

**The Impact of Chemical Additives and Chemical Transformations on
Water Quality in Hydraulic Fracturing**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

**Katherine Elizabeth Manz
May 2018**

Copyright © 2018 by Katherine E. Manz.
All rights reserved.

DEDICATION

This dissertation is dedicated to my family, especially my mom, dad, and brother, and to my soon-to-be-husband, whose patience, love, and understanding have encouraged me in pursuing my goals and dreams.

ACKNOWLEDGEMENTS

First, I would like to sincerely thank my advisor and mentor, Dr. Kimberly Carter, for her guidance and support. The opportunity to pursue interesting research topics and exposure to a wide range of techniques was instrumental in my scientific development.

Next, I would like to thank my committee members, Dr. Chris Cox, Dr. Qiang He, Dr. Terry Hazen, and Dr. Angel Palomino. I am very appreciative for the advice, encouragement, and insightful perspectives you have all provided me with over the past five years. I have learned so many new things from each of you, from articulate and effective communication skills to modeling reactions in software that I have never used before.

I would also like to thank the people who helped me along the way, especially the undergraduates and researchers I have collaborated with. I would especially like to thank undergraduates Jessica Lucchesi and Gregory Hearn for their help with the adsorption experiments presented in Chapter 2. I am also very grateful for the mentorship and generosity provided to me by Howard Cyr of UTK's Archaeological Research Laboratory (ARL).

Finally, I would like to thank my family and friends. I cannot express how grateful I am to my parents, Rose and Joe, and my brother, CJ, for their endless love and support in all of my endeavors. To my soon-to-be husband, Christopher, I could not have done this without your patience and understanding. There's no one else I would rather share my ups and downs with and I cannot wait to see where our adventures take us next!

ABSTRACT

The U.S. Energy Information Administration (EIA) predicts that electricity generation from natural gas will increase by 30 to 40% until 2040 [1]. Natural gas is produced via hydraulic fracturing, which does not come without environmental health and safety concerns. Many of the concerns are due to the insufficient knowledge about what hydraulic fracturing fluids contain pre-and post-fracture and how they impact water quality [2]. Consequently, knowledge gaps remain concerning how the additives transform and how they interact with the geological formations downhole. Failure to address this issue has caused the public to question whether the benefits outweigh the perceived risks as the environmental and ecosystem concerns surrounding hydraulic fracturing are still present [3].

To address these concerns, this research investigates the interactions and transformations of chemical additives used in hydraulic fracturing with one another and with shale rock. Specifically, the adsorption of a surfactant-like chemical, 2-butoxyethanol (2-BE), found in the chemical additive Revert Flow, and a non-surfactant chemical, 3-furaldehyde, found in enzyme breaker additives, will be monitored in shale rock and with granular activated carbon to assess the potential for chemical migration through geological formations. This dissertation will also investigate the reactions between 2-BE, shale rock, and chemical additives, including sodium persulfate and hydrochloric acid. In turn, the changes in shale properties, including particle size and heavy metal leaching, due to contact with chemical additives will be assessed. The organic byproducts produced or metals precipitated in each set of reactions will be used to determine how hydraulic fracturing fluids transform water quality.

Hydraulic fracturing transformations must be understood to evaluate how hydraulic fracturing fluids impact water quality. A better understanding of how chemicals interact under hydraulic fracturing conditions will increase awareness and knowledge of what the waste fluids contain, aid in developing environmental policies that protect the ecosystems surrounding a well, and facilitate spill preparedness to mitigate hydraulic fracturing pollution based on the information in this study.

TABLE OF CONTENTS

Chapter 1 Introduction.....	1
Introduction.....	2
Background	4
Chemical usage in hydraulic fracturing	4
Problems surrounding water and chemical usage.....	6
Chapter 2 Adsorption of hydraulic fracturing fluid components 2-butoxyethanol and furfural onto granular activated carbon and shale rock.....	9
Abstract	10
Introduction.....	10
Materials and Methods	11
Chemicals and Materials.....	11
Shale Rock and Solids TOC	11
Experimental Procedure.....	12
2-BE Concentrations	12
Furfural Concentrations.....	13
Results and Discussion	13
Adsorption of 2-BE and furfural onto shale rock.....	13
2-BE and furfural adsorption onto GAC in separate reaction vessels	15
Competitive adsorption of 2-BE and furfural onto GAC	26
Conclusion.....	34
Chapter 3 Degradation of Hydraulic Fracturing Additive 2-Butoxyethanol Using Heat Activated Persulfate in the Presence of Shale Rock	35
Abstract	36
Introduction.....	36
Materials and Methods	38
Chemicals	38
Shale Rock.....	38
Batch Oxidation Experiments.....	38
Sample Analysis.....	41
Statistics.....	42
Results and Discussion	42
Temperature Effects.....	42
pH Effects	55
Iron (II) and Shale Effects	55
Conclusion.....	68
Chapter 4 Characterization of Shale Particulates and Resulting Changes in Wastewater Quality due to Interaction with Hydraulic Fracturing Additives.....	69
Abstract	70
Introduction.....	70
Materials and Methods	71
Shale rock	71
Chemicals	74
Chemical additive solutions.....	74
Experimental procedure	74

Particle size, shape, and porosity analysis.....	74
Inorganic metal identification in liquid samples	75
Liquid samples pH and persulfate measurements	75
Statistical analysis.....	76
Results and Discussion	76
Impacts on shale particle physical and chemical properties.....	76
Mixing Speed Optimization for PSA Measurements.....	76
Particle size changes in the treated shale	78
Impact on shale minerology	82
Shale topology and mineral distribution	82
Impacts on water quality	87
Solution pH	87
Aqueous inorganic geochemistry	89
Time dependence of inorganic treatments	89
Conclusion.....	92
Chapter 5 Conclusion.....	99
References.....	101
Appendix	112
Vita.....	123

LIST OF TABLES

Table 2-1. Freundlich and Langmuir Isotherm Parameters for furfural and 2-BE at indicated temperatures and sodium chloride concentrations.	21
Table 2-2. Redlich-Peterson constants for the adsorption furfural and 2-BE onto GAC at 20, 35, 45, 55, and 65 °C with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride.	25
Table 2-3. Isosteric heats of adsorption for 2-BE and furfural with 0, 0.001, 0.1 mol L ⁻¹ of sodium chloride.	29
Table 2-4. Langmuir and Freundlich isotherm parameters for experiments containing both furfural and 2-BE at 20 and 65°C and 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride.	33
Table 3-1. WV7 Shale Minerology.....	40
Table 3-2. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at 20, 35, 45, 55, and 65°C with 21 mmol L ⁻¹ sodium persulfate (initial pH 6).	51
Table 3-3. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at varying initial pHs (55°C , 21 mmol L ⁻¹ sodium persulfate).	57
Table 3-4. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at varying Fe(II) concentrations (55°C , 21 mmol L ⁻¹ sodium persulfate, initial pH 6).	60
Table 3-5. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at varying Fe(II) concentrations (55°C , 21 mmol L ⁻¹ sodium persulfate, initial pH 6).	63
Table 4-1. Minerology of Untreated WV6 shale determined using XRD and verified with ICP using shale digestion.....	73
Table 4-2. Average D-10, 30, and 60 particle sizes measured at 2800 rpm on the PSA (n=3).....	80
Table 4-3. Minerology of treated shales in comparison to untreated particles measured using XRD patterns displayed in Figure 4-5 and Figure 4-6.....	83

LIST OF FIGURES

Figure 1-1. (a) Gas chromatogram of 2-BE containing hydraulic fracturing chemical additive, Revert Flow. 2-BE has a retention time of 8.748 minutes. (b) Mass spectrum of 2-BE in Revert Flow. Figure adapted from Manz and Carter, 2016 [41].	5
Figure 2-1. Furfural and 2-BE adsorption onto shale rock. Conditions: a) furfural, 20°C, b) furfural, 65°C, c) 2-BE, 20°C, and d) 2BE, 65°C.	14
Figure 2-2. Decreasing a) furfural and b) 2-BE concentrations due to adsorption onto GAC are shown for water, 0.1 mol L ⁻¹ sodium chloride, and synthetic hydraulic fracturing brine. The data was taken over the course of 511 h (21.3 days). The dashed line in b) represents the 2-BE half-life and shows that this decrease in concentration was due to 2-BE decay [41]. Furfural and 2-BE adsorption occurred within 24 h.	16
Figure 2-3. Percent removal of Furfural and 2-BE with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride in solution. The reaction conditions are a) furfural, 20°C, b) furfural, 65°C, c) 2-BE, 20°C, and d) 2-BE, 65°C.	17
Figure 2-4. Percent removal of 2-BE and furfural by GAC for 35, 45, and 55°C at different concentrations of sodium chloride.	18
Figure 2-5. Langmuir isotherm for furfural at a) 20 and b) 65°C and 2-BE at c) 20 and d) 65°C with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride.	20
Figure 2-6. Freundlich isotherms for furfural and 2-BE at 20 and 65°C with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride.	22
Figure 2-7. Linearized Redlich-Peterson isotherm for furfural and 2-BE at all temperatures tested (20, 35, 45, 55, and 65°C) with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride. Furfural data is displayed in parts a, b, and c, with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride, respectively. 2-BE data is displayed in parts d, e, and f, with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride, respectively.	24
Figure 2-8. Van't Hoff plot for furfural at a) 0 mol L ⁻¹ sodium chloride, b) 0.001 mol L ⁻¹ sodium chloride, and c) 0.1 mol L ⁻¹ sodium chloride.	27
Figure 2-9. Van't Hoff plot for 2-BE at a) 0 mol L ⁻¹ NaCl, b) 0.001 mol L ⁻¹ NaCl, and c) 0.1 mol L ⁻¹ NaCl.	28
Figure 2-10. Percent recoveries of experiments with both furfural and 2-BE in solution at 0, 0.001 0.1 mol L ⁻¹ sodium chloride. The conditions in each experiment are: a) furfural, 20°C, b) furfural, 65°C, c) 2-BE, 20°C, and d) 2-BE, 65°C.	30
Figure 2-11. Langmuir isotherms for competitive adsorption experiments with both furfural and 2-BE in solution at 20 and 65°C with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride in solution.	31
Figure 2-12. Freundlich isotherms for competitive adsorption experiments with both furfural and 2-BE in solution at 20 in (a) and (c) and 65°C in (b) and (d) with 0, 0.001, and 0.1 mol L ⁻¹ sodium chloride in solution.	32
Figure 3-1. Percent composition of elements detected in acid digestion and ICP analysis of unreacted WV7 shale.	39
Figure 3-2. Control experiments containing 2-BE in water at 20°C (no persulfate, initial pH 6). The concentration of 2-BE does not decrease over 375 hours.	43
Figure 3-3. Degradation of 2-BE at 20°C with 21 mmol L ⁻¹ persulfate (initial pH 6).	44

Figure 3-4. Decrease in (a) TOC, (b) pH, and (c) persulfate over the course of 2-BE degradation at 20°C with and initial dose of 21 mmol L ⁻¹ persulfate (initial pH 6)...	45
Figure 3-5. 2-BE concentration profile as temperature increases shown in (a) and pseudo-first-order natural log plot versus time in (b) (initial sodium persulfate dose 21 mmol L ⁻¹ , initial pH 6).	47
Figure 3-6. Decrease in (a) TOC, (b) pH, and (c) persulfate over the course of 2-BE degradation at 20, 35, 45, 55, and 65°C with and initial dose of 21 mmol L ⁻¹ persulfate (initial pH 6).	48
Figure 3-7. Full time scale of the decrease in (a) 2-BE, (b) persulfate, (c) pH, and (d) TOC over the course of 2-BE degradation at 35°C with and initial dose of 21 mmol L ⁻¹ persulfate (initial pH 6).	49
Figure 3-8. Full time scale of the decrease in (a) 2-BE, (b) persulfate, (c) pH, and (d) TOC over the course of 2-BE degradation at 45°C with and initial dose of 21 mmol L ⁻¹ persulfate (initial pH 6).	50
Figure 3-9. Arrhenius plots for 2-BE oxidation by 21 mmol L ⁻¹ persulfate (initial pH 6).	52
Figure 3-10. Decrease in persulfate concentration at 55°C with and without 2-BE in solution initial dose of 21 mmol L ⁻¹ persulfate, initial pH 6.	53
Figure 3-11. Mass spectra of butyric acid detected in experiment at 55°C containing 2-BE and 21 mmol L ⁻¹ persulfate, initial pH 6. Butyric acid was the only byproduct detected.	54
Figure 3-12. Degradation of 2-BE in solutions with varying pH (55°C, initial dose of 21 mmol L ⁻¹ persulfate). Initial pHs are 2, 6, and 11.	56
Figure 3-13. Decrease in TOC, pH, and persulfate concentration during 2-BE degradation in solutions with varying initial pH (55°C, initial dose of 21 mmol L ⁻¹ persulfate). Initial pHs are 2, 6, and 11.	58
Figure 3-14. Degradation of 2-BE in solutions with (a) Fe(II) and (b) shale rock (55°C, initial dose of 21 mmol L ⁻¹ persulfate, initial pH 2, initial 2-BE concentration 120 mg L ⁻¹). Legends indicate the mg L ⁻¹ concentration of Fe (II). Data below the limit of detection (0.957 mg L ⁻¹ 2-BE) were not used to calculate the rate constants reported in the text. Error bars represent standard error.	59
Figure 3-15. Decrease in TOC, pH, and persulfate concentration during 2-BE degradation in solutions with varying Fe(II) concentration (55°C, initial dose of 21 mmol L ⁻¹ persulfate, initial pH 2). Legend indicates the mg L ⁻¹ concentration Fe(II).	61
Figure 3-16. Decrease in TOC, pH, and persulfate concentration during 2-BE degradation in solutions with varying shale concentration (55°C, initial dose of 21 mmol L ⁻¹ persulfate, initial pH 2). Legend indicates the mg L ⁻¹ concentration Fe(II).	64
Figure 3-17. Unreacted WV7 shale rock SEM image.	65
Figure 3-18. XRD pattern of unreacted (bottom) and reacted (top) shale (55°C, initial dose of 21 mmol L ⁻¹ persulfate, initial pH 2, initial 2-BE concentration 120 mg L ⁻¹). Reacted shale was collected after the entire experiment was completed and filtered out of solution. The y-axis has been modified by taking log of intensity and stacking the plots in order to make the graphic clearer. Vertical lines show where minerals are depleted in the diffractogram of the reacted shale in comparison to the	

unreacted shale. Calcite and dolomite were the two minerals determined to be depleted from the shale.....	66
Figure 3-19. Dissolution of (a) major, (b) minor, and (c) trace metals from the shale rock over the course of 2-BE degradation activated by 21 mmol L ⁻¹ persulfate (initial pH 2).....	67
Figure 4-1. Metals detected in supernatant of untreated shale digestion using digestion and ICP. Results were used to verify XRD data. The major ion detected was Si, which comes from the major mineral quartz. The element with the second highest concentration was Fe, which comes from the pyrite in the shale. The third most concentrated element, Ca, in the shale could have come from several different minerals, including calcite, dolomite, gypsum, and lavendulan.	72
Figure 4-2. D ₁₀ , D ₃₀ , and D ₆₀ particle size measurements of dry, untreated shale at different mixing speeds in the PSA (n=5). Mixing speed was increased and decreased at regular intervals from 2500 to 2800, 3000, 3200, and 3500, then back down to 3200, 3000, 2800, and 2500-rpm.	77
Figure 4-3. D ₁₀ , D ₃₀ , and D ₆₀ particle size measurements of treated shales, including water, 0.07% HCl, 21 mmol L ⁻¹ persulfate, combined acid and persulfate, and the organic additives compared to untreated shale (n=3). Measurements were taken using the PSA.	79
Figure 4-4. Background particle size provided by WGA on the PSA. WGA is a cellulosic solid material that provides a background on the PSA size distribution measurements.	81
Figure 4-5. Diffraction pattern of inorganic treated shale particles in comparison to untreated shale particles obtained using XRD. Plots are log scale and the y-axis has been adjusted for ease of comparison. Hydrochloric acid depleted calcite, dolomite, gypsum, lavendulan, and some muscovite from the shale rock. Pyrite is depleted from the shale particles treated with persulfate.	84
Figure 4-6. Diffraction pattern of organic treated shale particles in comparison to untreated shale particles measured using XRD. Plots are log scale and the y-axis has been adjusted for ease of comparison. Organic additives depleted the same minerals from the shale as water treatment removed, including gypsum, some muscovite, and some calcite.	85
Figure 4-7. SEM images taken with HDBSD of the surface of (a) untreated, (b) water treated, and (c) combined HCl/persulfate treated shale. Bright spots in these images represent heavier elements in the surface minerals of the shale. The heavier elements are retained in untreated and water treated shale, but depleted from the HCl/persulfate treated shale.....	86
Figure 4-8. Average solution pH before and after the 8 days for each treatment (n=3). pH is buffered at 8.7 in the organic and water treatments. HCl and persulfate treated shales do not reach this buffering pH. HCl treated shale stays very acidic after the 8 days. The solution of persulfate treated shales decreased pH.....	88
Figure 4-9. Mass of individual inorganic metals leached into solution per mass of shale used in each treatment. The major metal, Si, is displayed in (a), minor metals are displayed in (b), and trace metals are shown in (c). Concentrations of each metal in the supernatant solutions were analyzed using ICP.....	90

Figure 4-10. Change in D-10, 30, and 60 particle size in each tested inorganic treatment over the course of 14 days. Each sample slurry was measured using the PSA. Error bars represent standard error (n=3).	91
Figure 4-11. Average pH profiles in each tested inorganic treatment over the course of 14 days. Error bars represent standard error (n=3).....	93
Figure 4-12. Average persulfate concentration in each treatment containing persulfate over the course of 14 days. By day 1, the remaining persulfate concentration was near the detection limits of the method used. Standard error was small, but error bars are displayed and represent standard error (n=3).	94
Figure 4-13. Dissolution of major ions over the course of 14 days as measured using ICP.	95
Figure 4-14. Dissolution of minor ions over the course of 14 days as measured using ICP.	96
Figure 4-15. Dissolution of trace ions over the course of 14 days as measured using ICP.	97

CHAPTER 1

INTRODUCTION

Introduction

As the U.S. strives for energy independence, hydraulic fracturing has enabled natural gas to become a reliable energy source [1, 4, 5]. Per unit of energy produced, natural gas produces a significantly reduced amount of greenhouse gases when compared to coal, including a decrease in sulfur dioxide, nitrogen oxide, carbon monoxide, and mercury and approximately half the amount of carbon dioxide [4]. Multistage horizontal hydraulic fracturing, or “fracing,” has proven to be a viable technology for tapping into unconventional natural gas reserves located approximately one mile below the Earth’s surface that would be otherwise uneconomical [6-8].

Horizontal drilling has allowed drilling companies to access unconventional natural gas and to optimize the amount of natural gas that may be extracted from the shale. Unconventional natural gas is contained in rock formations with low permeability and includes shale gas (located in the shale pores or adsorbed to the shale surface), coal-bed methane (located in coal deposits with extremely low permeability), tight gas (natural gas that has migrated into non-porous, impermeable rock such as limestone), and gas hydrates (crystalline gas formed by high pressures) [9]. Previously, drilling companies performed conventional drilling, which produces dry and wet gas extracted from the earth using naturally occurring pressure [10] in vertical wells [7]. Dry gas refers to shale that produces only methane gas; whereas, wet gas also contains liquid hydrocarbons [11]. Over time, production in conventional drilling decreases. Water injections are used to increase production until the process is no longer profitable. However, developments in hydraulic fracturing and horizontal drilling for unconventional natural gas have enabled drilling companies to produce 2.7 times more gas than conventional wells [12].

The process used in horizontal drilling enables natural gas companies to increase production rates and decrease production costs [13]. In horizontal drilling, wells are first drilled vertically and once the shale formation is reached, the well turns horizontal on a 500-ft radius and extends approximately 5,000-ft into the shale formation [14, 15]. From one vertical well, companies can drill horizontally into the shale formation in multiple directions, providing access to a larger surface area of shale rock. Once the well is drilled, cement and steel casings are used to line the wellbore in order to protect surrounding geological formations. The American Petroleum Institute has published industry guidance and best practice documents on casing length, thickness, tensile strength and composition [14]. A perforation gun is used to create holes in the casing at predetermined locations in 500-ft increments [15]. The first stage of perforation occurs at the furthest point out, or the “toe” of the wellbore. The second occurs five hundred feet closer to the heel, the third occurs 1,000 feet closer to the heel than the first perforation, and so on. After perforation is completed, fluids are used to create fractures. Acid, usually hydrochloric acid, is first used to clean out the borehole by disintegrating rocks and to alleviate initial fracture pressure. A chemical slurry, or “fracturing fluid,” is then pumped through the well. The high pressure of the fluid creates fissures in the shale rock at the perforation locations. Fracturing fluid is primarily composed of 98 to 99% water, about 1 to 1.9% proppant, and several other chemicals [16-18]. Proppant may consist of sand or ceramic particles that are used to “prop” the fissures open and allow for gas to escape when the hydraulic fluid pressure is released. The chemicals can include friction reducers, gelling agents, biocides, scale inhibitors, clay stabilizers, corrosion inhibitors, and surfactants. The gelling agent carries the proppants and may include a “breaking” agent.

Breaking agents facilitate cleaning out the wells after fracturing by breaking down gelling agents. Different types of breakers are used, such as persulfate, which is non-selective towards the gelling agent used, or hemicellulosic enzyme breakers, which are selective. After the chemical slurry has been injected, the final stage of fluid injection circulates freshwater in excess throughout the borehole in order to release the proppants from the fissures. In total, the process requires two to ten million gallons of water per well fractured [19].

