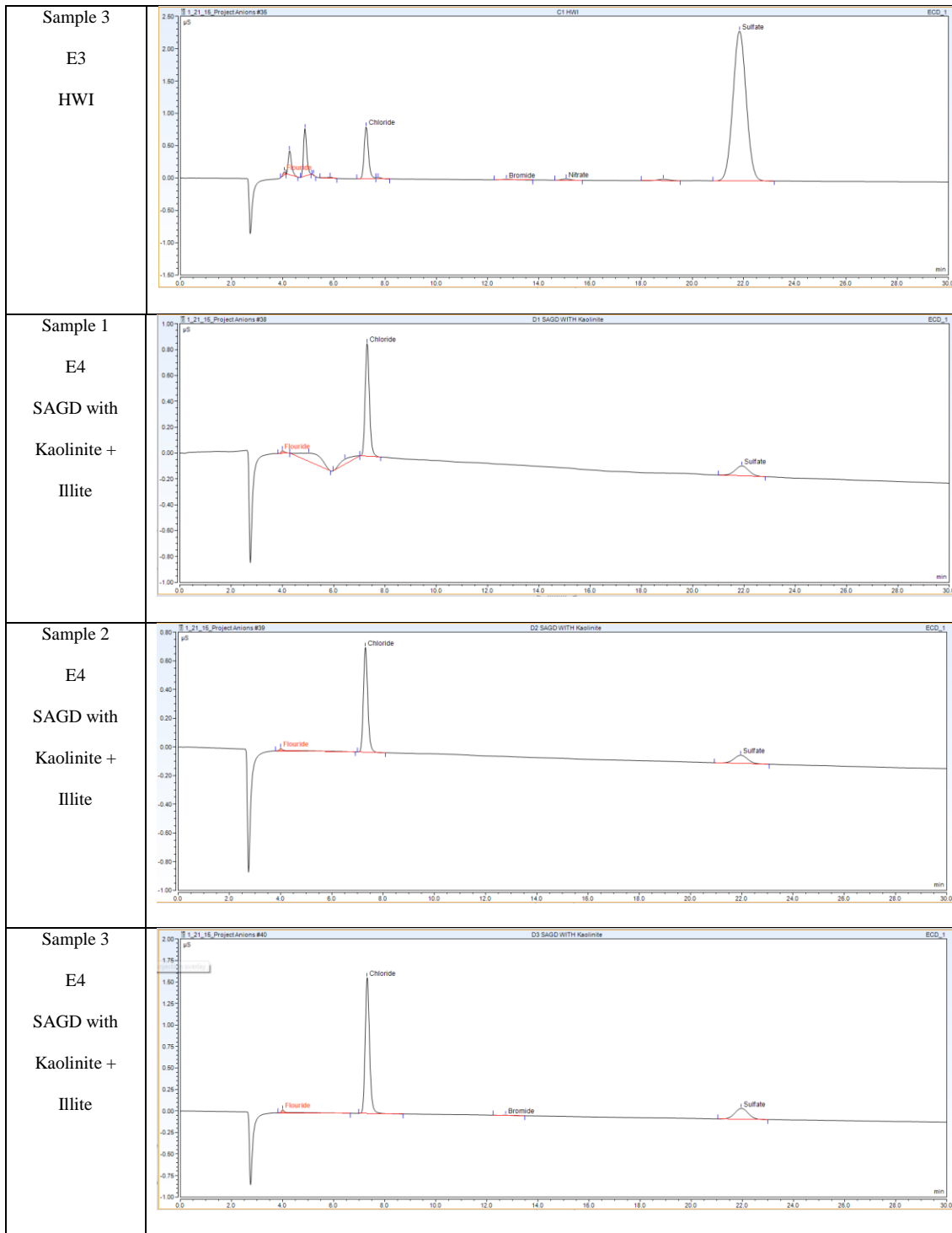


Table 29: Anion Chromatographs continued

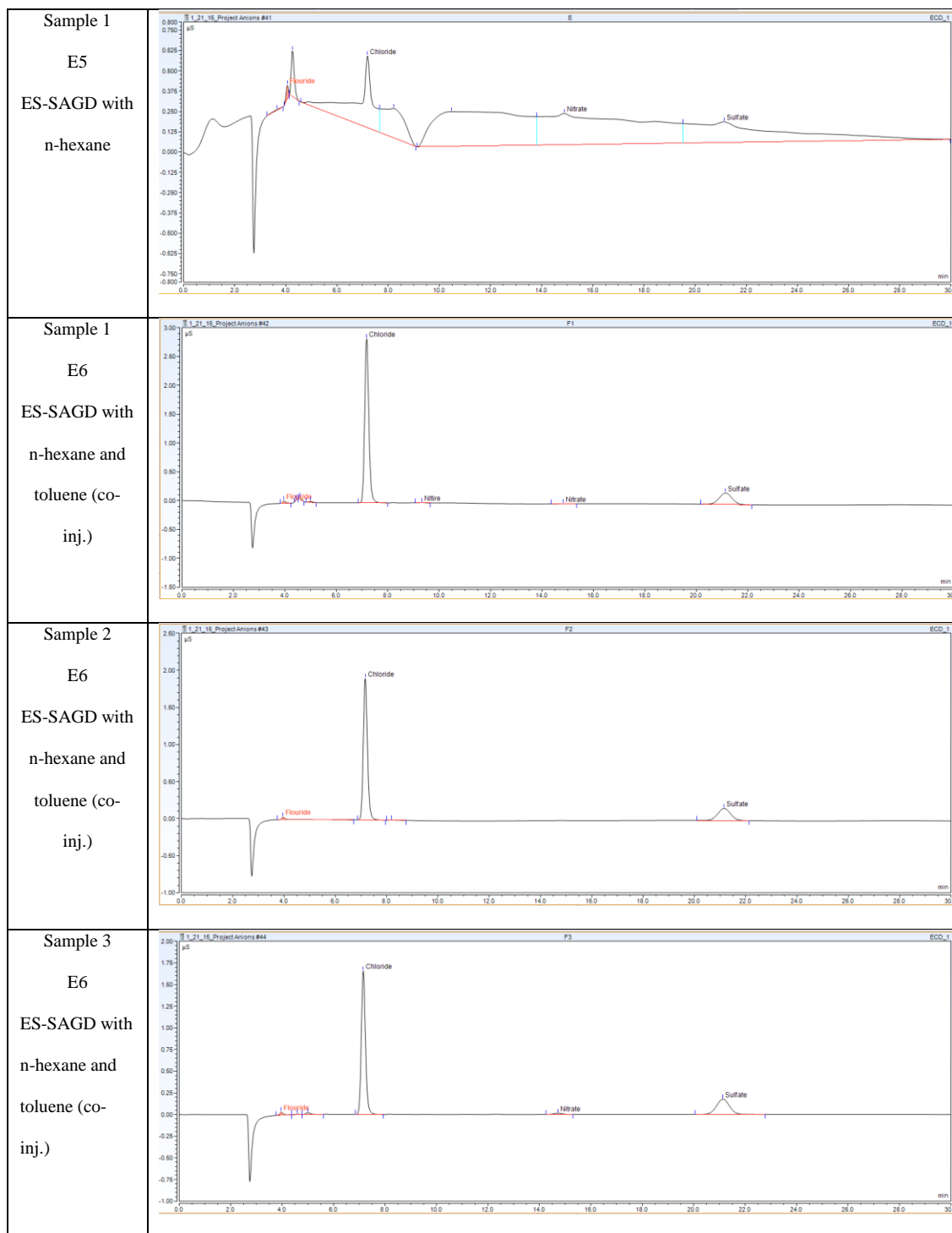


Table 29: Anion Chromatographs continued

<p>Sample 1 E7 ES-SAGD with cyclohexane and n-hexane</p>	
<p>Sample 1 E8 ES-SAGD with n-hexane and toluene (cyclic)</p>	
<p>Sample 2 E8 ES-SAGD with n-hexane and toluene (cyclic)</p>	
<p>Sample 1 E9 ISC</p>	