Once fluid injection is completed, a portion of the original volume returns to the well surface. This is known as the “flowback” stage. Consequently, “flowback” fluids are fluids that return to the surface, prior to production over a ten day period, and amount to 5 to 20% of the original fluid volume [20]. “Produced” waters are the fluids that return to the surface of the well once the well has been put into production and can amount to 10 to 300% of the injected volume. The flowback and produced fluids contain the natural gas that was extracted from the shale rock as well as the fluids added to the well and any geological fluids that may have been picked up along the way. Produced brine contains additional metals, organic compounds, and naturally occurring radionuclides (NORMs) [6]. The flowback and produced fluids are grouped as hydraulic fracturing wastewater.

Water usage in oil and gas development has generated environmental concerns [21-24], including the combined impacts of chemical and non-chemical stressors on water quality and the long and short-term impacts that the release of the wastewater may have to water quality and human health. The U.S. Environmental Protection Agency (EPA) considers transformation processes important to understanding the environmental impact of hydraulic fracturing for oil and gas on drinking water resources [25]. Currently, however, insufficient information is available on the transformation of chemical additives used in hydraulic fracturing and the transformation of shale particles from the geological formation. The deficit of knowledge on transformation processes in hydraulic fracturing is due to the focus of oil and gas development research related to water quality on identifying components of chemical additives and developing frameworks to assess potential toxicity of hydraulic fracturing fluid [17, 26-30]. The research has only recently shifted to a focus on transformation of shale and chemical additives in abiotic and biotic conditions [31-34]. In these studies, transformation of chemicals and shale rock does occur under hydraulic fracturing conditions, potentially causing more harmful or persistent byproducts that pose severe human health and environmental risks.

Not enough information is known about the transformation of hydraulic fracturing fluids and the impact of chemical use on the shale formations. To develop policies that protect surrounding water bodies and to shape water reuse standards, assessing the potential for fluid migration through the geological formations, evaluating how additives impact the physical and chemical characteristics of shale, and awareness of what the fluids might contain post-fracture are increasingly important. As shale constituents and additives react, more toxic and environmentally threatening contaminants may be produced; therefore, establishing these interactions is imperative to understanding the environmental consequences caused by hydraulic fracturing practices [33].

Background

Chemical usage in hydraulic fracturing

OGD companies use two to ten million gallons of water per well fractured [19]. Approximately 200,000 liters of chemical additives, including surfactants, acids, biocides, friction and viscosity reducers, and breaking agents, are added to this water [35, 36]. After well injection, a portion of the fluids return to the surface as flowback and produced waters, which contain materials naturally occurring in the shale formation [20]. These fluids have a high total dissolved solids (TDS) content ranging from 66,000 to 261,000 mg L⁻¹ or more [7].

Current hydraulic fracturing research focuses on listing chemical components of hydraulic fracturing fluids to determine environmental toxicity. An overwhelming number of chemicals have been identified in oil and gas development wastewater and reportedly added to fresh extraction water [7, 17, 26, 27, 37]. Of the reported chemical additives, at least 100 are known or suspected endocrine disrupters [37]. Endocrine disrupters are chemicals that interact with the endocrine system; exposure causes adverse developmental, reproductive, neurological, and immune consequences in humans and wildlife [38, 39]. Some of the endocrine disrupters detected by Kassotis *et al.* in water samples from a drilling-dense region of Colorado are 2-butoxyethanol (2-BE), 2-ethyl-1-hexanol, naphthalene, ethylene glycol, diethanolamine, sodium tetraborate decahydrate, diethylene glycol methyl ether, N,N-dimethyl-formamide, cumene, bronopol, bisphenol A (BPA), and styrene [37]. Endocrine disrupters pose an environmental threat to the ecosystem surrounding the well, as exposure to hydraulic fracturing flowback and produced water have shown endocrine disrupting potential in rainbow trout fish [40].

Hydraulic fracturing chemical additives, obtained from Weatherford International, a chemical supplier for oil and gas development companies in the Marcellus Shale region, have been analyzed for their small organic molecule content. The additives include an enzyme breaking agent and a viscosity reducer called "Revert Flow." The contents of the enzyme breaking agent were found to contain 3-furaldehyde, or "furfural," 5-hydroxymethylfurfural, 5-acetoxymethyl-2-furaldehyde, 1-methyl-1H-pyrazole-4-carboxaldehyde, 1-bromo-chloroethane, (E)-1,2-dichloroethylene, 2-fluoro-5-methoxypyrimidine (a cancer drug), chlorozotocin (used in cancer therapy), zearalenone (an estrogenic metabolite), and hemicellulosic compounds glucopyranose, galactapyranose, arbutin, and inositol [34]. Revert Flow was also characterized using GC/MS. Results, which are shown in Figure 1-1, revealed several known or potential endocrine disrupters in the additive Revert Flow, including 2-BE, 1-butoxy-2-propanol, and di-sec-butyl ether [41].

In a 2012 progress report published by the EPA describing the potential impacts of hydraulic fracturing fluids, 2-BE was listed as the fourth most often appearing chemical in products used by the oil and gas development industry [42]. As a common chemical ingredient in hydraulic fracturing fluids [4, 6, 17, 26, 43], 2-BE is completely miscible in water and most organic solvents [44]. 2-BE exhibits surfactant properties, forming micelles at concentrations greater than 120 g L⁻¹ [45]. Considered a potential indicator for hydraulic fracturing fluid spills, predictive studies have found 2-BE to be potentially mobile allowing for a higher probability of exposure via groundwater contamination [46].

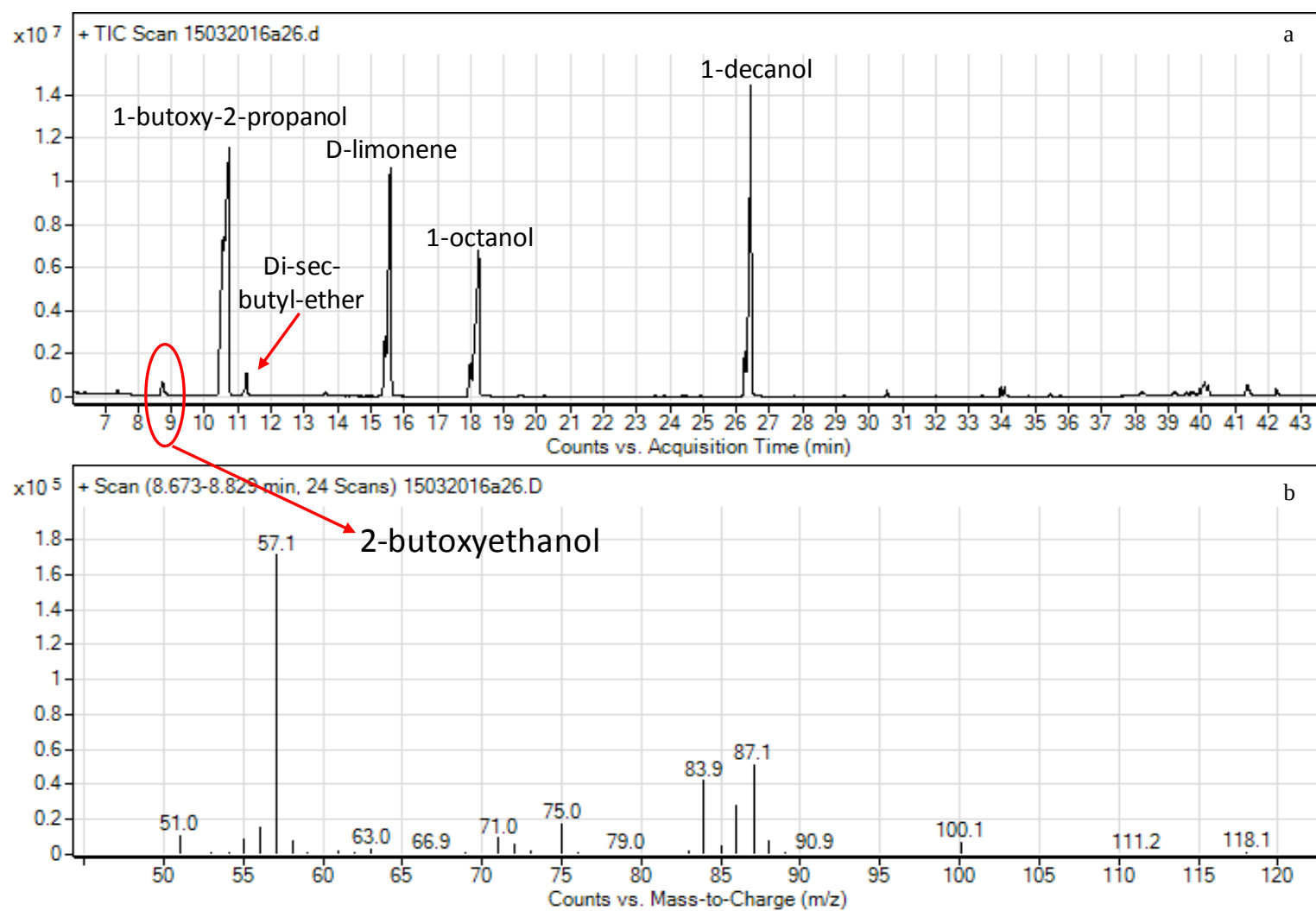


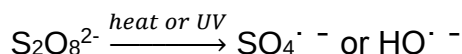
Figure 1-1. (a) Gas chromatogram of 2-BE containing hydraulic fracturing chemical additive, Revert Flow. 2-BE has a retention time of 8.748 minutes. (b) Mass spectrum of 2-BE in Revert Flow. Figure adapted from Manz and Carter, 2016 [41].

Furfural, or 3-furaldehyde, is another chemical additive used in hydraulic fracturing fluids and a variety of industries because of the chemical's resistance to heat, acid, and water [23, 26, 34, 47-49]. Furfural has been found in the resin material of proppants and as a component of an additive called LEB-10X, an enzyme breaking agent [34, 50, 51]. Furfural has very different chemical properties compared to 2-BE, but both are of concern due to evidence that hydraulic fracturing fluids have penetrated drinking water via leaks in the steel and cement casings of wells and their potential health risks [52-56].

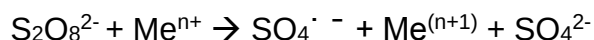
Problems surrounding water and chemical usage

Two major issues surrounding oil and gas development are water re-use and the potential for fluid migration into surrounding water bodies. Effectively re-using and recycling the water depends on the interactions that the TDS content and chemical additives have with chosen the treatment methods. Previously, hydraulic fracturing companies have used GAC as a treatment method for removing organic and toxic metal compounds [57]. While the chemical additives and naturally occurring chemicals interact with the chosen water treatment method, the chemicals also interact with the shale formation or migrate through the shale into drinking water aquifers [58]. To provide insight into the potential for groundwater contamination by these additives and effective treatment methods, a better understanding of the potential for migration of the fluids through shale formations and evaluation of current treatment methods is necessary. While furfural, a non-surfactant, has been shown to adsorb to several materials, including activated carbon [59-64], the adsorption onto shale rock has not been previously studied. Review of literature shows that no adsorption data currently exists for the surfactant 2-BE.

Another major issue surrounding natural gas production is insufficient attempts made towards understanding how any of the identified chemicals transform in the hydraulic fracturing environment. A key component missing in the attempt is the use of oxidizing breaking agents and how they transform the endocrine disrupters, such as 2-BE, used in hydraulic fracturing. Breakers, such as sodium persulfate, likely play a strong role in downhole transformation, with chemical and non-chemical stressors only influencing the extent to which persulfate can interact with individual components [34]. Persulfate breakers work by producing strong sulfate or hydroxyl radicals upon activation, as shown Reaction 1-1 and Reaction 1-2 [65, 66], to break down gelling agents, decrease fluid viscosity [67], and clean the wellbore in concentrations ranging from 0.125 mmol L⁻¹ to 47 mmol L⁻¹ [68-71]. Through investigating the interactions of persulfate, 2-BE, and shale rock, the environmental impacts of hydraulic fracturing can be better understood by gaining the ability to predict the contents of the fluids. Investigating the use of persulfate in this environment is essential to assessing the impacts of oil and gas development on water quality and the threat hydraulic fracturing spills pose to human and wildlife health.



Reaction 1-1



Reaction 1-2

The chemical additives, including persulfate, hydrochloric acid, and organics, used in hydraulic fracturing may also transform the shale rock. In regards to transformation studies focusing on shale rock, previous studies investigating the impact of synthetic hydraulic fracturing fluid, which contained a number of inorganic species and slightly acidic pH, on shale found that carbonate and gypsum precipitate from the shale [33]. However, no observations were made for persulfate and organic additives, which may cause further precipitation and demineralization of chemical species, including heavy metals. Heavy metals can be toxic to aquatic life in excess concentrations, so they are regulated by the EPA in natural water [72]. As shale constituents and organic additives react with persulfate, more toxic and environmentally threatening pollutants may be leached into the water; therefore, establishing these interactions is imperative to understanding the environmental consequences caused by oil and gas development practices [33].

In addition, exposure to hydraulic fracturing fluid may alter the physical characteristics of the shale formation. Once a wellbore is drilled and prepared, the first step in fracturing is perforation. During perforation, a blasting gun is used to create fissures in the shale rock, producing many small shale particles as a result of the explosions. As these small particles are exposed to hydraulic fracturing fluid and high mixing speeds when the fluids are returned to the well surface, the size of the particles may decrease due to the exposure to harsh chemicals. As the particles deteriorate, solution turbidity, colloidal particles, and suspended solids may increase. Compared to large particles, colloidal and suspended solids provide increased surface area for microbial growth to occur in aerobic and anoxic conditions [73-75]. While oil and gas development companies use biocides to reduce microbial activity, the elevated concentrations of organics and metals decreases biocide efficacy [76, 77]. Increasing small particles downhole as a result of exposure to hydraulic fracturing fluids could provide increased locations for microbial growth, which may result in increased sulfide production and souring of the natural gas [77].

The overall objective of the research presented in this dissertation is to address water quality issues caused by additive usage in hydraulic fracturing, namely chemical migration and transformations in hydraulic fracturing. Adsorption, kinetic, and geochemical interaction studies that improve understanding of migration and transformation are presented. Migration and transformation studies are required to understand how the fluids may behave in the environment post-fracture. This research is the beginning to having the ability to predict the contents of hydraulic fracturing fluids post-fracture, protecting water resources and ecosystems surrounding a well, and reducing exposure risks.

The rest of this dissertation is organized as follows. In Chapter 2, adsorption studies will be used to evaluate adsorption of surfactant (2-BE) and non-surfactant (3-furfuraldehyde) additives to shale rock and granular activated carbon (GAC). The goal is to assess the potential for hydraulic fracturing organic additives to migrate through the shale formation and to determine the interactions between GAC and surfactant and non-surfactant additives for removing these contaminants from solution for re-use. In Chapter 3, the transformation of 2-BE, a compound used to trace hydraulic fracturing spills and found in the chemical additive “Revert Flow,” will be investigated in the presence of oxidizing agents that are potentially activated by shale rock. In Chapter 4, the impact of

persulfate, acid, and organic additive use on the physical and chemical characteristics of shale will be determined. Leaching of materials from the shale rock into water as result of these additives will also be determined. Finally, conclusions are given in Chapter 5.

CHAPTER 2
ADSORPTION OF HYDRAULIC FRACTURING FLUID COMPONENTS 2-
BUTOXYETHANOL AND FURFURAL ONTO GRANULAR ACTIVATED
CARBON AND SHALE ROCK

A version of this chapter was originally published by Katherine E. Manz, Gregory Haerr, Jessica Lucchesi, and Kimberly E. Carter:

Katherine E. Manz, Gregory Haerr, Jessica Lucchesi, Kimberly E. Carter.
“Adsorption of hydraulic fracturing fluid components 2-butoxyethanol and furfural onto granular activated carbon and shale rock.” *Chemosphere* 164 (2016): 585-592.

Abstract

The objective of this study was to understand the adsorption ability of a surfactant and a non-surfactant chemical additive used in hydraulic fracturing onto shale and GAC. Experiments were performed at varying temperatures and sodium chloride concentrations to establish these impacts on the adsorption of the furfural (a non-surfactant) and 2-Butoxyethanol (2-BE) (a surfactant). Experiments were carried out in continuously mixed batch experiments with Langmuir and Freundlich isotherm modeling. The results of the experiments showed that adsorption of these compounds onto shale does not occur, which may allow these compounds to return to the surface in flowback and produced waters. The adsorption potential for these chemicals onto GAC follows the assumptions of the Langmuir model more strongly than those of the Freundlich model. The results show uptake of furfural and 2-BE occurs within 23 h in the presence of DI water, 0.1 mol L⁻¹ sodium chloride, and in lab synthesized hydraulic fracturing brine. Based on the data, 83% of the furfural and 62% of the 2-BE was adsorbed using GAC.

Introduction

Water reuse and recycling is a major issue surrounding the extraction of natural gas from shale rock formations via hydraulic fracturing. For each well fractured, hydraulic fracturing companies use two to ten million gallons of water [19]. According to Howarth *et al.*, approximately 200,000 liters of chemical additives are added to this water, making a chemical slurry [36]. Hydraulic fracturing fluids contain surfactants, acids, biocides, scale inhibitors, friction reducers, corrosion inhibitors, clay stabilizers, breaking agents, and iron controllers [35]. Once a well is completed, a portion of the original injected volume returns to the surface as flowback and produced waters [20]. Flowback and produced waters contain fluids naturally occurring in the shale formation, resulting in high TDS content ranging from 66,000 to 261,000 mg L⁻¹ or more [7].

Treating these waters is largely dependent on the chemical additives used in the fluids and their interactions with chosen treatment methods. Previously, hydraulic fracturing companies have used GAC as a treatment method for removing organic and toxic metal compounds [57]. Not only are all of the chemical additives and naturally occurring constituents able to interact with the chosen treatment method, it is also plausible that these additives may interact with the shale formation surrounding the well or migrate through the shale into drinking water aquifers [58].

Furfural, a non-surfactant, and 2-BE, a surfactant, are chemical additives used in hydraulic fracturing fluids and a variety of industries [26]. Furfural is produced through the decomposition of plant biomass and is used as a preservative, fungicide, herbicide, disinfectant, a precursor to other compounds and synthetic resins, and as a demulsifying agent in petroleum refining [47-49]. Furfural is a strong inhibitor of dark fermentation

process, which is one of the first steps of anaerobic digestion [78] and is found in the resin material of proppants because of its high resistance to heat, acid, and water [50, 51].

2-BE has been used in herbicides, pesticides, food additives, corrosion resistant coatings, cosmetics, and as a dispersant in solutions used by the EPA to clean up oil and gas spills [79-82]. 2-BE is a well-known surfactant and has the ability to lower surface tension between two liquids. For this reason, 2-BE is used as a product stabilizer in hydraulic fracturing fluids [35]. Both furfural and 2-BE have become a concern due to evidence that hydraulic fracturing fluids have penetrated drinking water via leaks in the steel and cement casings of wells and their potential health risks [52-56].

Understanding the potential for chemical constituents from hydraulic fracturing to migrate through shale formations offers insight into their potential to cause groundwater, while evaluating the ability to remove these contaminants is necessary to provide effective treatment strategies should contamination occur. Previously conducted adsorption studies have found activated carbon, zeolites, nanoporous silica based MCM-48 material, and polymeric resins are capable of adsorbing furfural [59-64], however; review of literature shows that no adsorption data currently exists for 2-BE. Therefore, the objectives of this study were 1) to determine if adsorption onto granular activated carbon (GAC) may be used to remove the chemical additives, 2-BE and furfural, from solution; 2) to understand how these two compounds may compete for adsorption sites; and 3) to better understand the interaction between these chemical additives with shale.

Materials and Methods

Chemicals and Materials

Optima grade dichloromethane, sodium chloride, and $\geq 95\%$ practical grade 2-butoxyethanol (2-BE) were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). 99% furfural and ≥ 85 wt. % phosphoric acid in water were purchased from Sigma-Aldrich (St. Louis, MO 63178, USA). Deionized water was produced using a Milli-Q Plus water purification system (Darmstadt, Germany). The activated carbon, NORIT® GAC 1240, with a 12-40 mesh size was obtained from ACROS Organics (New Jersey, USA) and was used as received. This material was chosen because it is commercially available and has previously been shown to remove furfural from aqueous solutions [59].

Shale Rock and Solids TOC

WV7 shale rock from a depth of 6,582.5 m was obtained from the West Virginia Geological Survey (Morgantown, WV 26508) and was crushed and sieved using a No. 10 and 18 mesh with a mean diameter of 1.00 to 2.00 mm. The total organic carbon (TOC) of the shale and GAC used was measured with a Shimadzu TOC analyzer equipped with an ASI autosampler and a SSM-5000A solid sample module (Kyoto, Japan). TOC was calculated by subtracting inorganic carbon (IC) from the total carbon (TC). For TC analysis, solid samples were heated in a 900°C oven that was connected to the detector. For IC analysis, samples were acidified in the sample boat using 1 part ≥ 85 wt. % phosphoric acid mixed with 2 parts water and immediately introduced into a 150°C oven attached to the detector. Samples of GAC and shale were measured in triplicate and

standard error for these samples were less than 2%. The TOC content of the shale used in this study was 4.4%, whereas the TOC of the GAC was 70%.

Experimental Procedure

Aqueous solutions of 2-BE, furfural, and both 2-BE and furfural were prepared in 2-liter glass volumetric flasks using deionized water. The solutions were prepared in DI water, a 0.001 mol L⁻¹ sodium chloride solution, a 0.1 mol L⁻¹ sodium chloride solution, or with hydraulic fracturing brine. The hydraulic fracturing brine was composed in the laboratory and its chemical make-up has been previously described [41]. All solutions were mixed using a magnetic stir bar at least 24 hours prior to the experiment. The initial and final pHs were measured using a Fisher Scientific Accumet XL benchtop meter (Pittsburgh, PA 15275, USA). Initial concentration of 2-BE and furfural ranged from 500 to 700 mg L⁻¹. Adsorption isotherms by GAC or shale were performed in small batch experiments using 125 mL volume in borosilicate glass serum bottles closed with a rubber septum and aluminum crimped seal. GAC or shale was added to each vial in weights of 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, and 0.5 g. The vessel containing 0 g of GAC was used to account for volatilization and losses of the compounds not due to adsorption. The vials were stirred continuously using a water bath shaker at constant temperatures of 20, 35, 45, 55, and 65°C (New Brunswick Scientific Co, Inc, Model G76, Edison, NJ USA) for 24 hours in order to achieve equilibrium between the solid and liquid phases were reached [59, 60, 83]. Samples were taken after 24 hours to measure the 2-BE and/or furfural concentration. The absorbed amount was calculated using Equation 2-1, where q_A is the adsorbent-phase concentration of 2-BE or furfural at equilibrium, V is the volume, M is the weight of GAC, C_i is the concentration of 2-BE or furfural, and C_A is the concentration of furfural or 2-BE in solution.

$$q_A = \frac{V}{M} * (C_i - C_A) \quad \text{Equation 2-1}$$

2-BE Concentrations

2-BE concentrations were determined using GC/MS. The liquid-liquid extraction procedure and GC/MS parameters have been previously described [41]. 15 mL samples from each experiment were collected in borosilicate scintillation vials with silicon-lined caps. 3 mL of the sample was used for extraction and quantification of 2-BE and the rest was used for pH measurements. Dichloromethane (DCM) was used as the extraction solvent. 3 mL of DCM was added to the sample vial and the sample was vortexed using a 115V Mini Vortex Mixer (Fisher Scientific, Pittsburgh, PA 15275, USA). The solution was allowed to equilibrate for 10 minutes and separated using a 6 mL polypropylene syringe (Fisher Scientific, Pittsburgh, PA 15275, USA). The extraction was repeated 3 times and after each extraction the DCM fraction was collected in a separate scintillation vial and weighed to determine the total volume of DCM used. The 2-BE concentration was determined using calibration curves made from analysis of 2-BE standards at the start of each GC/MS run and a detailed description of this method and quantification procedure for 2-BE was previously described [41].

An Agilent 7890B Gas Chromatograph (GC) equipped with 5977A Mass Selective Detector (MSD) system, 7963 auto-sampler, and an Agilent J&W DB-1 capillary column, with dimensions of 60m x 0.25 mm inner diameter and 0.25- μ m film thickness, was used to determine the 2-BE concentrations (Santa Clara, CA 95051, USA). Ultra-high purity helium purchased from Airgas Corporation (Knoxville, TN 37921, USA) was used as the carrier gas with the flow rate maintained at 2.5 mL min⁻¹. The GC was operated in split-less mode and the pressure maintained in the instrument was 33.974 psi. Each sample was injected using a 10 μ L needle with an injection volume of 3.5 μ L. The initial temperature of the GC was 40°C and was held for 4 minutes. The temperature ramp was 10°C per min to 230°C, which was held for 3 minutes. The 2-BE peak on the chromatogram was between 9.5 and 10 minutes.

Furfural Concentrations

Furfural concentrations were determined using a ThermoFisher Scientific Evolution 600 UV/Vis spectrophotometer (Madison, WI 53711, US). The maximum wavelength for furfural was determined to be at 258 nm. For samples containing 2-BE and furfural, 2-BE was determined to have no maximum wavelength and, therefore, did not interfere with furfural measurements. The furfural concentration was calculated using calibration curves made by measuring standards of known furfural concentrations. Standards were created by dissolving a known amount of furfural in distilled water or salt water, depending on the sample matrix, and successively diluting the stock solution with the same solvent.

Results and Discussion

Adsorption of 2-BE and furfural onto shale rock

Figure 2-1 (a) and (b) display the uptake of furfural by shale at 20 and 65°C in 0 and 0.1 mol L⁻¹ sodium chloride. As shown in these Figures, the concentration of furfural remains consistent as the mass of shale rock is increased regardless of the temperature and chloride concentration. This experiment was also performed at 35, 45, 55°C and with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride at all temperatures, with similar results observed. Furthermore, as the mass of shale increased, the concentration of furfural remained constant. This suggests that furfural does not adsorb to shale rock and is potentially mobile in the shale formation.

Similar experiments were performed with 2-BE and the shale. The results for the 2-BE experiments displayed similar trends at the same temperatures and salt concentrations and are shown in Figure 2-1 (c) and (d). These results imply that neither 2-BE nor furfural adhere or adsorb to the shale because the shale does not contain enough organic matter or the sites are not sufficient for adsorption of the chemicals [84-86], though the TOC content of the shale used was 4.4%. The results also suggest that these two hydraulic fracturing chemical additives may have the capability to migrate through shale formations when present in the flowback and produced waters [52].

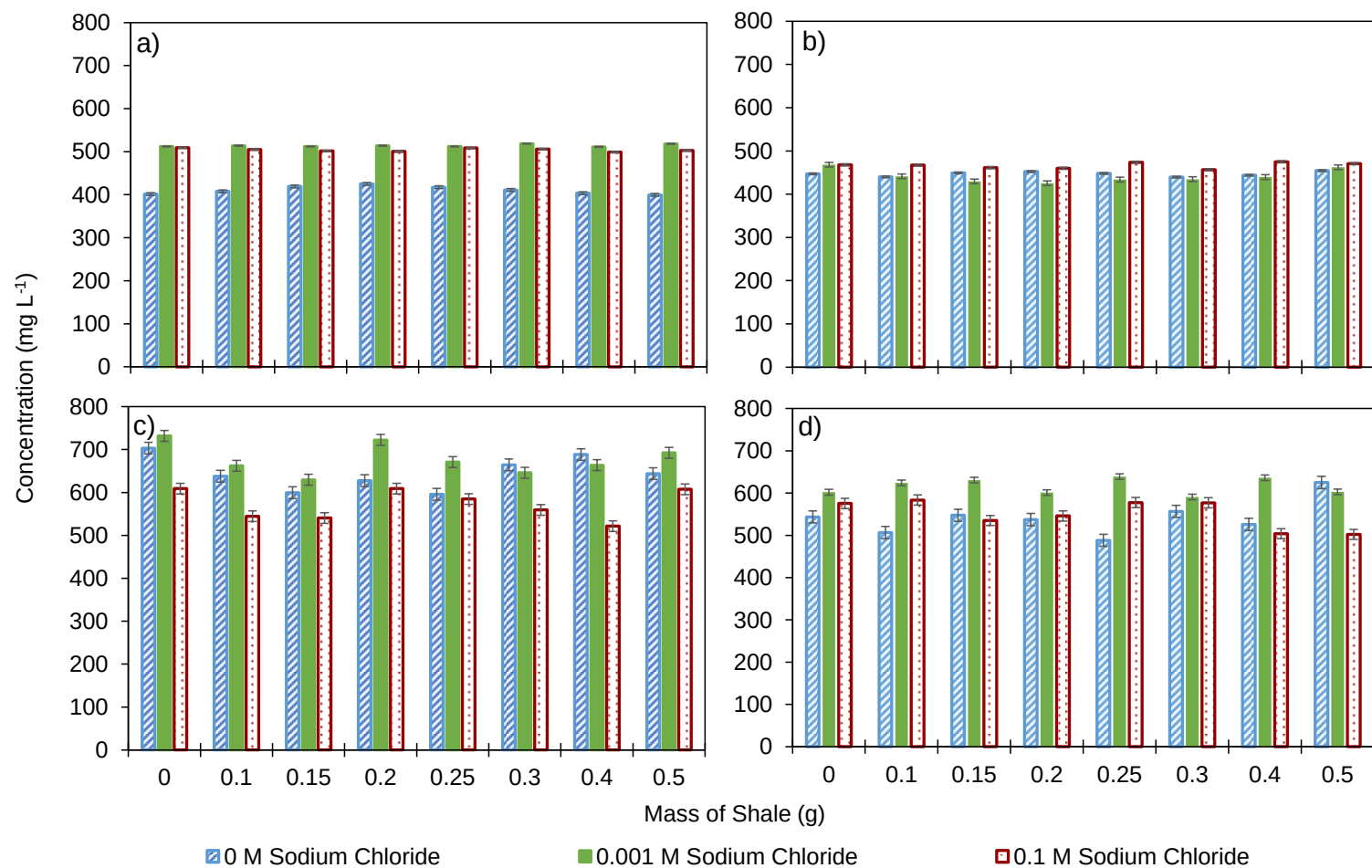


Figure 2-1. Furfural and 2-BE adsorption onto shale rock. Conditions: a) furfural, 20°C, b) furfural, 65°C, c) 2-BE, 20°C, and d) 2BE, 65°C.

2-BE and furfural adsorption onto GAC in separate reaction vessels

Time dependence of 2-BE and furfural adsorption

Figure 2-2 displays the decrease in concentration over the course of 21 days for furfural and 2-BE in reaction vessels containing water, 0.1 mol L⁻¹ sodium chloride, and hydraulic fracturing brine with 0.5g GAC. Adsorption and desorption equilibrium was achieved within 23 hours for both furfural and 2-BE. For 2-BE, maximum adsorption in all solution matrices occurred within 4.75 hours. After 22.3 hours in the presence of GAC, decreasing 2-BE concentrations occur due to the hydrolysis half-life [87]. Adsorption of 2-BE in hydraulic fracturing brine mimicked adsorption from water and sodium chloride. At 22.3 hours, the overall removal of 2-BE is 64, 60, and 62% in water, hydraulic fracturing brine, and sodium chloride. For furfural, the overall removal was 85, 83, and 86% in water, hydraulic fracturing brine, and sodium chloride at 22.3 hours.

Effects of temperature and salt concentration

Figure 2-3 and Figure 2-4 display the percent removal of furfural and 2-BE from solutions containing different salt concentrations using GAC at 20, 35, 45, 55°C, and 65°C. For furfural, greater percent removal is obtained at lower temperatures, which agrees with the findings of Sahu *et al.* [59] studies on furfural adsorption to commercial grade activated carbon [59]. In addition to temperature effects, the influence of salt concentrations was observed. At room temperature, the highest percent of furfural removal was observed when no sodium chloride was in solution, as seen in Figure 2-3 (a). At each temperature, the percent of furfural removed is approximately the same, independent of salt concentration as shown in Figure 2-3 and Figure 2-4. The average difference between the percent removal at one mass of GAC and for all 3 salt concentrations was 3.7%, while the highest percent difference was 7.76% for 0.4 g of GAC at 20°C, the lowest percent difference was 0.09% for 0.3 g of GAC at 35 °C.

Maximum adsorption of 2-BE at each weight of GAC varies with temperature and sodium chloride concentration. The greatest percent removal of 2-BE was observed in the solution containing 0.1 mol L⁻¹ of sodium chloride. Increasing the salt concentration also had little to no effect on the adsorptive properties of 2-BE. At 35, 45, 55, and 65 °C, furfural adsorption is not affected by salt concentration. Studies have shown that the sodium chloride concentration has variable effects on adsorption capacity, enhancing adsorption capacity for anionic organic molecules and having little to no effect on non-ionized compounds [88].

However, increasing temperature did impact 2-BE adsorption. Control experiments were performed at each temperature to monitor decrease in 2-BE due to potential volatilization. 2-BE At 65°C, a greater proportion of 2-BE is absorbed than at room temperature for all salt concentrations. 2-BE is classified as a small-size surfactant [89] and 2-BE is zwitterionic, having both cationic and anionic centers within the neutral molecule [90]. In the presence of ionic solutions, surfactant adsorption is accompanied by counter-ion adsorption [91] suggesting that, in addition to the adsorption monolayer being formed at the surface of the GAC, a bilayer may also form at the cationic or anionic center of 2-BE that is not already attached to the GAC – providing additional adsorption of 2-BE. The variation of adsorption at different temperatures may be due to variation in bilayer.

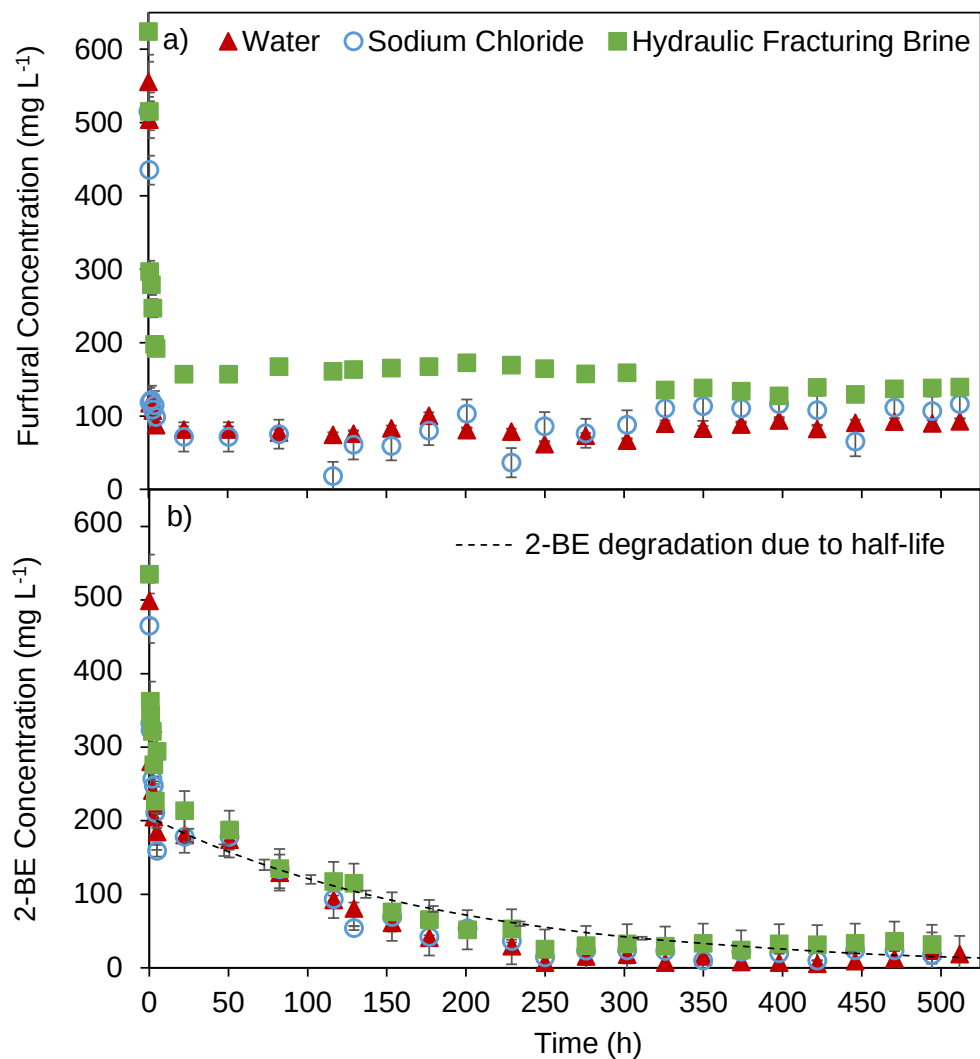


Figure 2-2. Decreasing a) furfural and b) 2-BE concentrations due to adsorption onto GAC are shown for water, 0.1 mol L⁻¹ sodium chloride, and synthetic hydraulic fracturing brine. The data was taken over the course of 511 h (21.3 days). The dashed line in b) represents the 2-BE half-life and shows that this decrease in concentration was due to 2-BE decay [41]. Furfural and 2-BE adsorption occurred within 24 h.

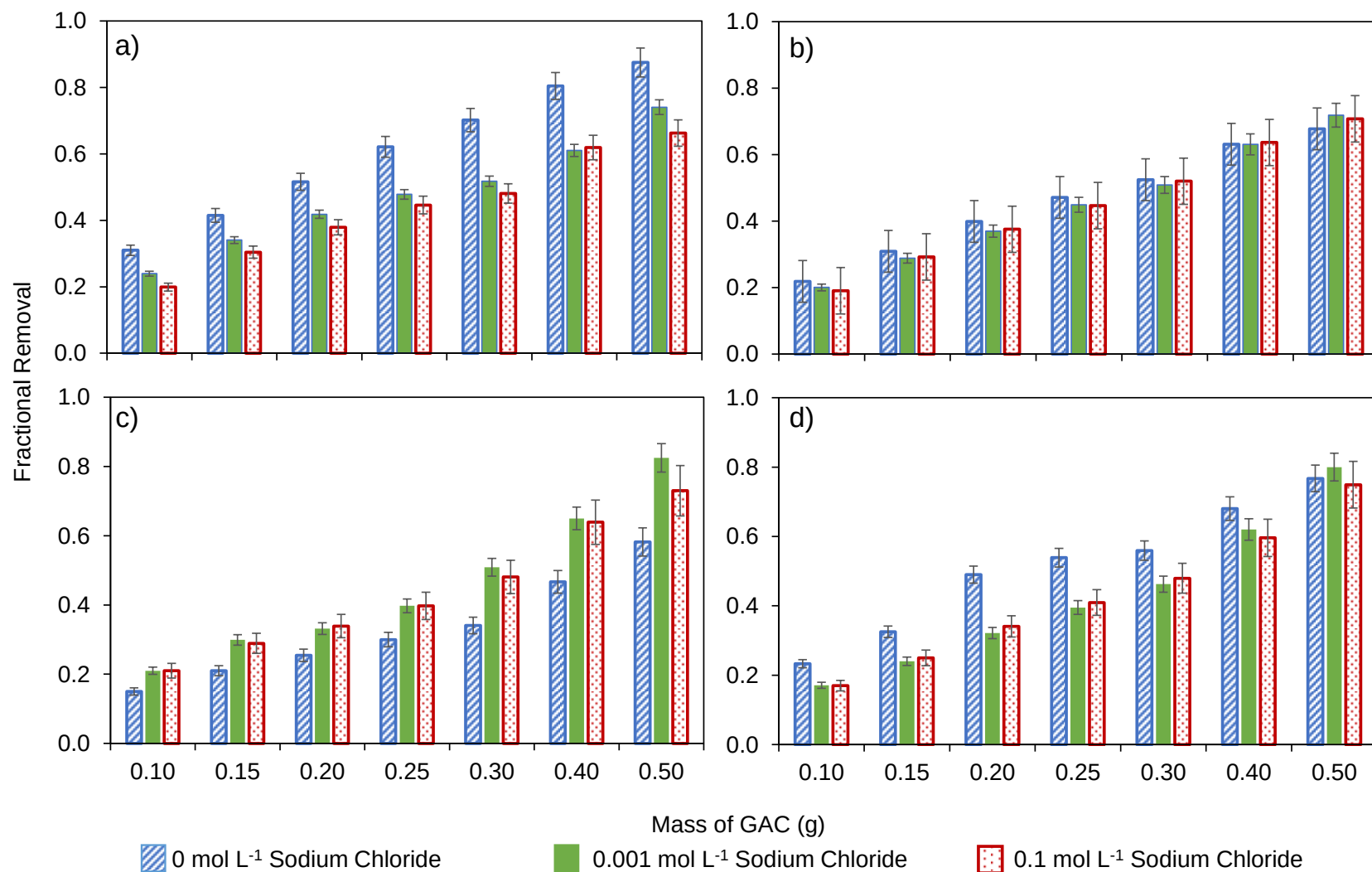


Figure 2-3. Percent removal of Furfural and 2-BE with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride in solution. The reaction conditions are a) furfural, 20°C, b) furfural, 65°C, c) 2-BE, 20°C, and d) 2-BE, 65°C.

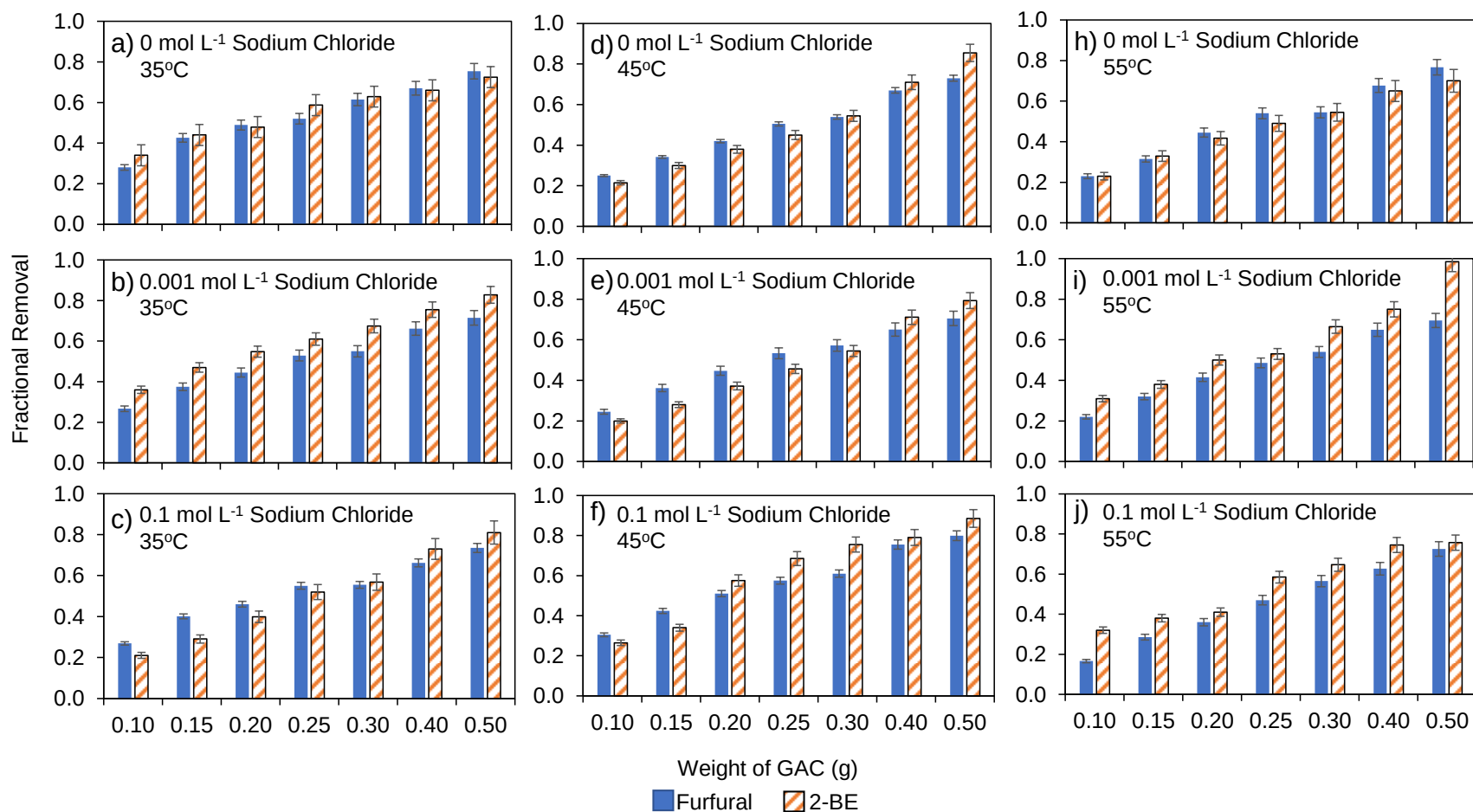


Figure 2-4. Percent removal of 2-BE and furfural by GAC for 35, 45, and 55°C at different concentrations of sodium chloride.