Table 29: Anion Chromatographs continued

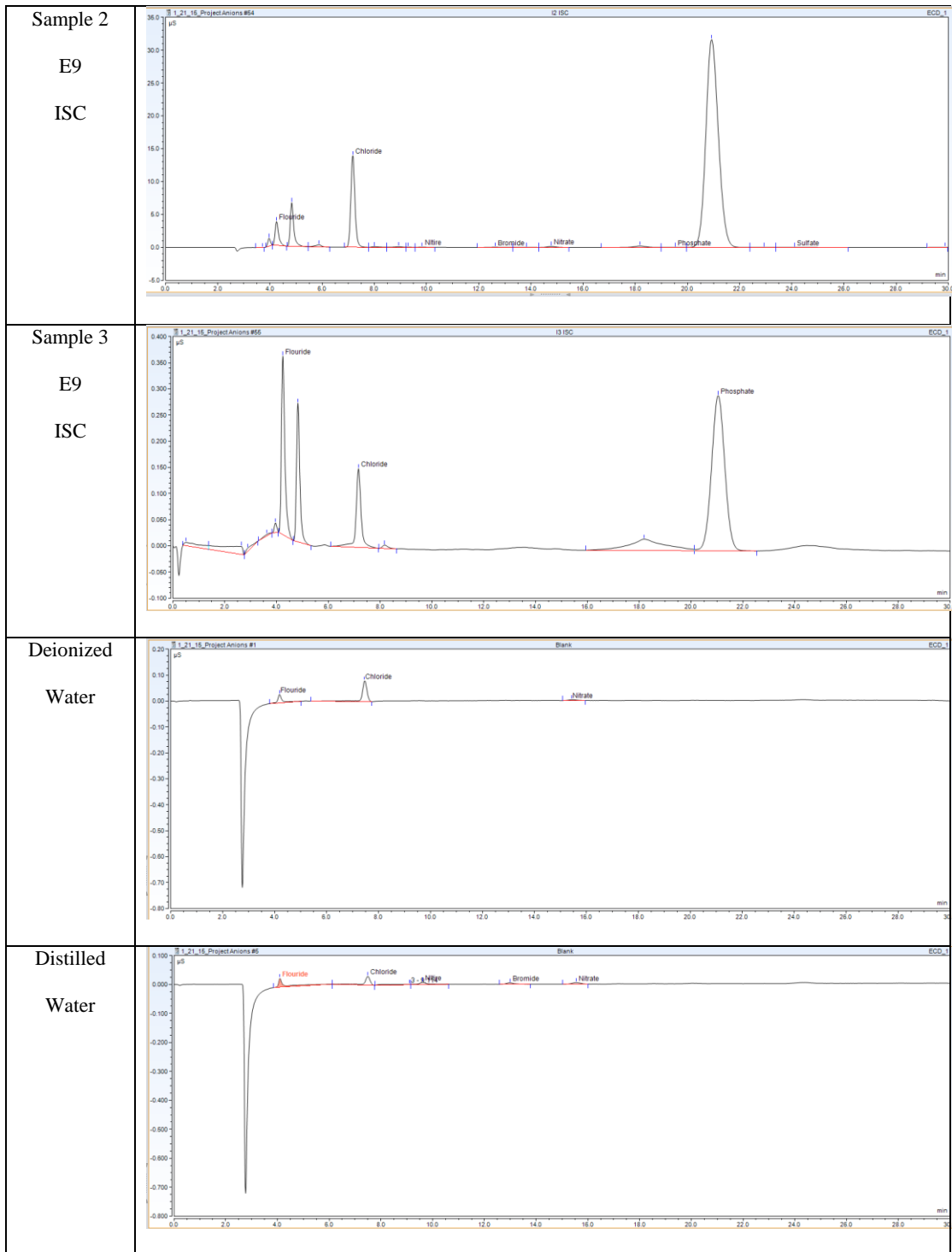


Table 29: Anion Chromatographs continued

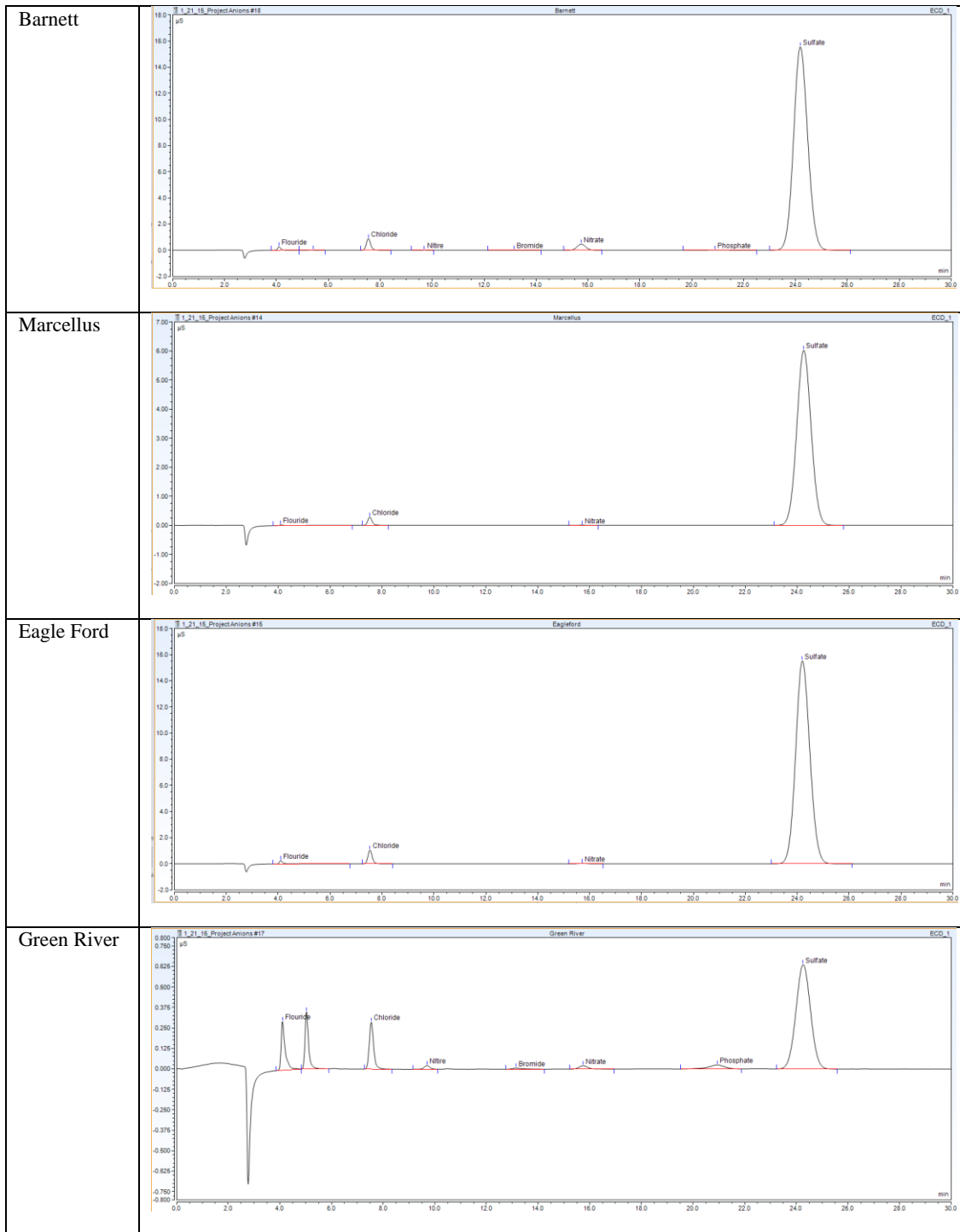


Table 30: Clay Minerals determined by XRD Analysis, wt.%

Shale Formation (Before or After Water Interaction)	Smectite	Chlorite	Kaolinite	Illite	Illite with Smectite Layers
Barnett (After)	0	4.5	5.3	32.8	14.7
Barnett (Before)	0	3.1	4.4	28.9	20.9
Eagle Ford (After)	0	0	4.7	0	0
Eagle Ford (Before)	0	0	4.8	0	0
Green River (After)	0	0	0	4.3	3.5
Green River (Before)	0	0	0	2.9	3.5
Marcellus (After)	1.2	0.3	0.2	18.7	5.4
Marcellus (Before)	1.4	0.8	0	19.4	3.8

Table 31: Other Minerals Determined by XRD Analysis Before and After Water-Rock Interaction

Shale Formation (Before or After Water Interaction)	Calcite	Dolomite	Quartz	K-Feldspar	Plagioclase	Pyrite	Apatite	Zeolites	Gypsum
Barnett (After)	0.1	0	28.8	1.1	0.9	2	9.3	0	0.5
Barnett (Before)	0	0	28.5	1.1	0.8	2.1	9.7	0	0.5
Eagle Ford (After)	65.3	2.5	21.1	0	0	1.8	1.1	0	3.5
Eagle Ford (Before)	63.4	3.6	21.7	0	0	1.9	1.5	0	2.6
Green River (After)	0.4	73.7	5.2	3.9	2.6	0	0.6	5.4	0.4
Green River (Before)	0.2	76	5	3.8	2.1	0	1	5.1	0.4
Marcellus (After)	31.8	4.5	30.1	0	1.8	4.7	1.1	0	0.2
Marcellus (Before)	31.6	4.7	30	0	1.6	5.4	1.1	0	0.2