Langmuir and Freundlich Isotherms

Langmuir and Freundlich isotherms models were applied to the data for both furfural and 2-BE [92, 93]. Figure 2-5 displays the Langmuir isotherms for furfural and 2-BE experiments. The Langmuir isotherm assumes adsorbent is uniform with a fixed number of adsorption sites, reversible equilibrium with the aqueous phase, and monolayer adsorption with no interactions between the molecules [92].

The Langmuir parameters for furfural and 2-BE are shown in the Table 2-1. These parameters were found by fitting the data to the linearized form of the Langmuir isotherm, shown in Equation 2-2, where C_A is concentration of furfural or 2-BE in solution, q_A is the adsorbent-phase concentration of 2-BE or furfural at equilibrium, Q_M is the maximum adsorbent phase concentration of 2-BE or furfural when the adsorbent is saturated, and K_L is the Langmuir adsorption constant of 2-BE or furfural [92]. For furfural, values of K_L ranged from 2.05×10^{-3} to $160 \times 10^{-3} \text{ L mg}^{-1}$. For 2-BE, values ranged from 2.17×10^{-3} to $63.6 \times 10^{-3} \text{ L mg}^{-1}$.

$$\frac{C_A}{q_A} = \frac{1}{K_L Q_M} + \frac{C_A}{Q_M} \quad \text{Equation 2-2}$$

Shown by the data plotted in Figure 2-5 using the Langmuir model, sodium chloride concentration had a more significant impact on the adsorption of 2-BE than furfural. The slope of the Langmuir plot is the inverse of Q_M , which means that the slope is equal to the mass of adsorbent per mass of adsorbate. At 20 and 65°C, the slope of each furfural line varies only slightly for all salt concentrations. For 2-BE at room temperature, the isotherm with the greatest slope is the one where no sodium chloride was present in solution. However, at 65°C, the isotherm with the greatest slope is the one with the 0.1 mol L⁻¹ of sodium chloride.

Figure 2-6 displays Freundlich isotherms for furfural and 2-BE at 20 and 65°C with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride. Freundlich isotherms are used to model heterogeneous adsorption and assume, unlike the Langmuir model, that individual sites have different energies and more than one layer of adsorption can occur [92, 93]. Freundlich isotherms were plotted using Equation 2-3, where $1/n$ is the unit-less adsorption intensity parameter [92]. The Freundlich parameter values at all temperatures and salt concentrations for furfural and 2-BE are displayed in Table 2-1. The slope, $1/n$, of the Freundlich isotherm indicates the adsorption intensity. For both Furfural and 2-BE, the highest adsorption intensity was observed at 35°C. This indicates that adsorption is more favorable at this temperature. Overall, Freundlich isotherms exhibited lower R^2 values than the Langmuir isotherms for both 2-BE and furfural. This suggests that the assumptions made in the Langmuir model are better suited for these contaminants.

$$\log q_A = \log K_F + \frac{1}{n} \log C_A \quad \text{Equation 2-3}$$

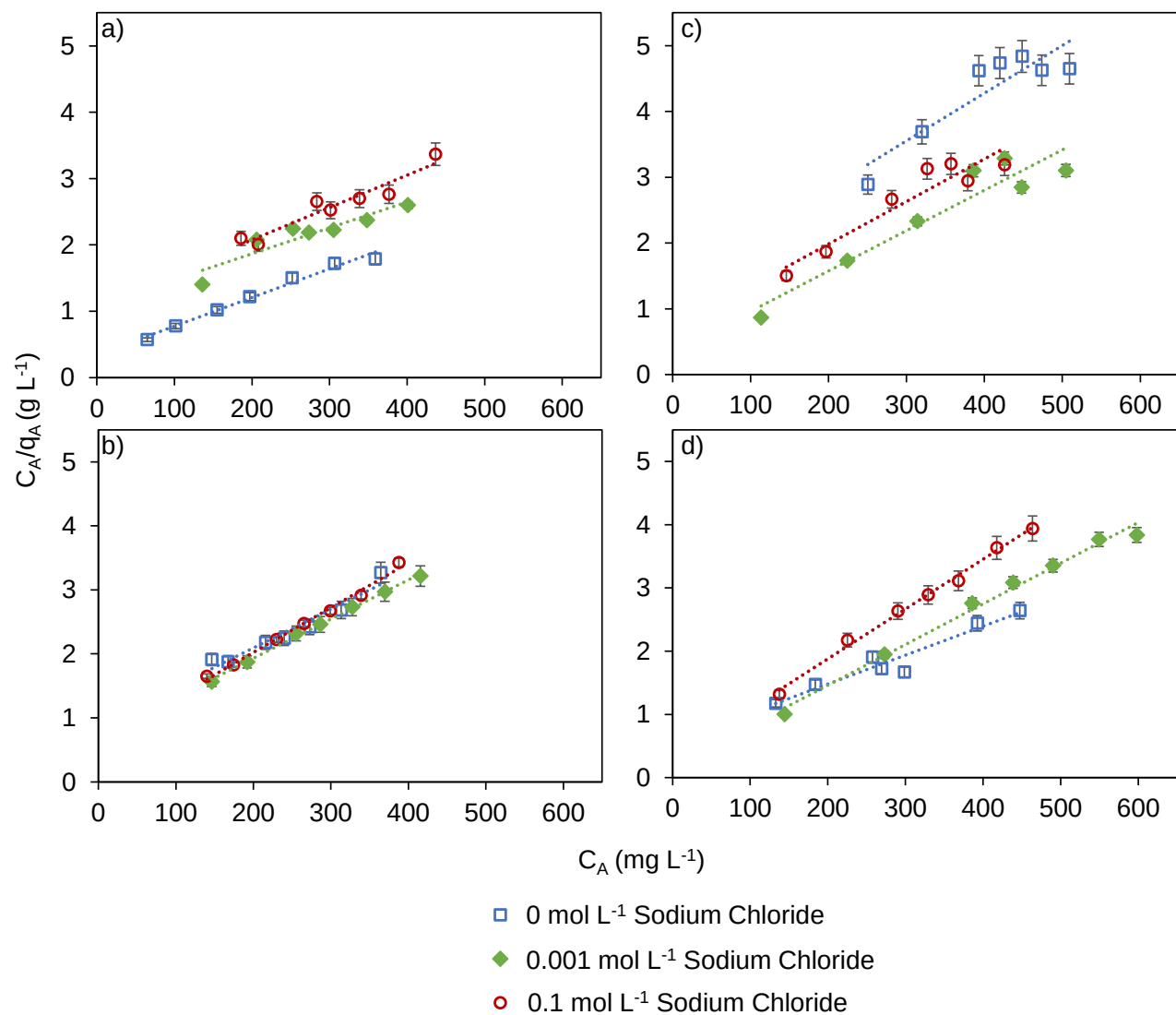


Figure 2-5. Langmuir isotherm for furfural at a) 20 and b) 65°C and 2-BE at c) 20 and d) 65°C with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride.

Table 2-1. Freundlich and Langmuir Isotherm Parameters for furfural and 2-BE at indicated temperatures and sodium chloride concentrations.

Constituent	[Sodium Chloride] (mol L ⁻¹)	T (°C)	Langmuir			Freundlich		
			Q _M (mg g ⁻¹)	K _L x 10 ⁻³ (L mg ⁻¹)	R ²	$\frac{1}{n}$	K _F $\left(\left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^{\frac{1}{n}}\right)$	R ²
Furfural	0	20	231	12.6	0.98	0.308	31.6	0.98
		35	450	2.05	0.96	0.818	1.53	0.88
		45	254	3.97	0.96	0.489	8.43	0.97
		55	139	14.0	0.95	0.301	20.4	0.77
		65	205	4.34	0.98	0.514	6.20	0.97
	0.001	20	256	3.59	0.86	0.482	8.41	0.89
		35	387	2.12	0.92	0.643	3.81	0.97
		45	312	2.88	0.91	0.608	4.52	0.93
		55	207	4.87	0.99	0.476	8.11	0.97
		65	163	8.72	0.99	0.309	20.0	0.99
	0.1	20	283	2.71	0.90	0.562	5.10	0.93
		35	347	2.51	0.85	0.641	3.85	0.94
		45	270	5.07	0.93	0.503	9.26	0.95
		55	93.9	160	0.94	0.129	45.3	0.44
		65	143	11.1	0.99	0.298	20.1	0.94
2-BE	0	20	138	5.27	0.83	0.278	17.6	0.51
		35	422	2.17	0.94	0.904	1.07	0.93
		45	194	24.7	0.99	0.078	109	0.60
		55	207	4.87	0.99	0.476	8.11	0.97
		65	219	8.07	0.94	0.358	20.0	0.78
	0.001	20	163	17.7	0.92	.0971	78.9	0.91
		35	609	2.26	0.91	0.594	8.16	0.96
		45	196	24.8	0.99	0.114	89.4	0.93
		55	252	6.11	0.89	0.444	12.9	0.95
		65	155	37.2	0.99	0.0339	119	0.94
	0.1	20	155	9.32	0.95	0.244	28.2	0.90
		35	145	33.9	0.94	0.145	57.7	0.71
		45	183	63.6	0.95	0.180	64.3	0.91
		55	195	7.87	0.93	0.487	11.7	0.95
		65	127	25.9	0.95	0.115	58.1	0.98

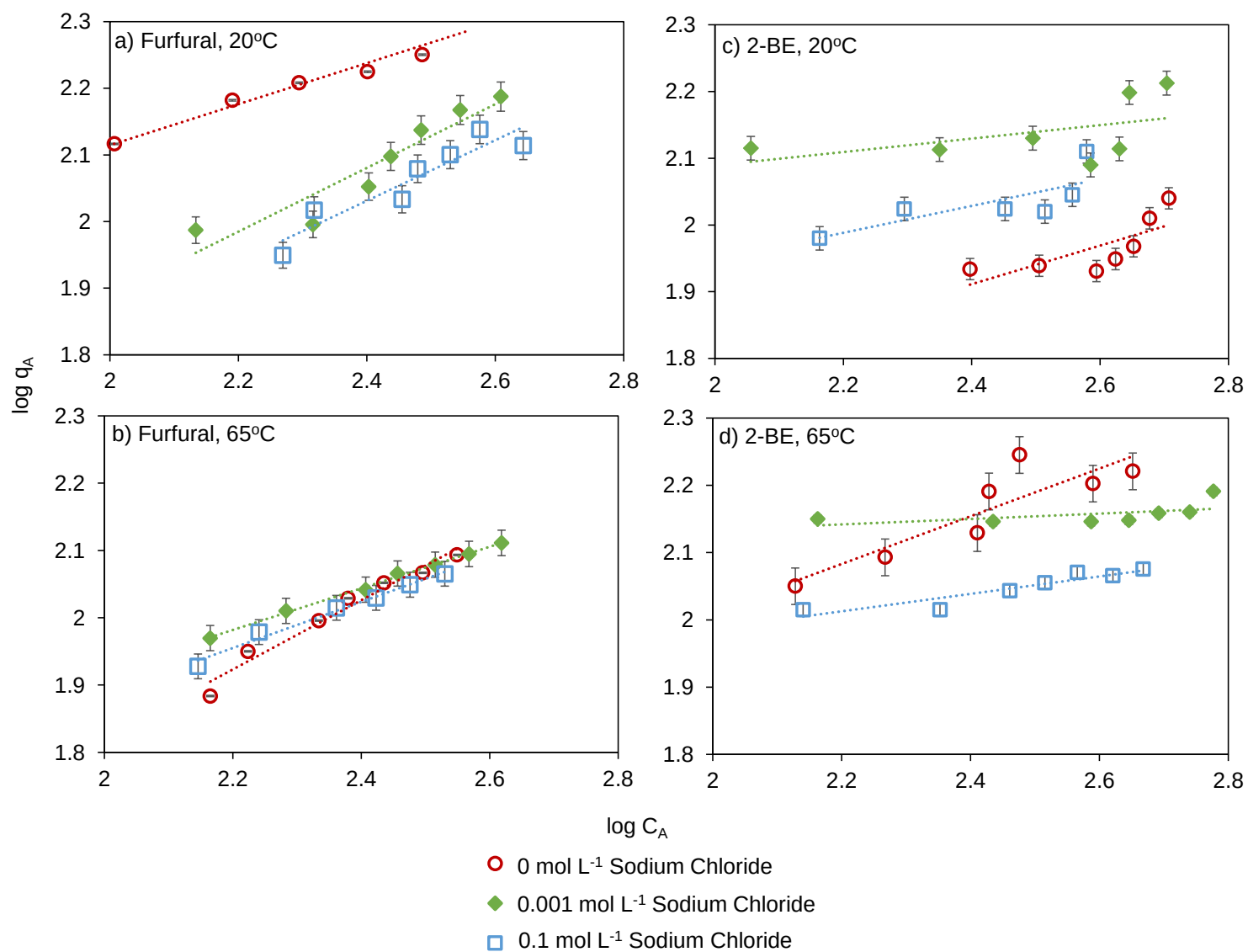


Figure 2-6. Freundlich isotherms for furfural and 2-BE at 20 and 65°C with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride.

Redlich-Peterson Isotherms

The Redlich-Peterson isotherm is a three parameter isotherm that uses assumptions from both the Langmuir and Freundlich isotherms [94-98]. Therefore, the Redlich-Peterson isotherm adsorption mechanism is not uniform and does not follow monolayer adsorption. The Redlich-Peterson model is determined using Equation 2-4, where q_e is the equilibrium adsorbent-phase concentration of 2-BE or furfural (mg g^{-1}), K_{RP} is the Redlich-Peterson isotherm constant (L g^{-1}), a_R is a constant (L mg^{-1}), β is a constant that lies between 0 and 1, and C_e is the liquid-phase adsorbent concentration (mg L^{-1}). The linearized form of this equation is Equation 2-5.

Figure 2-7 displays the linearized Redlich-Peterson isotherms for 2-BE and furfural experiments with 0, 0.001, and 0.1 mol L^{-1} sodium chloride at 20, 35, 45, 55, and 65°C and Table 2-2 displays the resulting Redlich-Peterson constants. When β equals 1, the Redlich-Peterson isotherm reduces to the Langmuir equation [94]. The Redlich-Peterson isotherm reduces to Henry's equation (Equation 2-6) when β equals 0 and reduces to the Freundlich isotherm when the $a_R C_e^\beta$ term is much larger than 1 [94, 95]. Henry's isotherm is a one parameter isotherm that assumes the amount of absorption is proportional to the partial pressure of the absorbate and is described by the linear Equation 2-6, where q_e and C_e are the same as in the Redlich-Peterson isotherm and K_{HE} is the Henry's adsorption.

For 2-BE, β was approximately equal to 1 and all R^2 values were 1.00 for all temperatures and salt concentrations tested (20, 35, 45, 55, 65°C and 0, 0.001, 0.1 mol L^{-1} sodium chloride). Little variation was observed in the β values for 2-BE. In all cases tested for 2-BE, the Redlich-Peterson isotherm reduces to the Langmuir isotherm. β values for furfural are between 0.85 and 0.88 and R^2 values were 1.00 for all temperatures and salt concentrations tested. The β values for furfural are also very close to one; however, the slightly lower values compared to 2-BE indicates that furfural does not obey the Langmuir isotherm as well as 2-BE. Adsorption capacity is indicated by the ratio of K_{RP} to a_R . Values of K_{RP}/a_R for 2-BE vary between 2.7 and 3.8 and for furfural vary between 12 and 20,000. Furfural exhibited more variation in K_{RP}/a_R values, which indicates that the adsorption capacity varies more with temperature and salt concentration for furfural. Overall, the Redlich-Peterson data indicate that 2-BE reduces to the Langmuir isotherm and that the furfural isotherm is approaching the Langmuir isotherm; however, the adsorption of both 2-BE and furfural were not influenced by salt concentration or temperature according to the consistent K_{RP} values.

$$q_e = \frac{K_{RP} C_e}{1 + a_R C_e^\beta} \quad \text{Equation 2-4}$$

$$\ln \frac{C_e}{q_e} = \beta \ln C_e - \ln K_{RP} \quad \text{Equation 2-5}$$

$$q_e = K_{HE} C_e \quad \text{Equation 2-6}$$

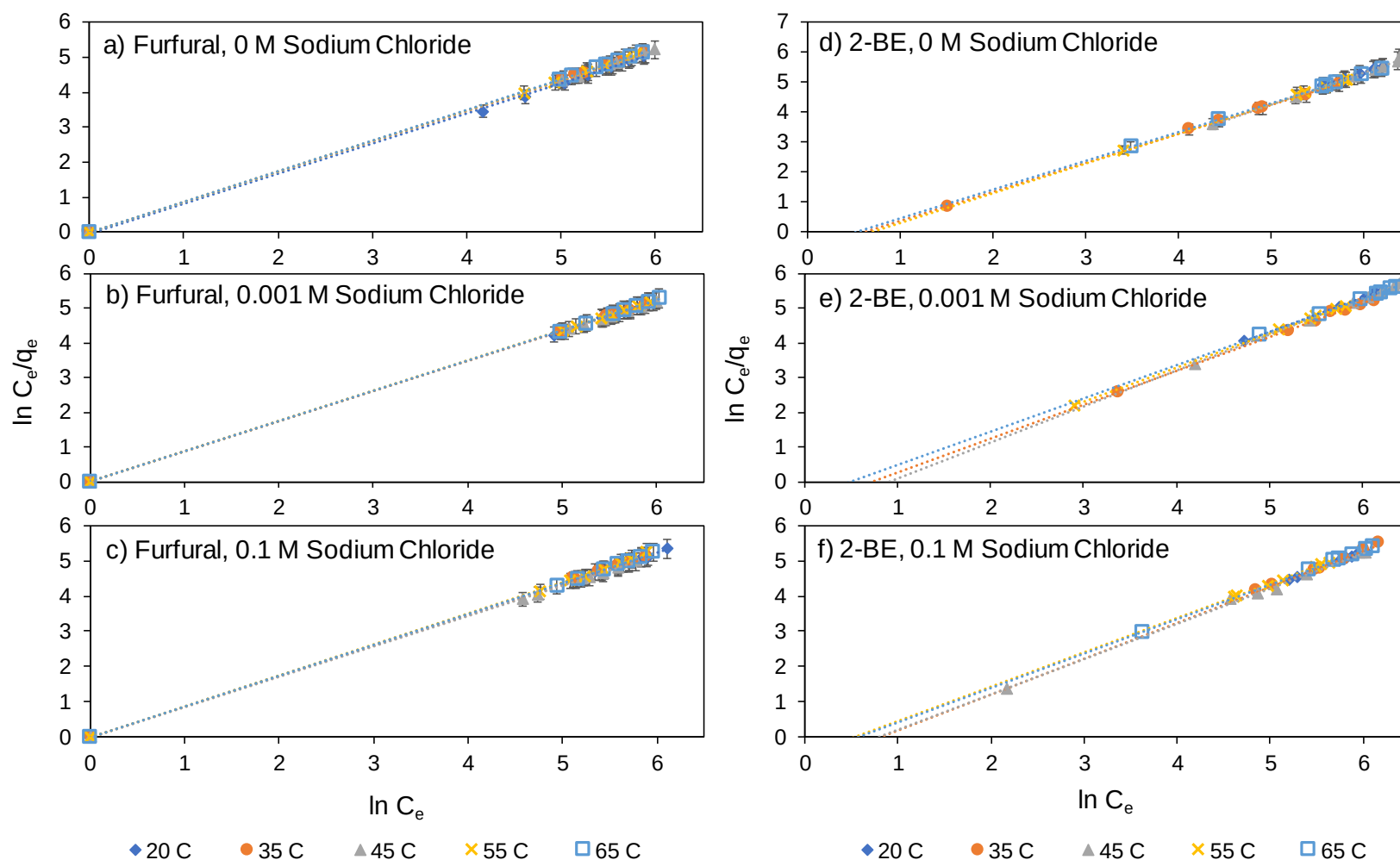


Figure 2-7. Linearized Redlich-Peterson isotherm for furfural and 2-BE at all temperatures tested (20, 35, 45, 55, and 65°C) with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride. Furfural data is displayed in parts a, b, and c, with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride, respectively. 2-BE data is displayed in parts d, e, and f, with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride, respectively.

Table 2-2. Redlich-Peterson constants for the adsorption furfural and 2-BE onto GAC at 20, 35, 45, 55, and 65 °C with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride.

Constituent	[Sodium Chloride] (mol L ⁻¹)	T (°C)	Langmuir		
			β	K_{RP} (L g ⁻¹)	$\frac{K_{RP}}{a_R}$
Furfural	0	20	0.857	1.04	29.2
		35	0.862	0.997	322
		45	0.867	1.00	228
		55	0.872	1.01	83.7
		65	0.873	1.00	557
	0.001	20	0.868	1.00	557
		35	0.865	0.999	20,000
		45	0.865	1.00	1001
		55	0.871	1.03	295
		65	0.873	1.01	113
	0.1	20	0.871	1.03	324
		35	0.864	0.997	285
		45	0.859	1.01	126
		55	0.879	1.02	63.5
		65	0.875	1.09	12.5
2-BE	0	20	0.951	1.48	3.79
		35	0.965	1.80	3.06
		45	1.07	3.09	2.74
		55	0.992	1.94	2.93
		65	0.963	1.65	3.29
	0.001	20	0.973	1.74	3.14
		35	0.969	2.001	2.88
		45	1.04	2.58	2.72
		55	0.981	1.87	2.99
		65	0.955	1.57	3.47
	0.1	20	0.964	1.74	3.13
		35	1.01	2.24	2.78
		45	0.998	2.19	2.79
		55	0.971	1.68	3.23
		65	0.974	1.75	3.12

Isosteric Heats of Adsorption

Van't Hoff plots for furfural at 0, 0.001, and 0.1 mol L⁻¹ of sodium chloride are displayed in Figure 2-8. Isosteric heats of adsorption (Q_{iso}) for each GAC loading were calculated using the Van't Hoff plots and Equation 2-6, where R is the universal gas constant, T is the temperature, and K_D is the partitioning coefficient of the adsorbate [93]. For all weights of GAC used, at 0 and 0.001 mol L⁻¹ sodium chloride, the Van't Hoff plots display negative slopes, indicating that the adsorption reaction is endothermic, thus requiring energy for the adsorption to take place. For solutions with 0.1 mol L⁻¹ sodium chloride, all weights of GAC displayed negative slopes with the exception of the plots for 0.4 (3.2 g L⁻¹) and 0.5 g (4 g L⁻¹) GAC. For these doses of GAC, the Van't Hoff plot displays a positive slope, indicating an exothermic reaction. Sahu *et al.* have previously reported furfural adsorption as an endothermic process, with the isosteric heat of adsorption as -12.45 kJ mol⁻¹ in a solution of 10 g L⁻¹ commercial grade activated carbon and no sodium chloride in solution [59]. The differences in these values may be attributed to the amount of GAC in solution. At the lower weights of GAC tested in this study, there are less adsorption sites, requiring more energy input for furfural adsorption. Table 2-3 displays furfural Q_{iso} values for each weight of GAC and sodium chloride concentration tested in this study.

$$Q_{iso} = R \left[\frac{d(\ln K_D)}{d\left(\frac{1}{T}\right)} \right]_{loading} \quad \text{Equation 2-6}$$

Table 2-3 also displays Q_{iso} values for 2-BE at all salt concentrations. Van't Hoff plots used to determine Q_{iso} may be found in Figure 2-9. The adsorption processes with 2-BE are endothermic when there is 0.001 mol L⁻¹ sodium chloride in solution. For all doses of GAC tested with 0 and 0.1 mol L⁻¹ sodium chloride, the adsorption process of 2-BE onto GAC is exothermic.

Competitive adsorption of 2-BE and furfural onto GAC

Figure 2-10 displays percent removal of 2-BE and furfural at 20 and 65°C and salt concentrations of 0, 0.001, and 0.1 mol L⁻¹ sodium chloride with both contaminants in solution. The Langmuir and Freundlich plots are displayed in the Figure 2-11 and Figure 2-12, respectively, and Table 2-4 contains the resulting Langmuir and Freundlich constants. At 65°C, more 2-BE appears to be adsorbed than furfural. This is due to the poor stability of 2-BE at high temperatures. At room temperature, a greater percentage of furfural is removed than 2-BE. This indicates that furfural adsorption onto GAC occurs more preferentially than 2-BE, since heat stability is not a factor in this case. This was not expected since GAC favors adsorption of nonpolar compounds [60]. Furfural is a polar molecule, while 2-BE has both polar and nonpolar ends. However, at low temperatures and low concentrations, 2-BE is more susceptible to aggregate [89, 99]. If the 2-BE is aggregating at these lower temperatures, less 2-BE will adsorb to the GAC.

When GAC is used in water treatment for hydraulic fracturing fluids, 2-BE and furfural are of importance because their degrees of adsorption vary when other

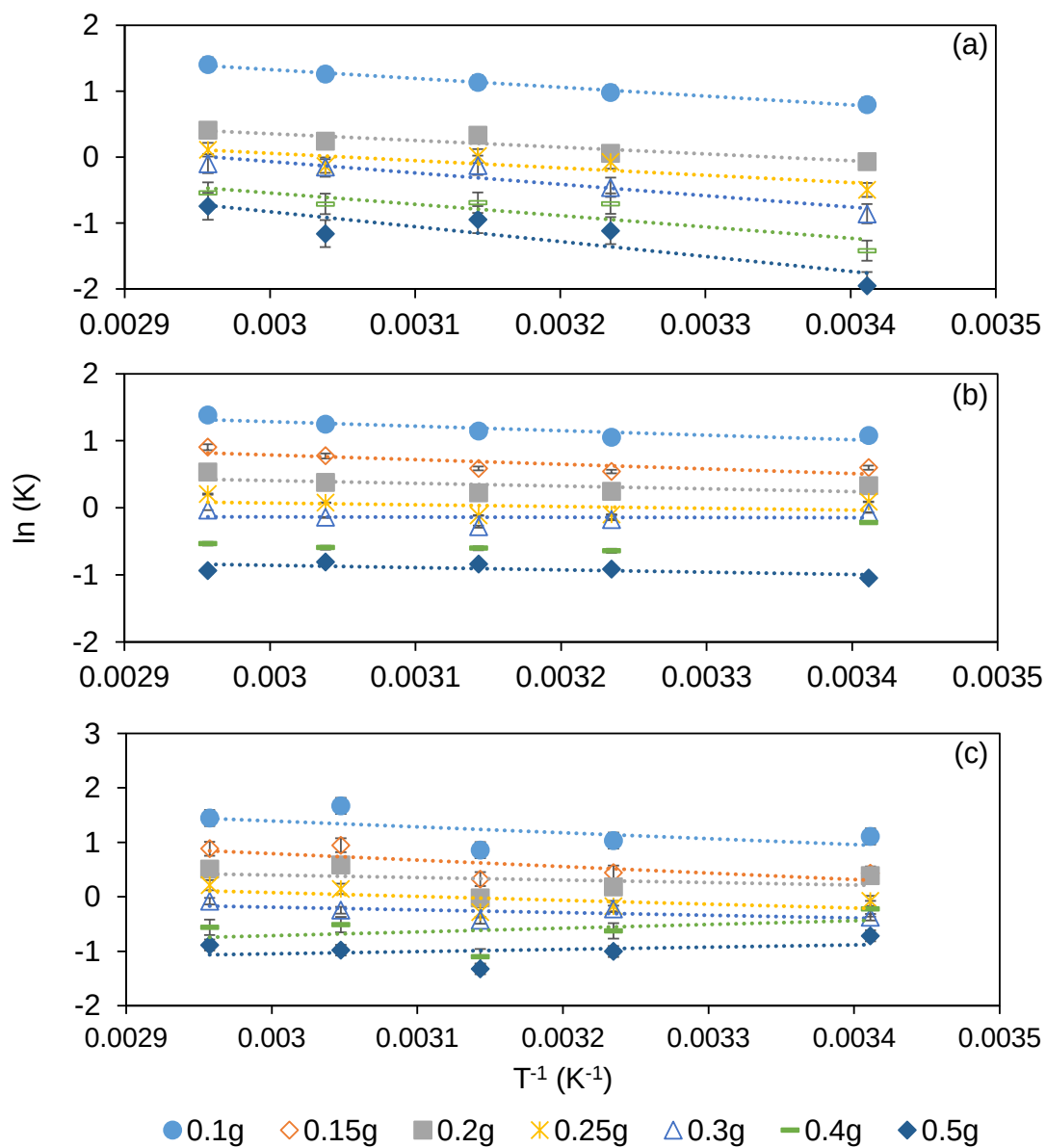


Figure 2-8. Van't Hoff plot for furfural at a) 0 mol L^{-1} sodium chloride, b) 0.001 mol L^{-1} sodium chloride, and c) 0.1 mol L^{-1} sodium chloride.

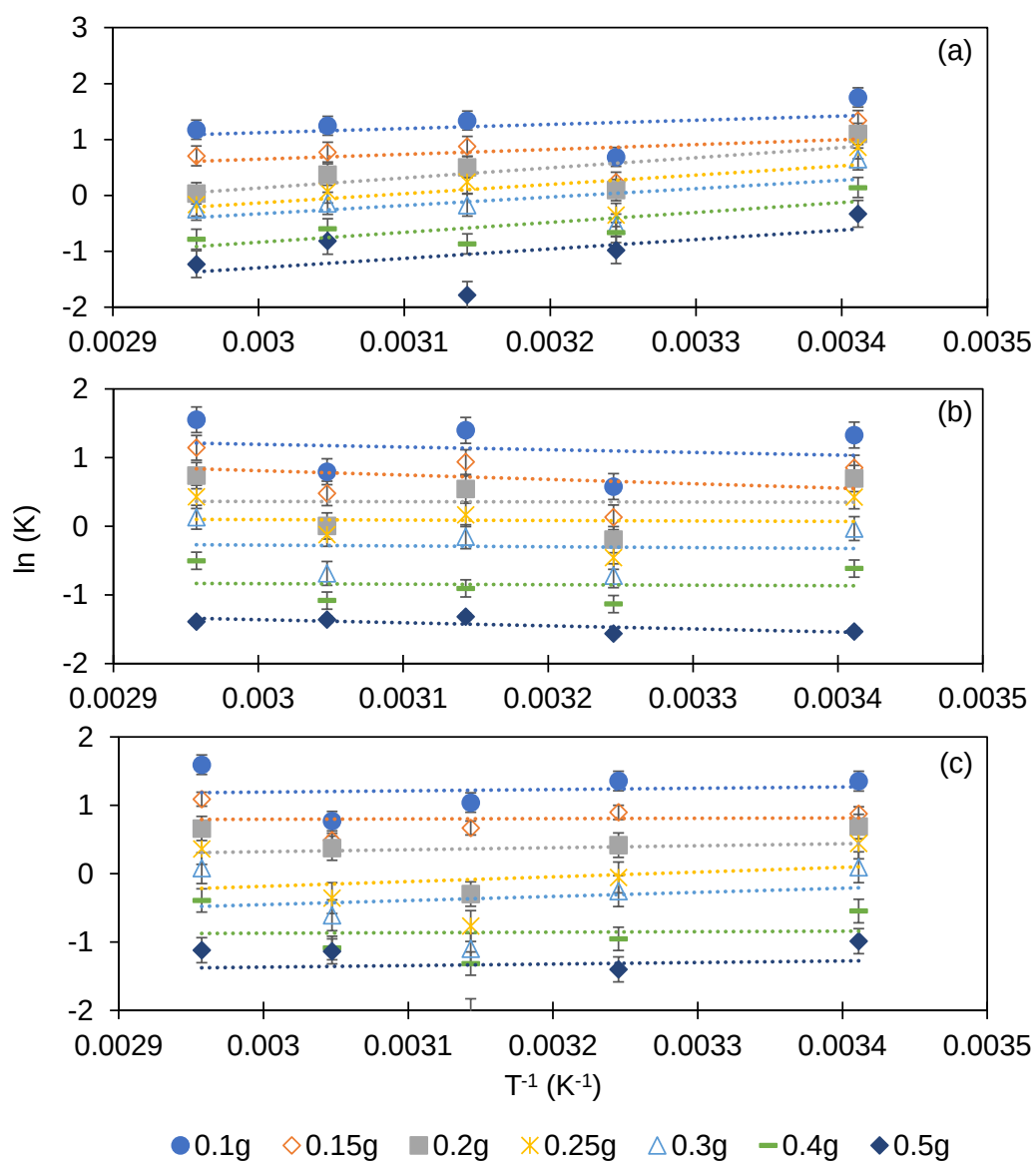


Figure 2-9. Van't Hoff plot for 2-BE at a) 0 mol L^{-1} NaCl, b) 0.001 mol L^{-1} NaCl, and c) 0.1 mol L^{-1} NaCl.

Table 2-3. Isosteric heats of adsorption for 2-BE and furfural with 0, 0.001, 0.1 mol L⁻¹ of sodium chloride.

[Sodium Chloride] (mol L ⁻¹)	Mass of GAC (g)	Q _{iso} (kJ mol ⁻¹)	
		Furfural	2-BE
0	0.1	11.09	6.20
	0.15	10.23	7.30
	0.2	8.49	15.0
	0.25	9.30	13.8
	0.3	14.28	12.5
	0.4	14.26	14.8
	0.5	18.85	14.0
0.001	0.1	5.65	-3.30
	0.15	5.73	-5.27
	0.2	5.10	-0.166
	0.25	4.91	-0.551
	0.3	3.72	-0.995
	0.4	2.86	-0.565
	0.5	2.87	-3.66
0.1	0.1	9.01	1.55
	0.15	9.90	0.423
	0.2	3.77	2.42
	0.25	5.87	5.80
	0.3	4.14	4.97
	0.4	-5.70	0.611
	0.5	-3.45	1.84

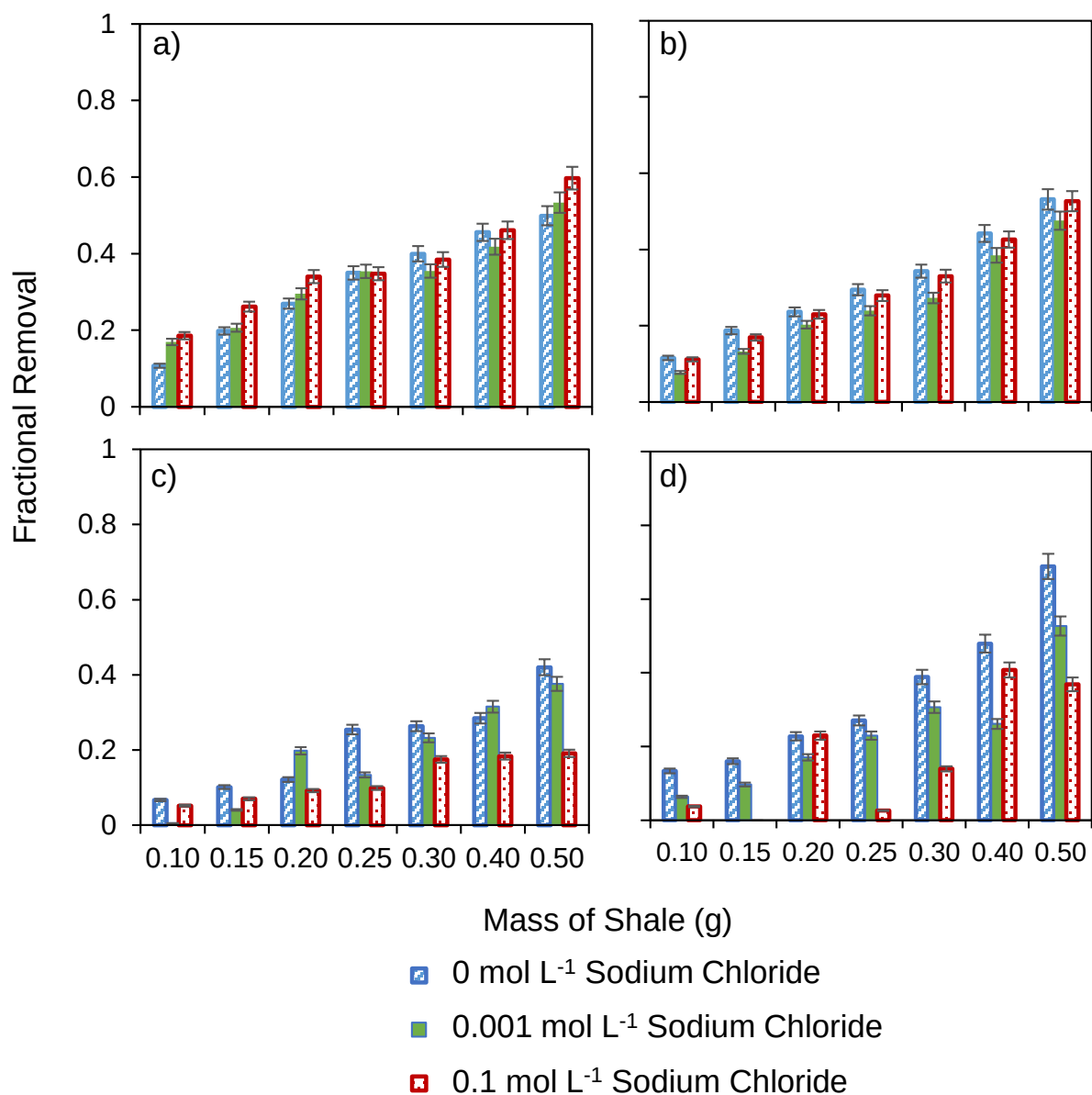


Figure 2-10. Percent recoveries of experiments with both furfural and 2-BE in solution at 0, 0.001 0.1 mol L⁻¹ sodium chloride. The conditions in each experiment are: a) furfural, 20°C, b) furfural, 65°C, c) 2-BE, 20°C, and d) 2-BE, 65°C.

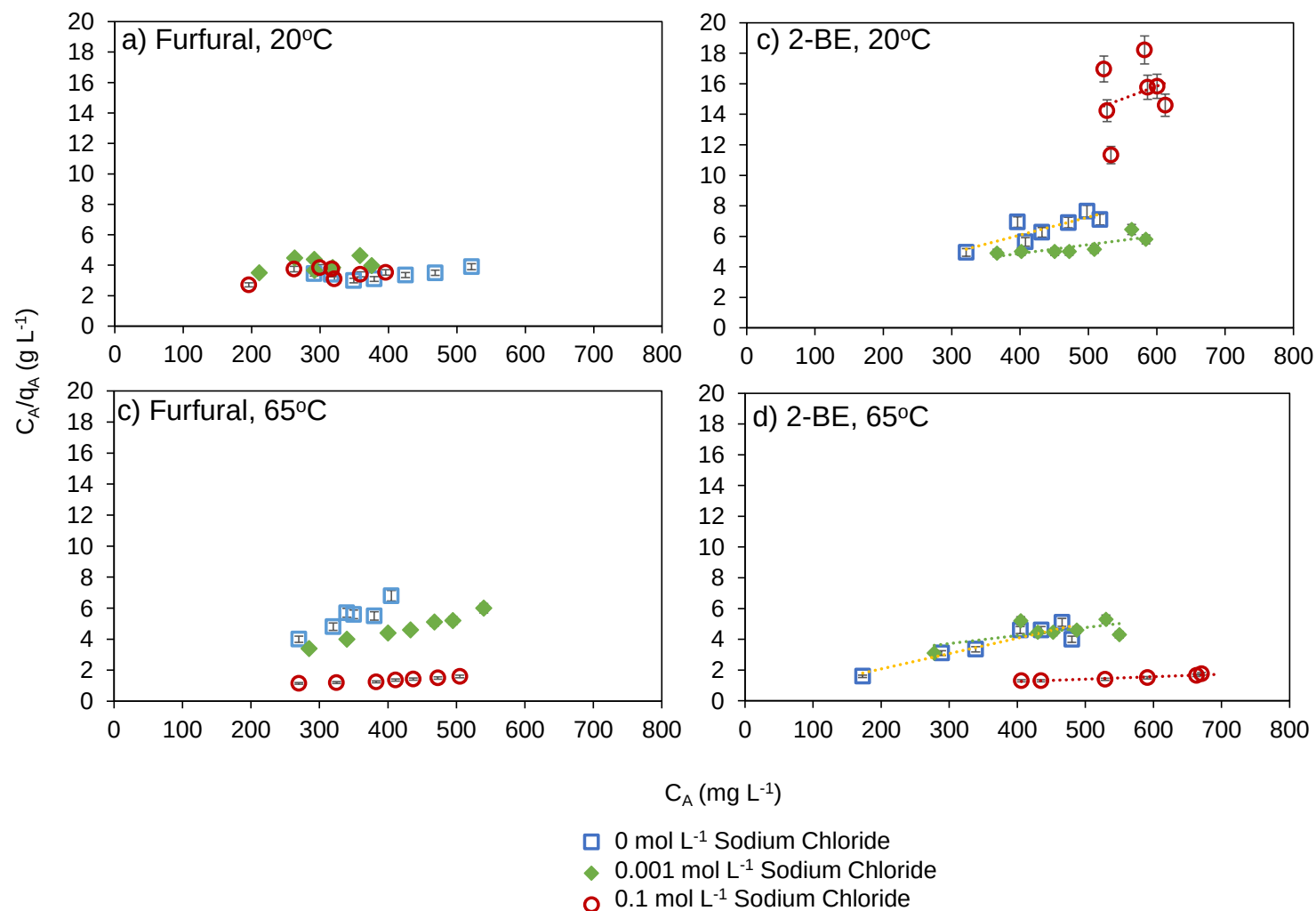


Figure 2-11. Langmuir isotherms for competitive adsorption experiments with both furfural and 2-BE in solution at 20 and 65°C with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride in solution.

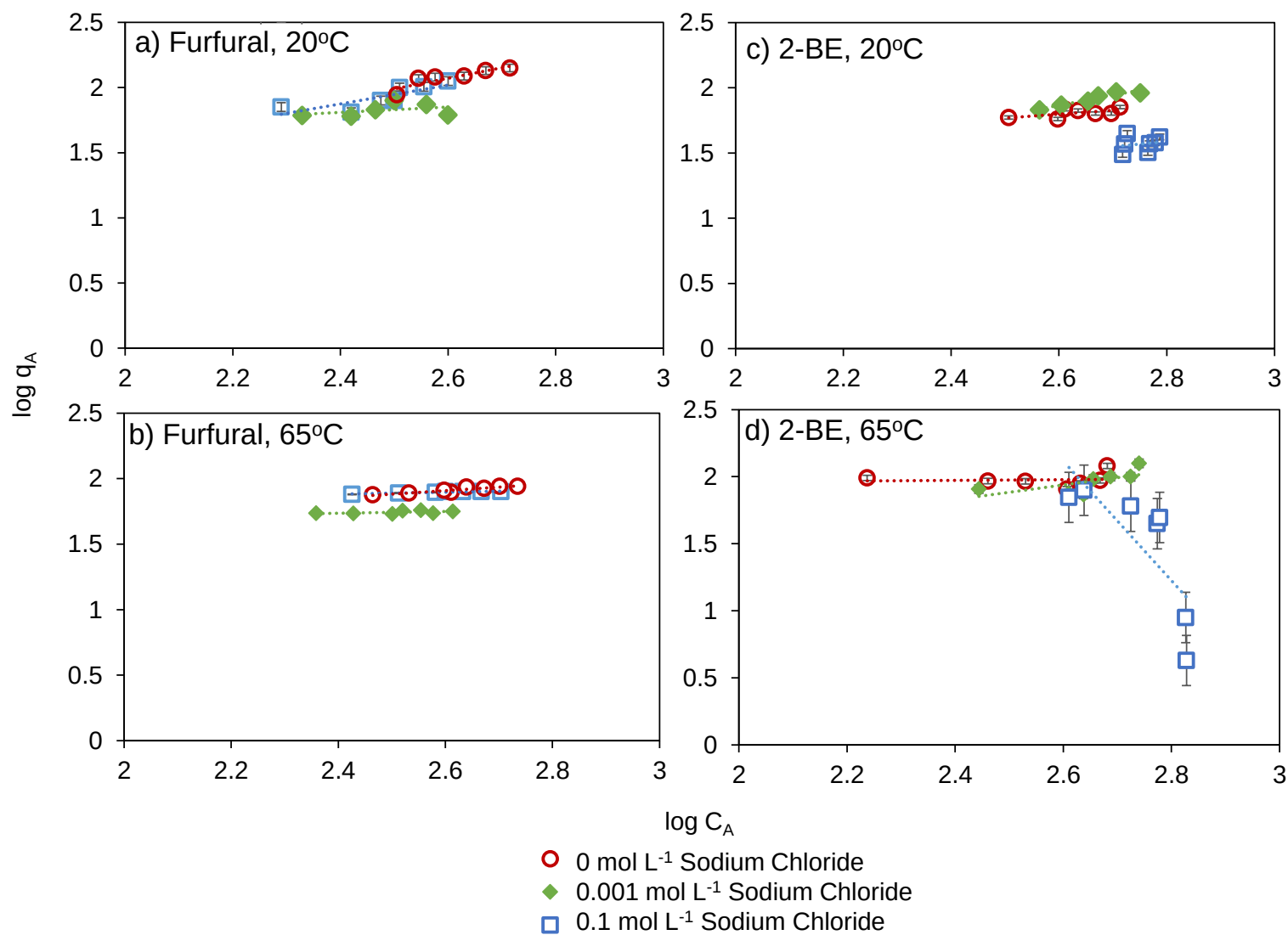


Figure 2-12. Freundlich isotherms for competitive adsorption experiments with both furfural and 2-BE in solution at 20 in (a) and (c) and 65°C in (b) and (d) with 0, 0.001, and 0.1 mol L⁻¹ sodium chloride in solution.

Table 2-4. Langmuir and Freundlich isotherm parameters for experiments containing both furfural and 2-BE at 20 and 65°C and 0, 0.001, and 0.1 mol L⁻¹ sodium chloride.

[Sodium Chloride] (mol L ⁻¹)	Constituent	T (°C)	Langmuir			Freundlich		
			Q_M (mg g ⁻¹)	K_L (x 10 ⁻³ L mg ⁻¹)	R^2	$\frac{1}{n}$	K_F $\left(\left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^{\frac{1}{n}}\right)$	R^2
0	Furfural	20	530	5.84	0.32	0.808	0.956	0.85
		65	106	9.74	0.97	0.194	27.2	0.72
	2-BE	20	82.9	17.1	0.71	0.204	18.9	0.15
		65	101	11.8	0.84	6.00 x 10 ⁻⁴	94.9	0.19
0.001	Furfural	20	371	14.9	0.18	0.707	1.56	0.69
		65	516	2.06	0.94	0.117	38.8	0.77
	2-BE	20	59.4	204	0.18	0.283	6.21	0.17
		65	648	1.62	0.95	-4.42	3.92 x 10 ¹³	0.61
0.1	Furfural	20	328	19.4	0.16	0.759	0.972	0.71
		65	58.1	18.3	0.94	0.0614	39.2	0.18
	2-BE	20	1570	1.03	0.62	0.665	1.53	0.90
		65	164	13.4	0.46	0.316	13.9	0.24

many of the tested conditions, 2-BE has less adsorption capacity than furfural. Rather than adsorbing to the GAC, the 2-BE forms aggregates with itself at low temperatures. The critical micelle concentration for 2-BE is approximately a mole fraction of 0.02; however, temperature can alter the critical micelle concentration especially in water-rich solutions and reportedly does not have a distinct critical micelle concentration [44, 89, 100, 101]. This leaves more open sites on the GAC for the furfural to adsorb. Despite the known surfactant properties of 2-BE, at high temperatures, 2-BE appears to adsorb to GAC more preferentially than furfural.

Conclusion

In summary, hydraulic fracturing chemical additives furfural and 2-BE interact differently with GAC and shale and are very dependent on the temperature of the solutions that they are in. Neither 2-BE nor furfural adsorb to shale rock. This implies that these chemical additives may be able to migrate through shale formations and into water resources. GAC may be used to adsorb 2-BE and furfural from hydraulic fracturing fluids. Adsorption onto GAC occurs within 23 hours for both contaminants. Adsorption is even quicker for 2-BE, occurring within 4.75 hours. According to the Redlich-Peterson isotherms, 2-BE adsorption onto GAC reduces to the Langmuir model, while furfural adsorption is approaching the Langmuir isotherm. 2-BE and furfural compete for adsorption sites. At lower temperatures, furfural adsorption takes place to a greater degree than 2-BE adsorption. 2-BE adsorption is influenced by temperature and salt concentration. High temperatures are best for 2-BE adsorption, which is most likely due to 2-BE's surfactant properties and poor stability at high temperatures.

CHAPTER 3
DEGRADATION OF HYDRAULIC FRACTURING ADDITIVE 2-
BUTOXYETHANOL USING HEAT ACTIVATED PERSULFATE IN THE
PRESENCE OF SHALE ROCK

Abstract

Changes in fluid composition during hydraulic fracturing for natural gas production can impact well productivity and the water quality of the fluids returning to the surface during productivity. Shale formation conditions can influence the extent of fluid transformation. Oxidizers, such as sodium persulfate, likely play a strong role in fluid transformation. This study investigates the oxidation of 2-butoxyethanol (2-BE), a surfactant used in hydraulic fracturing, by sodium persulfate in the presence of heat, pH changes, Fe (II), and shale rock. Increasing temperature and Fe (II) concentrations sped up 2-BE oxidation, while pH played little to no role in 2-BE degradation. The presence of shale rock impeded 2-BE oxidation with increasing shale concentrations causing decreasing pseudo-first-order reaction rate constants to be observed in comparison to oxidation without iron or shale at 55°C. Over the course of reactions containing shales, dissolved solids were tracked to better understand how reactions with minerals in the shale impact water quality.

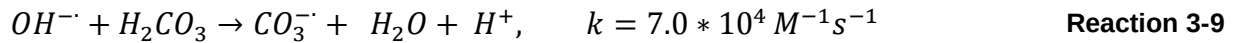
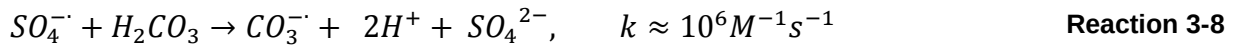
Introduction

Extracting oil and natural gas from unconventional shale reservoirs requires hydraulic fracturing with high volumes of water mixed with chemical additives [7, 102]. Chemical additives include surfactants and oxidizing breakers that likely transform during the fracturing process [32, 103]. Transformation of additives and shale may impact the flowback and produced water quality that returns to the surface during natural gas production.

Hydraulic fracturing wastewater spills are a concern due to potential contamination of water aquifers. While many chemicals have been identified in hydraulic fracturing flowback and produced fluids, the transformed fluids are the source of pollution when spills occur. Surfactants are consistently found in hydraulic fracturing waters [32]. 2-BE is a commonly identified surfactant found in hydraulic fracturing additives including the foaming agent, Revert Flow [17, 23, 41, 46, 52, 104-106]. Revert Flow improves production by decreasing surface tension, thus preventing water blocking during the HF process. While the harsh physical conditions downhole may stimulate organic additive transformation, HF operators also use strong oxidizing agents such as persulfate salts [17, 107, 108]. Hydraulic fracturing companies use sodium persulfate as a breaker to decrease fluid viscosity and decompose gelling agents [67]. Persulfate has the potential to speed up and enhance transformations, therefore; persulfate is a key component to understanding how additives transform during the hydraulic fracturing treatment of a well.

Certain conditions faced in the wellbore may activate persulfate and speed up transformations caused by oxidation reactions [34]. The extent of the oxidation reactions are dependent upon the well conditions. The persulfate anion has an oxidation potential of 2.01 V, which was been determined by Reaction 3-1 [109]. Persulfate may be activated, using heat, as shown in Reaction 3-2 [109, 110], to form sulfate radicals, which have greater oxidation potential ($E^0 = 2.7$ V) than the persulfate anion. The sulfate radical is non-selective and may react with any matter in solution, including water. The sulfate radical reacts with water according to Reaction 3-3 [66, 110, 111], which causes a decrease in pH as the reaction proceeds. Reaction 3-3 also forms the hydroxyl radical one of the most powerful oxidizing agents ($E^0 = 2.81$ V) [112, 113]. In basic conditions, the sulfate radical may react with hydroxide to form a hydroxyl radical. Although hydraulic

fracturing companies add acid to their fluids, the fluid pH may vary as the fluids contact the shale formation. Once the shale formation has been contacted, other reactions may occur that impede or enhance persulfate activation. Certain metals and anions in the shale have different impacts on persulfate reactions. For example, transition metals, especially iron, can activate persulfate according to Reaction 3-5 and increase the production of sulfate radicals [65, 66]. However, certain anions, such as carbonates, can negatively impact persulfate oxidation. In acidic hydraulic fracturing conditions, carbonates that dissolve from the minerals of the shale are likely in the form of carbonic acid as shown in Reactions 3-6 and 3-7. The sulfate and hydroxyl radicals may react with carbonic acid to form the carbonate radical ($E^0 = 1.78$ V at pH 7.0), as shown in Reactions 3-8 and 3-9 [114-116]. Despite having an oxidation potential, carbonates are considered to also have scavenging effects on persulfate oxidation [109, 111] because they can decrease the amount of organic that is degraded in solution [117, 118].



Addition of shale to persulfate reactions in the hydraulic fracturing environment has not been previously investigated. Persulfate activation through increased formation temperatures and pressures has been previously investigated by the authors [119]. As persulfate activation was observed under hydraulic fracturing conditions, the shale constituents may impede or enhance the activation. For example, shale contains minerals that contain iron, which may activate persulfate and enhance oxidation of additives. Minerals found in shale include pyrite, hematite, goethite, and limonite. Shale also contains minerals, such as chlorite and gypsum, which may prevent oxidation of additives because these minerals contain carbonates.

The objective of this study is to address the potential persulfate activation using shale rock and the impact it has on 2-BE degradation and water quality. Fluid conditions that mimic those used during a fracture, including temperature, pH, iron, and shale rock,

are systematically introduced. Further impacts persulfate usage has on hydraulic fracturing water quality are evaluated through quantification of metals leached into solution during shale-activated reactions. Determination of 2-BE oxidation reactions with persulfate in the presence of shale will enable a better understanding of the impacts persulfate utilization has on flowback and produced water quality.

Materials and Methods

Chemicals

Solutions were prepared using deionized water (Milli-Q Plus purification system, Darmstadt, Germany). Chemical used, including 2-BE (95%), Optima grade dichloromethane, ferrous sulfate (>99%), hydrochloric acid (35-38%), sodium persulfate (>98%), TraceMetal™ grade nitric acid, sodium persulfate (>98%), sodium bicarbonate (>99%), potassium iodide (>99%), and SPEX CertiPrep™ calibration standard 2 without mercury (5% nitric acid), were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). Revert Flow (RF) was received from Weatherford International (Houston, Texas, USA).

Shale Rock

WV-7 shale rock used in this study was obtained from the Marcellus shale play at a depth of 6621.1 m (West Virginia Geological Survey, Morgantown, WV 26508, USA). The shale was crushed with a mortar and pestle and sieved to a mean diameter of 1.00-2.00 mm using No. 10 and 18 sized meshes. Bulk shale mineralogy was determined using X-Ray diffraction (XRD) and verified using acid digestion and inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. Diffraction patterns were collected using a Panalytical Empyrean XRD with Cu source (Almelo, Netherlands) and ICP-OES data was collected with a ThermoFisher Scientific iCAP DUO 7400 (Waltham, MA 02451). Figure A1 in the appendix displays the resulting diffractogram of the unreacted WV7 shale and Figure 3-1 displays the ICP digestions results. Bulk mineralogy of the shale is listed in Table 3-1 and contained calcite, dolomite, muscovite-2M1, rubidium zinc silicon oxide, pyrite, and quartz. Microscope observations were made using a Zeiss scanning electron microscope (SEM) (model EVO-MA15) equipped with an Energy-dispersive X-ray (EDS) detector (Bruker, model X Flash 6130).

Batch Oxidation Experiments

Chemicals used and their supplier are listed in SI. In HF practices, surfactants are used in total concentrations ranging from 500 to 1800 mg L⁻¹ [17], while the HF additive supplier suggested Revert Flow concentration of 1 gallon Revert Flow per 1000 gallons water [41]. Revert Flow was determined to be 1.0328 g mL⁻¹ and contained 3.31wt% 2-BE [41]. Therefore, the 2-BE concentration in HF fluids may be as low as 34 mg L⁻¹. Solutions in this study contained 120 mg L⁻¹ 2-BE for ease of measurement and were prepared 12 hours prior to experiments, which allowed for overnight mixing in amber jars. Fe (II) concentrations used to activate persulfate ranged from 0 to 100 mg L⁻¹. Fe (II) was

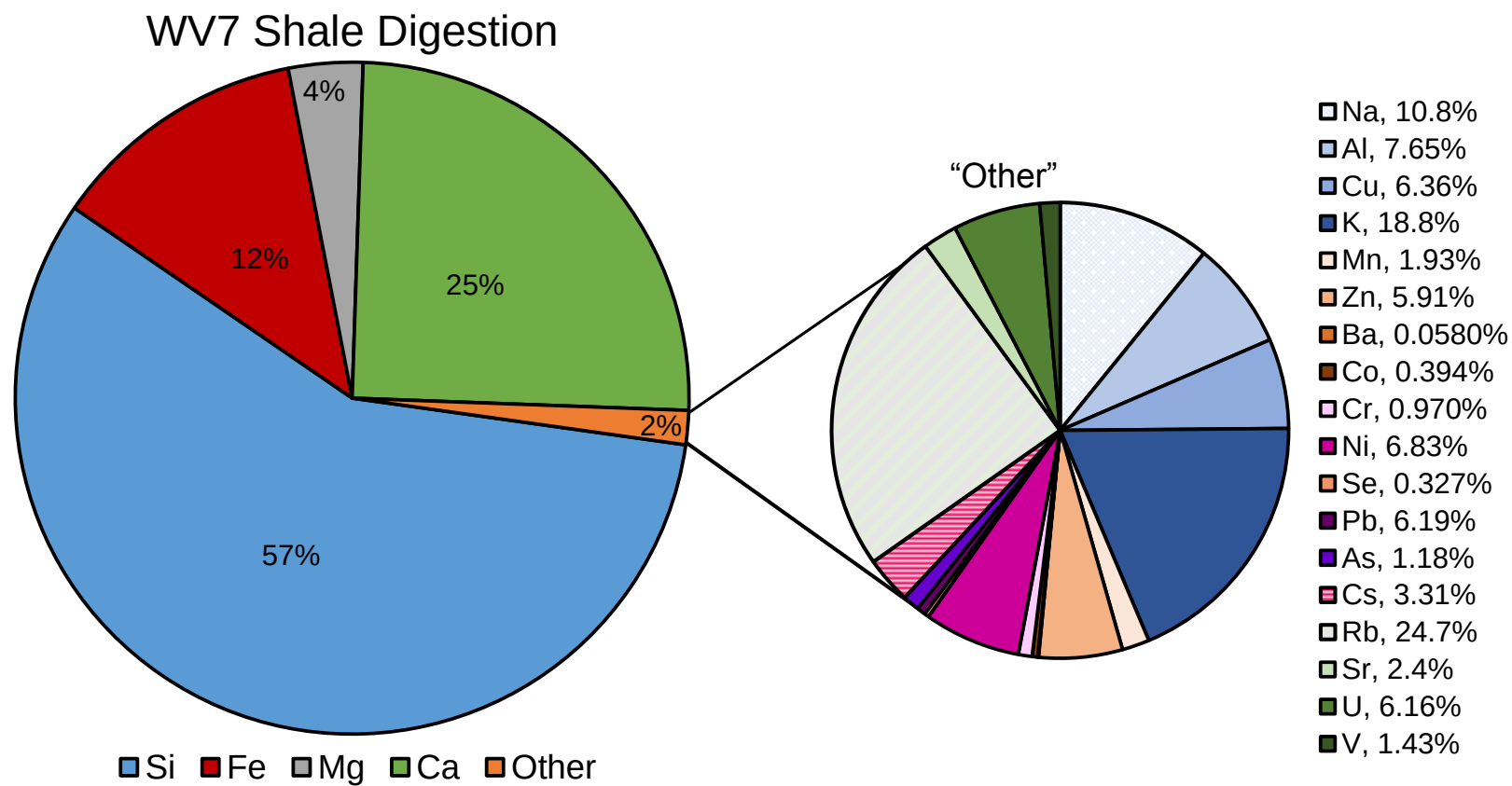


Figure 3-1. Percent composition of elements detected in acid digestion and ICP analysis of unreacted WV7 shale.

Table 3-1. WV7 Shale Minerology.

Mineral Name		Approximate Designation
Calcite		Major
Dolomite		Minor
Muscovite – 2M1		Minor
Rubidium Zinc Silicon Oxide		Trace
Pyrite		Minor
Quartz		Major
Designation		
Major	>25%	
Minor	10-25%	
Trace	<10% clearly in sample	

used because 2+ is the same oxidation state as the pyrite found in the WV shale rock. Acidic conditions such as those used in the industry, 0.012 to 15% [23, 120-122], were achieved using 0.07% hydrochloric acid as listed by FracFocus [34]. pH was measured with a Fisher Scientific Accumet XL600 benchtop pH meter (Pittsburgh, PA 15275, USA). Experiments were performed in triplicate using 250-mL volumes in capped 1-L amber borosilicate jars. The jars were placed in a shaking water bath (New Brunswick Scientific Co, Inc, Model G76, Edison, NJ USA) 12 hours prior to experiment start at temperatures of 20, 35, 45, 55, and 65°C. Experiments were spiked with a concentrated solution of stock sodium persulfate to a final concentration of 21 mmol L⁻¹ to initiate experiments. Fracing fluids can return to the surface of the well from the first day after fluids are injected and may continue to flow out for several years following injection [123]. However, 2-BE was degraded much faster than this time frame. Therefore, experiments were carried out for 8 hours, with the exception of experiments performed at 20, 35, and 45°C because persulfate activation was slower at these temperatures than at higher temperatures. Samples were taken at designated times between 0 and 480 minutes in 10-mL volumes. Samples were immediately extracted for 2-BE [41] and analyzed for pH, TOC, and persulfate concentration. Mass balance calculations were performed to minimize sampling effects. Control experiments were performed without persulfate to account for the 2-BE oxidation at high temperatures and possible 2-BE absorption onto shale or Fe (II).

Sample Analysis

2-BE concentration was determined using an Agilent 7890B gas chromatograph (GC) (Santa Clara, CA 95051) equipped with a splitter that connected to a 5977A Mass Selective spectrometer (MS) and a flame ionization detector (FID), allowing simultaneous MS and FID analysis. The liquid-liquid extraction procedure and GC parameters have been previously described [41]. In short, 3-mL of sample was pipetted into a scintillation vial containing 3-mL of methylene chloride and vortexed using a 115V Mini Vortex Mixer (Fisher Scientific, Pittsburgh, PA 15275). The solution was separated using a 6-mL polypropylene syringe (Fisher Scientific, Pittsburgh, PA 15275) and the methylene chloride was collected in a separate vial. The extraction procedure was repeated three times. Calibration curves were made using known 2-BE concentration dissolved in methylene chloride. Extractions were repeated with hexane to detect additional reaction byproducts as different compounds have different affinities for different solvents. The GC-MS-FID was operated in split-less mode and equipped with an Agilent 7963 auto-sampler and an Agilent J&W DB-1 (30-m x 0.25-mm ID x 0.25-μm film thickness) capillary column. Ultra-high purity helium (Airgas Corporation, Knoxville, TN 37921) was used as the carrier gas and maintained at 2.5 mL min⁻¹. Samples (2.5-μL injection volume) were analyzed in triplicate. The GC was held at an initial temperature of 40°C for 4 minutes, and the temperature was ramped up 10°C min⁻¹ to 180°C, and held at 180°C for 3 minutes before ramping back down. The limit of detection of this method is 0.957 mg L⁻¹ 2-BE [41].

Total Organic Carbon (TOC) was measured using a TOC-LCSH/CSN series standalone analyzer equipped with an ASI autosampler and a high sensitivity catalyst (Shimadzu, Kyoto, Japan). TOC standards were made using a known amount of 2-BE in 2.5% hydrochloric acid. TOC was determined using the difference between the total carbon (TC) and inorganic carbon (IC) concentrations.

A modified spectrophotometric/iodometric method was used to measure the persulfate anion [124, 125]. Briefly, 166 g L⁻¹ KI and 12 g L⁻¹ NaHCO₃ were added to DI water and mixed until all components dissolved. Depending on the anticipated persulfate concentration, 20 to 50-μl of sample was added to a scintillation vial containing 2.5-mL of the KI/NaHCO₃ solution. The mixture reacted for 20 minutes and measured using a UV/Vis spectrophotometer (Thermo Fisher Scientific, Model Evolution 600 Madison, WI 53711, US) at the maximum wavelength of 352 nm. Standards were prepared by pipetting 20-μl of a 22-mM persulfate solution into 2.5, 3, 4, 5, and 7.5 mL aliquots of the KI/NaHCO₃ solution.

Metals leaching from the shale were measured using ICP-OES. Concentrations were determined by comparison to serial dilutions of a standard solution containing 10 mg L⁻¹ of the following metals: Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Pb, Rb, Se, Sr, Ti, U, V, and Zn.

Statistics

For all sample analysis, standard error (SE) of the data was calculated using Equation 3-1, where SE is standard error, *s* is sample standard deviation, and *n* is the number of observations. SE is represented by error bars in the Figures. Statistical analysis was performed using JMP Pro software from SAS, version 12.0.1 (Cary, NC 27516) to determine if the mean observed reaction rate constant for each experimental condition was significantly different from the other conditions tested. One-way analysis of variance (ANOVA) paired with a post-hoc Tukey-Kramer honest significant difference (HSD) test was used ($\alpha = 0.05$).

$$SE = \frac{s}{\sqrt{n}}$$

Equation 3-1

Results and Discussion

Temperature Effects

Figure 3-2 displays the degradation of 2-BE in water at 20°C without persulfate in an amber jar (pH 6). Previous studies have shown that 2-BE is susceptible to photo-degradation at 20°C when experiments are performed in clear glassware [41, 126]. Figure 3-2 shows little to no 2-BE degrades over 22,500 minutes, or 15.6 days, in the dark environment of the amber jar, which is similar to well-bore conditions. Figure 3-3 shows the degradation of 2-BE with the addition of 21 mM persulfate at 20°C (a) and the pseudo-first-order plot in (b). Figure 3-3 (a) shows 65% of the initial 2-BE concentration degraded after 22,500 minutes. The plot of concentration versus time displayed a greater R² value than the natural log of the concentration versus time plot, which indicates that the reaction order with respect to 2-BE is pseudo zero-order at room temperature with a rate constant of 2.24 x10⁻⁵ M s⁻¹. Figure 3-4 displays the TOC, pH and persulfate concentration after 22,500 minutes. TOC and persulfate decreased by 22 and 15%, respectively, while the

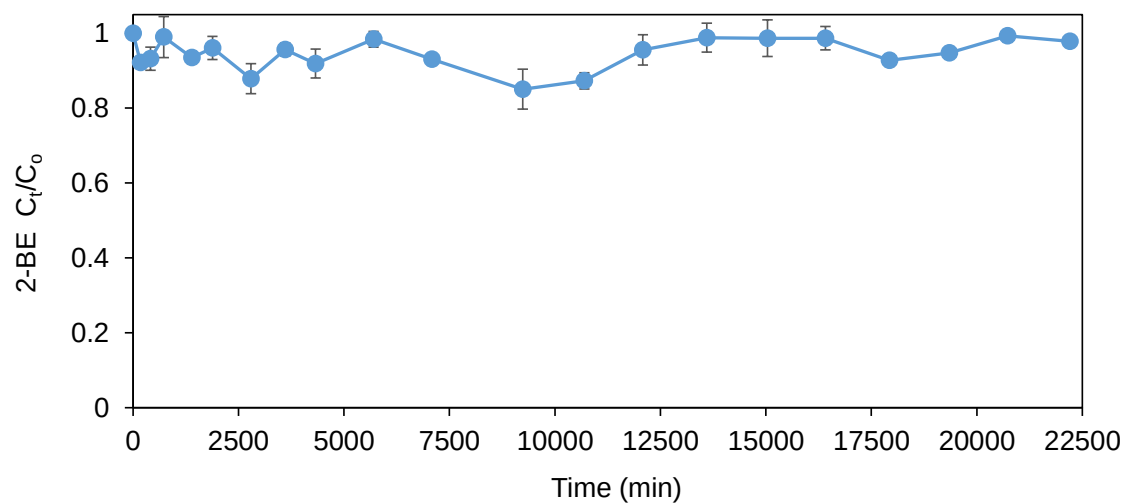


Figure 3-2. Control experiments containing 2-BE in water at 20°C (no persulfate, initial pH 6). The concentration of 2-BE does not decrease over 375 hours.

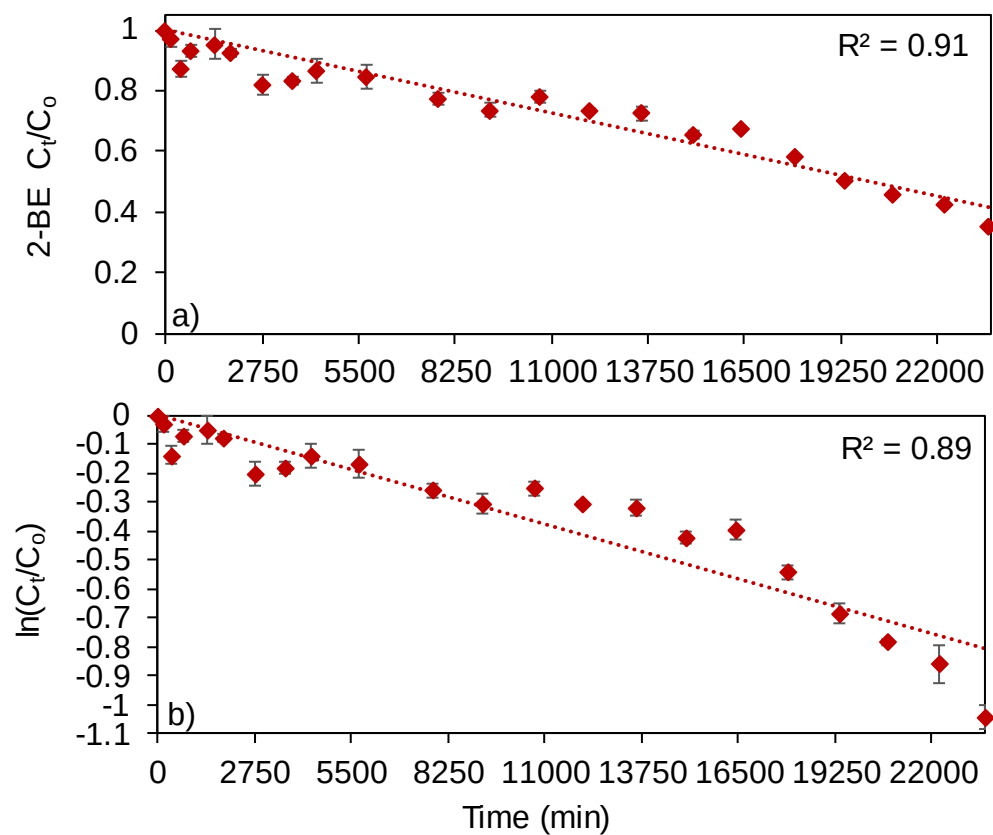


Figure 3-3. Degradation of 2-BE at 20°C with 21 mmol L⁻¹ persulfate (initial pH 6).

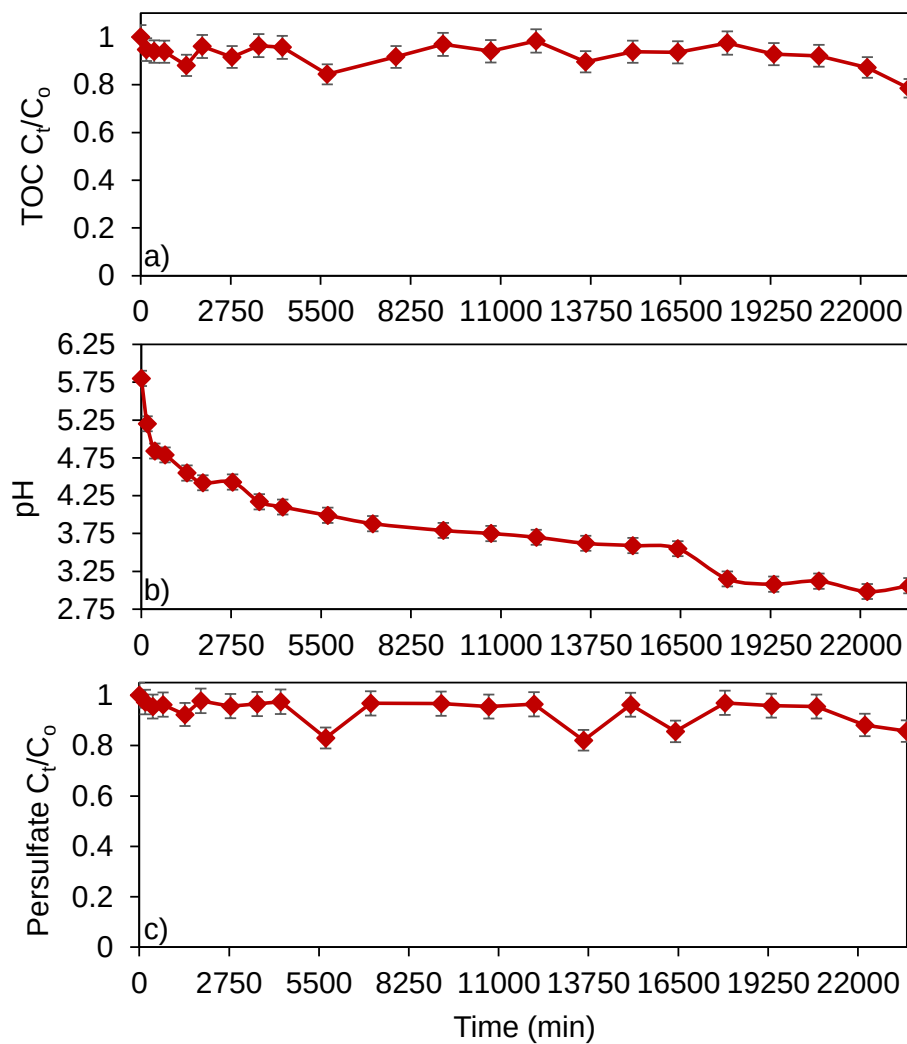


Figure 3-4. Decrease in (a) TOC, (b) pH, and (c) persulfate over the course of 2-BE degradation at 20°C with and initial dose of 21 mmol L⁻¹ persulfate (initial pH 6).

pH decreased from 6 to 3.06. The persulfate-induced oxidation of 2-BE at low temperatures suggests the persulfate anion may play a role in 2-BE degradation. The persulfate reduction half-reaction is shown in Reaction 3-1. The direct oxidation of 2-BE by the persulfate anion is feasible as this strong oxidizing anion possesses a redox potential of 2.01V [109].

The oxidation of 2-BE at higher temperatures (35-65°C) is shown in Figure 3-5. The corresponding TOC, pH, and persulfate profiles are shown in Figure 3-6. The full-time scale for 2-BE, TOC, pH, and persulfate degradation at 35 and 45°C is shown in Figure 3-7 and Figure 3-8, respectively. Both the 2-BE and persulfate degradation increased as temperature increased from 35 to 65°C. These results were expected as increasing temperatures lead to persulfate activation, which increases production of sulfate radicals (Reaction 3-2) [109, 110]. As temperature increases, more radicals are produced and these radicals may further oxidize the 2-BE in solution. The sulfate radical reacts with water (Reaction 3-3) [66, 110, 111], producing hydrogen ions and the observed pH drop. As shown in Figure 3-5 (b), a pseudo-first-order rate model describes 2-BE oxidation well for higher temperatures. Table 3-2 summarizes the resulting reaction rate constants and half-lives. Values for $k_{\text{obs},2\text{BE}}$ at 35, 45, 55, and 65°C were 1.034×10^{-5} , 6.243×10^{-5} , 4.074×10^{-4} , and $1.312 \times 10^{-3} \text{ s}^{-1}$, respectively. Figure 3-9 shows the Arrhenius plot for this data of 2-BE by all oxidants produced in thermal persulfate activation. The plot of natural log of k_{obs} versus the inverse temperature fit the Arrhenius model with $R^2=0.997$. The average activation energy was $146.95 \pm 4.44 \text{ kJ mol}^{-1}$. The temperature dependence of this reaction is likely due to the persulfate decomposition and increased production of radicals.

As shown in Figure 3-5, at 65°C, 2-BE completely degrades within 50 minutes of the reaction. At 55°C complete 2-BE degradation does not occur until 240 minutes. Since 2-BE degradation occurs more quickly at higher temperatures, this suggests that the persulfate was heat-activated to produce sulfate radicals as described in Reaction 3-2. Figure 3-10 compares the persulfate disappearance at 55°C with and without 2-BE present. Without 2-BE, the k_{obs} for persulfate activation is $3.53 \times 10^{-6} \text{ s}^{-1}$ at 55°C, which agrees with values previously reported by House ($4.55 \times 10^{-6} \text{ s}^{-1}$ at 56°C) [110]. With 2-BE, the $k_{\text{obs,persulfate}}$ value is $1.04 \times 10^{-5} \text{ s}^{-1}$ at 55°C. The increasing persulfate disappearance with 2-BE in solution suggests that the radicals produced by thermal persulfate activation degrade 2-BE while direct oxidation via the persulfate anion may also occur [127].

Figure 3-11 displays the mass spectra for the byproduct detected under the reaction conditions at 55°C. Butyric acid (BA) was the only byproduct detected, appearing between the 30 and 300 minutes reaction times. The concentration of BA was low and less than the GC/MS's limit of quantification. As shown in Figure 3-3, 2-BE degradation slowed down compared to the degradation before 30 minutes. This suggests that BA, or the unidentified byproducts produced, compete with 2-BE for the radicals formed by persulfate. As observed by the TOC data in Figure 3-6 at 55°C, once BA is no longer detected after 300 minutes, TOC removal occurs more rapidly, suggesting that BA is more resistant to persulfate oxidation than the other byproducts produced. According to the TOC data, other reaction byproducts may exist, but were not detected with the available GC/MS methods. The increase in TOC removal after BA disappearance suggests that the subsequent byproducts breakdown more easily than BA.

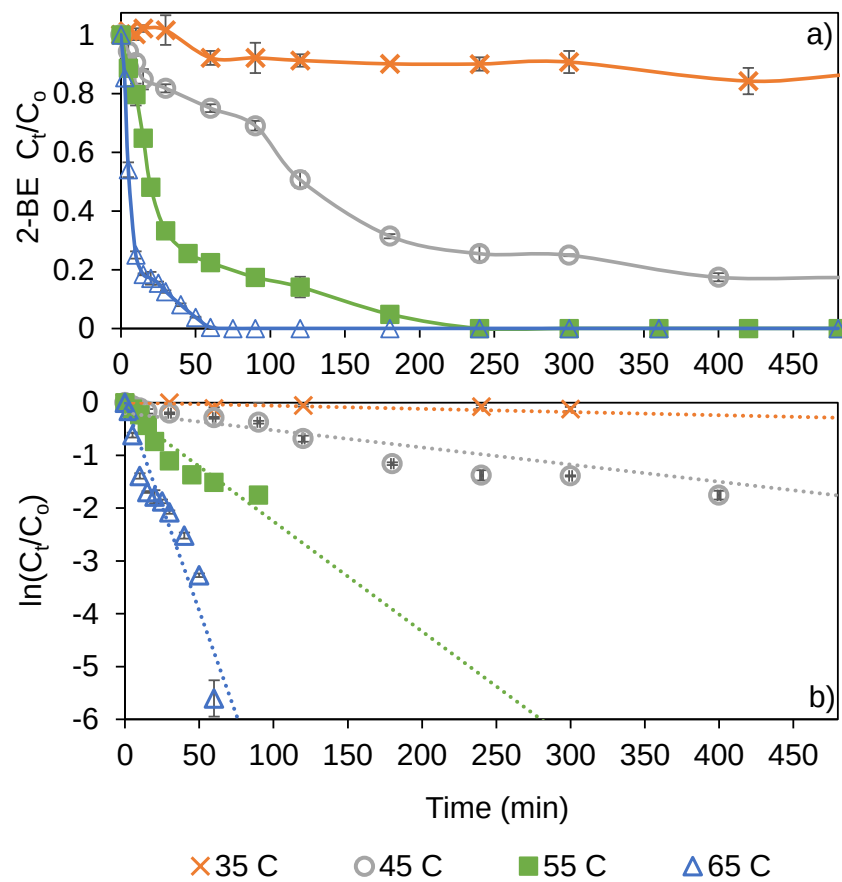


Figure 3-5. 2-BE concentration profile as temperature increases shown in (a) and pseudo-first-order natural log plot versus time in (b) (initial sodium persulfate dose 21 mmol L^{-1} , initial pH 6).

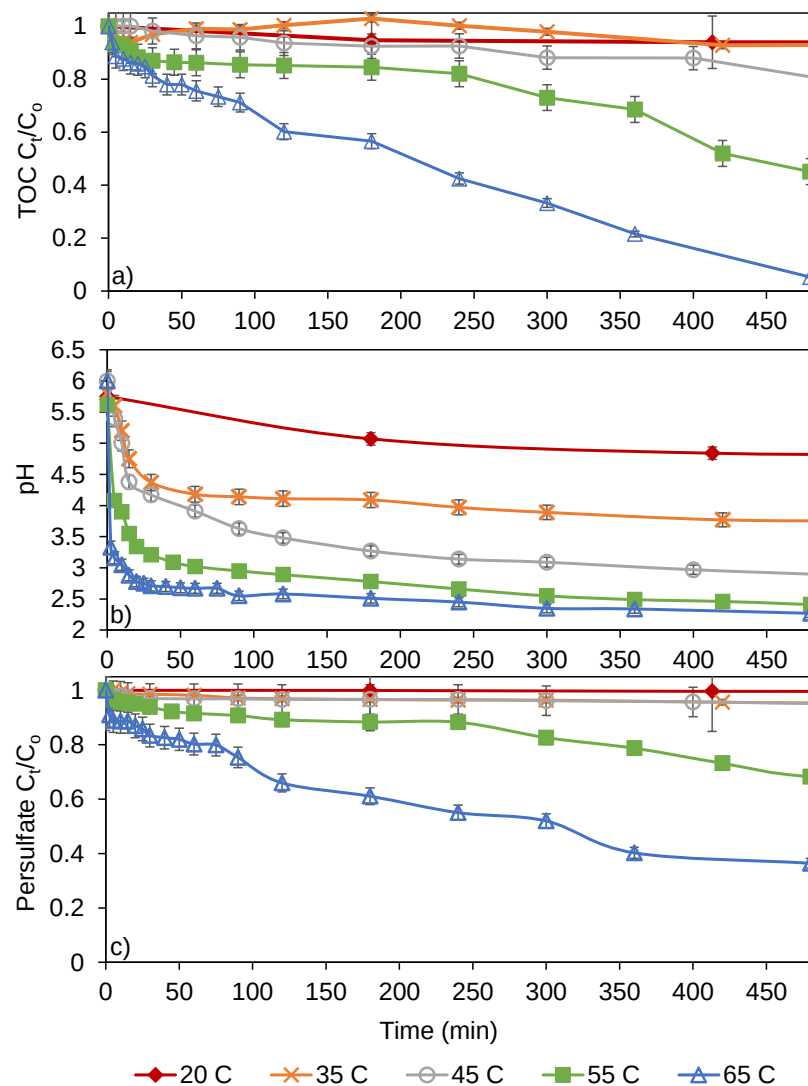


Figure 3-6. Decrease in (a) TOC, (b) pH, and (c) persulfate over the course of 2-BE degradation at 20, 35, 45, 55, and 65°C with an initial dose of 21 mmol L⁻¹ persulfate (initial pH 6).

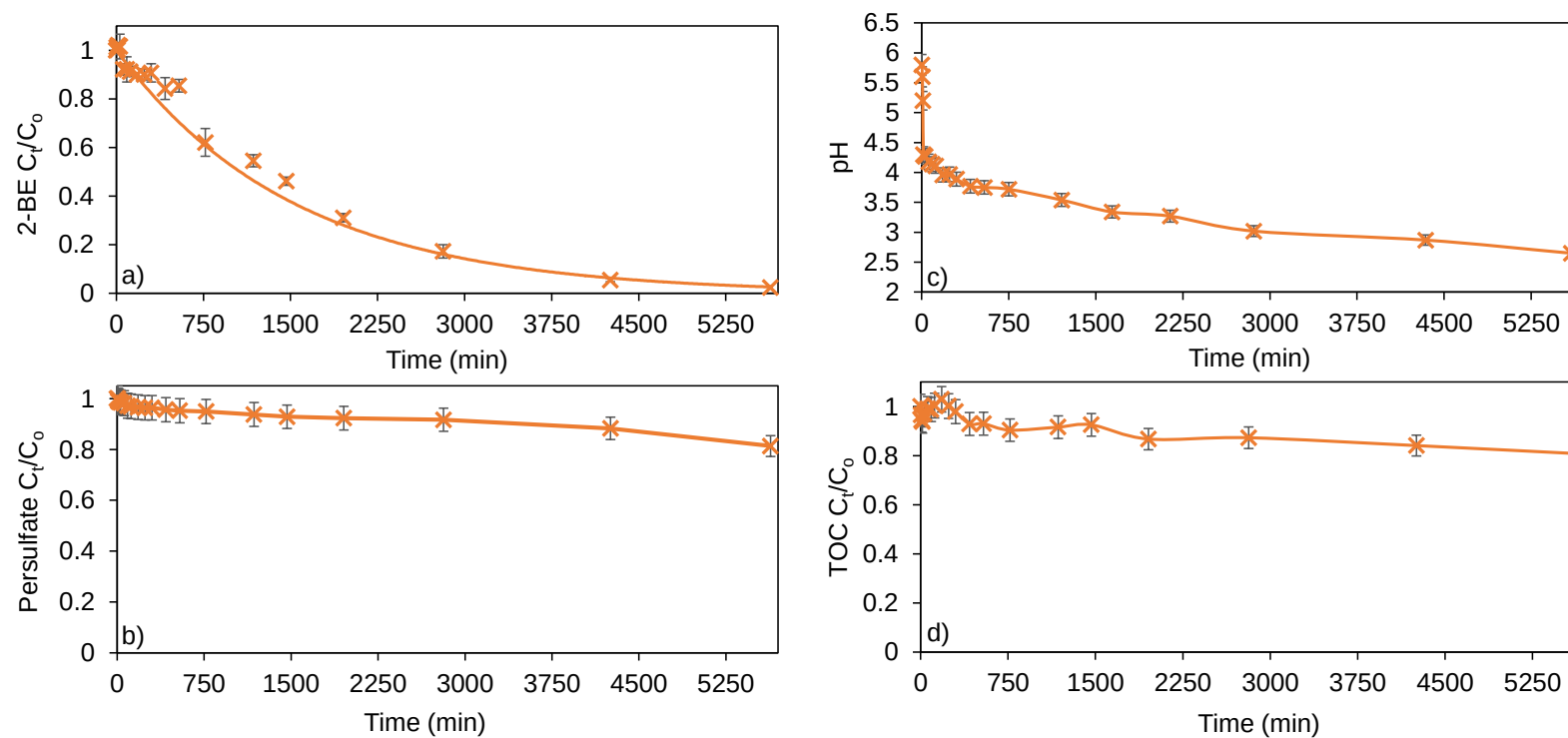


Figure 3-7. Full time scale of the decrease in (a) 2-BE, (b) persulfate, (c) pH, and (d) TOC over the course of 2-BE degradation at 35°C with an initial dose of 21 mmol L⁻¹ persulfate (initial pH 6).

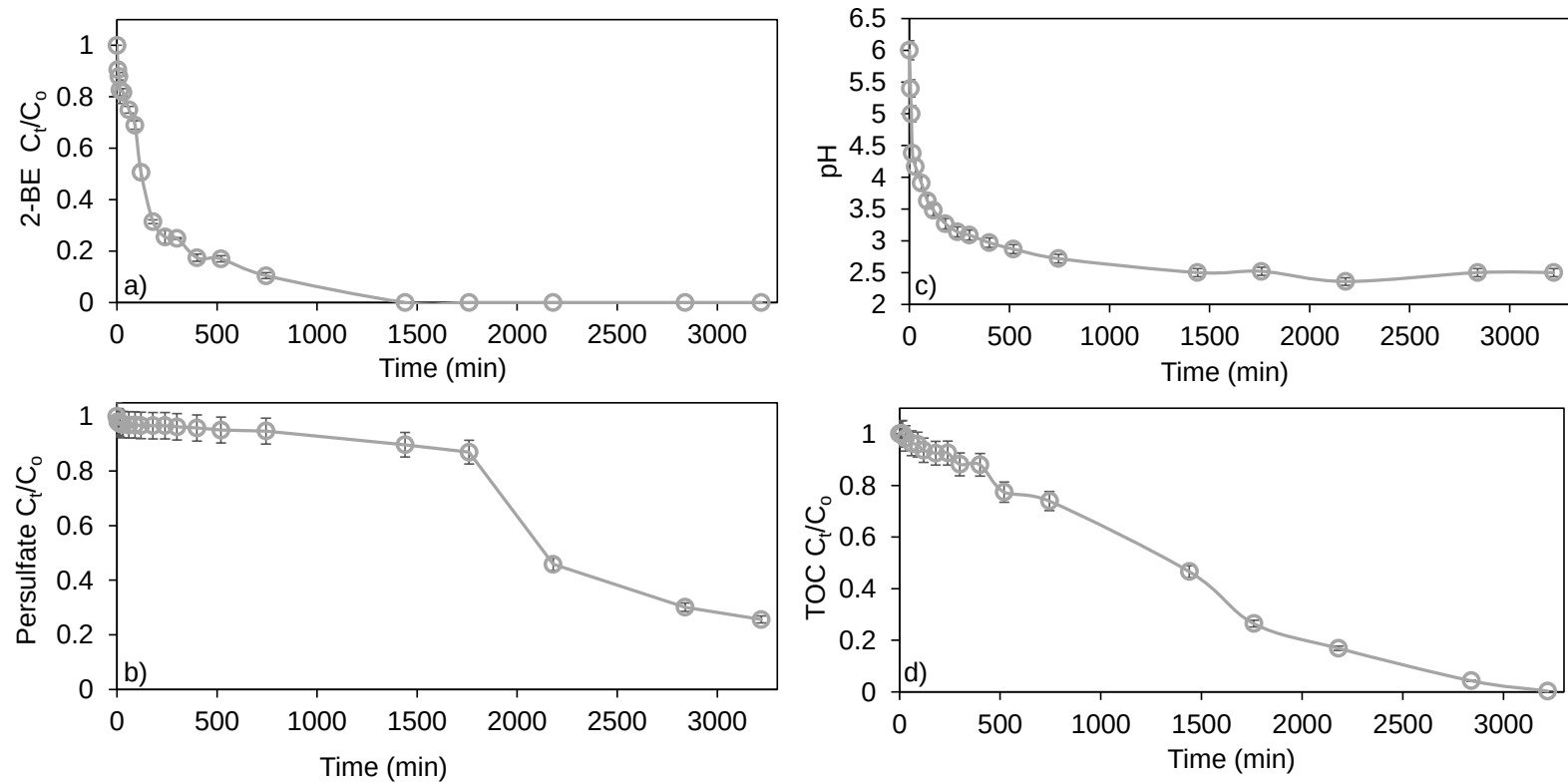


Figure 3-8. Full time scale of the decrease in (a) 2-BE, (b) persulfate, (c) pH, and (d) TOC over the course of 2-BE degradation at 45°C with an initial dose of 21 mmol L⁻¹ persulfate (initial pH 6).

Table 3-2. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at 20, 35, 45, 55, and 65°C with 21 mmol L⁻¹ sodium persulfate (initial pH 6).

T (°C)	k (s ⁻¹)	Half- life (h)
20	3.425x10 ⁻⁷	337
35	1.034x10 ⁻⁵	18.6
45	6.243x10 ⁻⁵	3.08
55	4.074x10 ⁻⁴	0.473
65	1.312x10 ⁻³	0.147

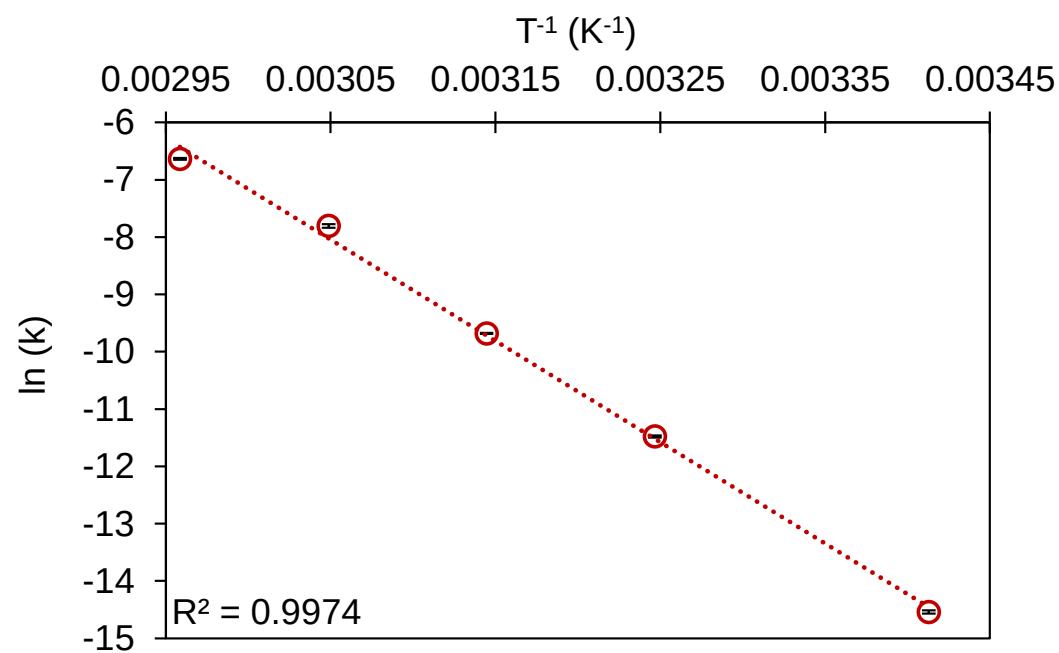


Figure 3-9. Arrhenius plots for 2-BE oxidation by 21 mmol L⁻¹ persulfate (initial pH 6).

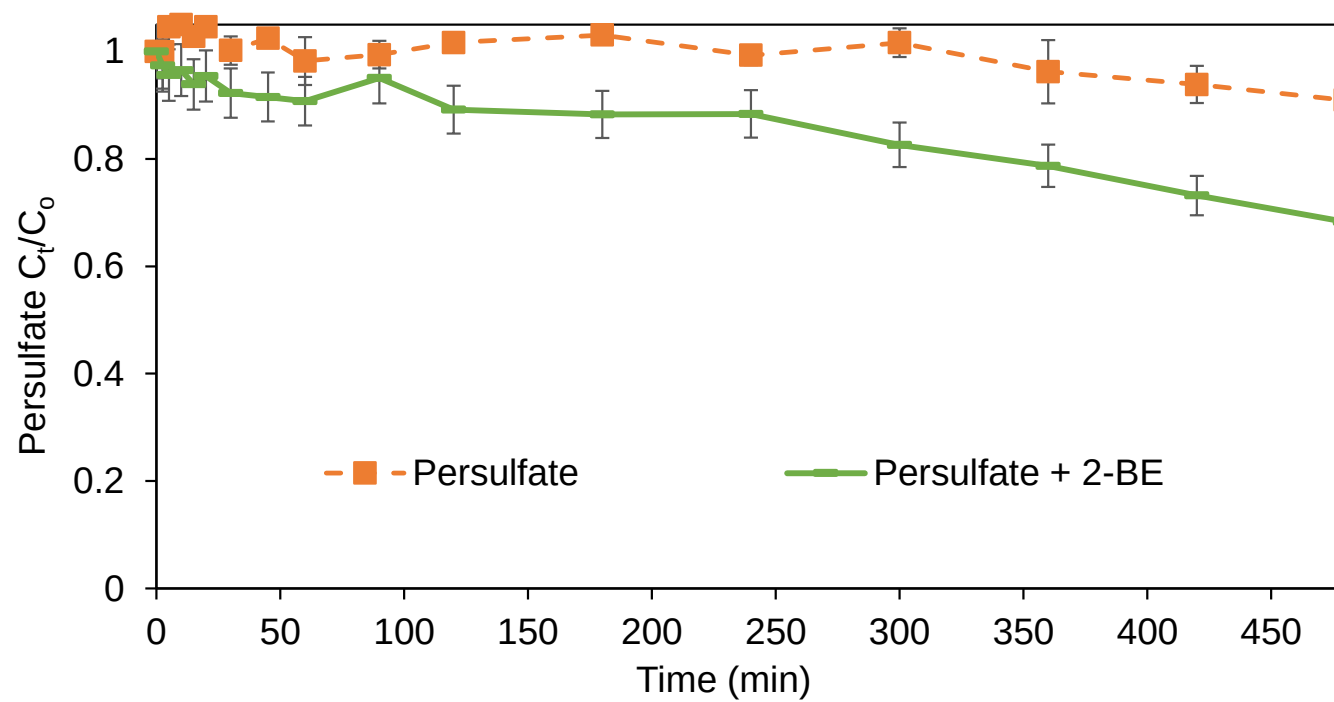


Figure 3-10. Decrease in persulfate concentration at 55°C with and without 2-BE in solution initial dose of 21 mmol L⁻¹ persulfate, initial pH 6.

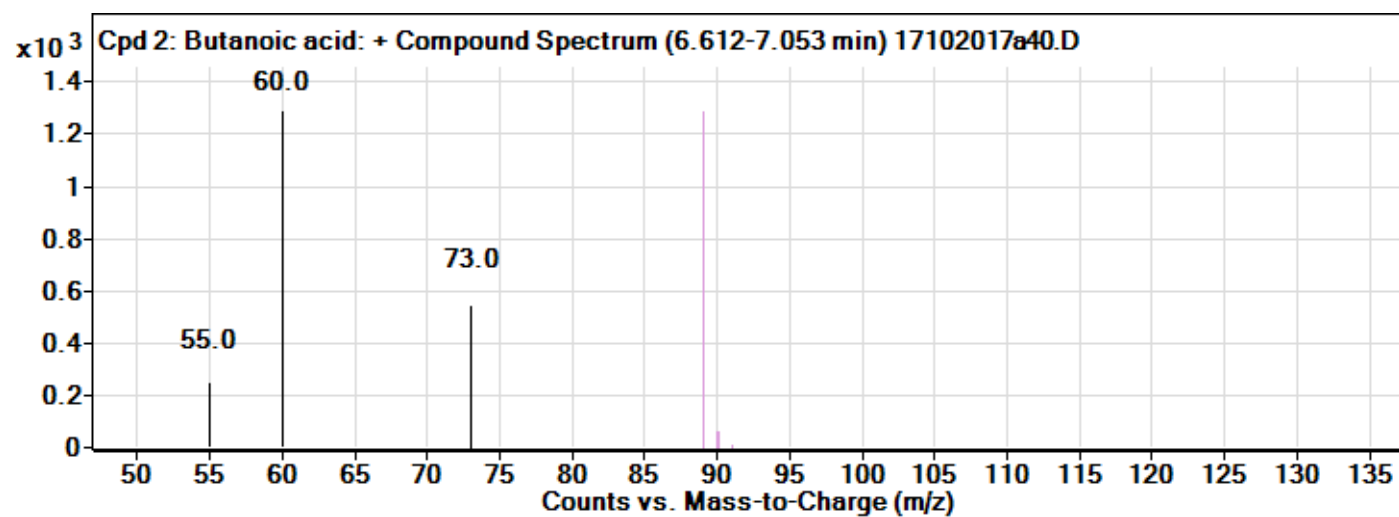


Figure 3-11. Mass spectra of butyric acid detected in experiment at 55°C containing 2-BE and 21 mmol L⁻¹ persulfate, initial pH 6. Butyric acid was the only byproduct detected.

pH Effects

Figure 3-12 shows the decreasing 2-BE concentrations at initial pH 2, 6, and 11. The k_{obs} and half-life values are summarized in Table 3-2. Initial pH had little impact on 2-BE degradation. One-way ANOVA with Tukey's HSD post-hoc test was performed to evaluate differences in the mean pseudo-first-order reaction rate constants between the three pHs ($k_{\text{obs},2\text{-BE}} = 3.061 \times 10^{-4} \text{ s}^{-1}$ at pH 2, $4.074 \times 10^{-4} \text{ s}^{-1}$ at pH 6, $3.302 \times 10^{-4} \text{ s}^{-1}$ at pH 11). At the 95% confidence interval, the mean pseudo-first-order reaction rate constant at pH 6 is significantly different from the reaction rate constants at pH 2 and 11. However, the pseudo-first-order reaction rate at pH 2 and pH 11 are not significantly different from one another. Figure 3-13 shows the TOC, pH and persulfate profiles for the reactions at all pHs. Over 480 minutes, 15% less TOC degraded at pH 2 and 11 than pH 6. At all three pHs, the same amount of persulfate was consumed. Thus, pH played little to no role in the degradation of 2-BE by persulfate at 55°C.

At all pHs, the sulfate radical may react with water to produce a hydroxyl radical, as shown in Reaction 3-3 [66, 110, 111]. At alkaline pHs, the sulfate radical reacts with hydroxide to produce a hydroxyl radical and sulfate as shown in Reaction 3-3 [127]. However, at high temperatures the effect of pH on organic oxidation is less pronounced than at low temperatures [119, 128]. This suggests that the activation of persulfate at 55°C according to Reaction 3-2 is a much faster than Reaction 3-3 and Reaction 3-4. Over the course of a fracture, pH may change as the fluids come in contact with the shale rock or as persulfate reactions occur. The data indicate that the higher temperatures, such as those observed in the well-bore, play a stronger role in the oxidation of 2-BE than the variation in pH over the course of a fracture would play.

Iron (II) and Shale Effects

Figure 3-14 (a) displays decrease in 2-BE as Fe(II) is added to solution at 55°C with an persulfate dose of 21 mmol L⁻¹ (initial pH 2). The resulting $k_{\text{obs},2\text{-BE}}$ and half-life values are summarized in Table 3-4. Control experiments showed that the addition of Fe(II) without persulfate did not cause the 2-BE concentration to decrease in water, while persulfate addition and increasing Fe(II) concentrations increased the rate of 2-BE degradation [129]. The observed increase in 2-BE degradation is due to persulfate activation by Fe(II) that produces additional sulfate radicals, as shown in Reaction 5. To compare the resulting mean $k_{\text{obs},2\text{-BE}}$ values, one-way ANOVA with Tukey's HSD post-hoc test was performed. The mean $k_{\text{obs},2\text{-BE}}$ for 0 mg L⁻¹ Fe(II) ($3.061 \times 10^{-4} \text{ s}^{-1}$) was not statistically different from the mean rate constant for 5 mg L⁻¹ Fe(II) ($3.360 \times 10^{-4} \text{ s}^{-1}$) ($\alpha=0.05$). The mean $k_{\text{obs},2\text{-BE}}$ for 10 mg L⁻¹ Fe(II) ($3.680 \times 10^{-4} \text{ s}^{-1}$) was not statistically different from 5 nor 15 mg L⁻¹ Fe(II) ($4.354 \times 10^{-4} \text{ s}^{-1}$) ($\alpha=0.05$). The mean $k_{\text{obs},2\text{-BE}}$ values for 20 ($4.790 \times 10^{-4} \text{ s}^{-1}$), 50 ($7.525 \times 10^{-4} \text{ s}^{-1}$), and 100 ($1.130 \times 10^{-3} \text{ s}^{-1}$), mg L⁻¹ Fe(II) were significantly different from each other and all other tested Fe(II) concentrations ($\alpha=0.05$). At all iron concentrations, 2-BE was completely oxidized within 180 minutes at 55°C. Figure 3-15 displays the TOC, pH, and persulfate concentration profiles for the experiments with Fe(II) in solution (55°C, persulfate dose of 21 mmol L⁻¹, initial pH 2). As expected, as more iron was added to solution, TOC and persulfate concentrations decreased at faster rates.

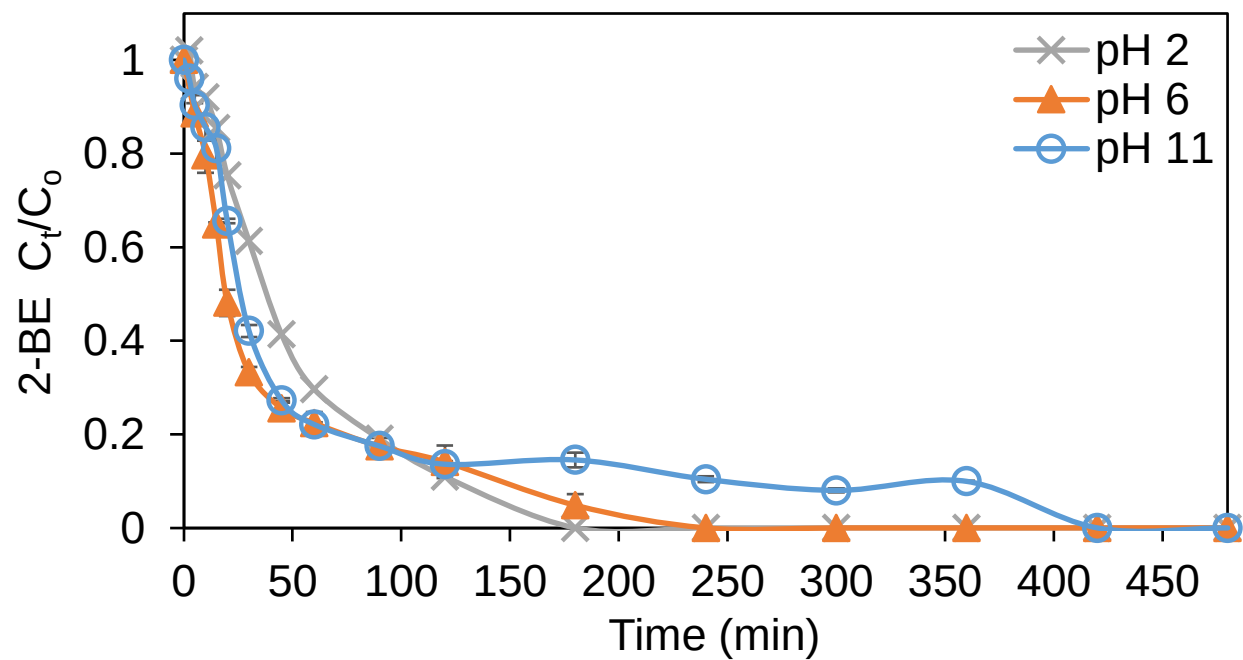


Figure 3-12. Degradation of 2-BE in solutions with varying pH (55°C, initial dose of 21 mmol L⁻¹ persulfate). Initial pHs are 2, 6, and 11.

Table 3-3. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at varying initial pHs (55°C , 21 mmol L⁻¹ sodium persulfate).

Initial pH	k (s⁻¹)	Half-life (h)
2	3.061x10 ⁻⁴	0.629
6	4.074x10 ⁻⁴	0.473
11	3.302x10 ⁻⁴	0.583

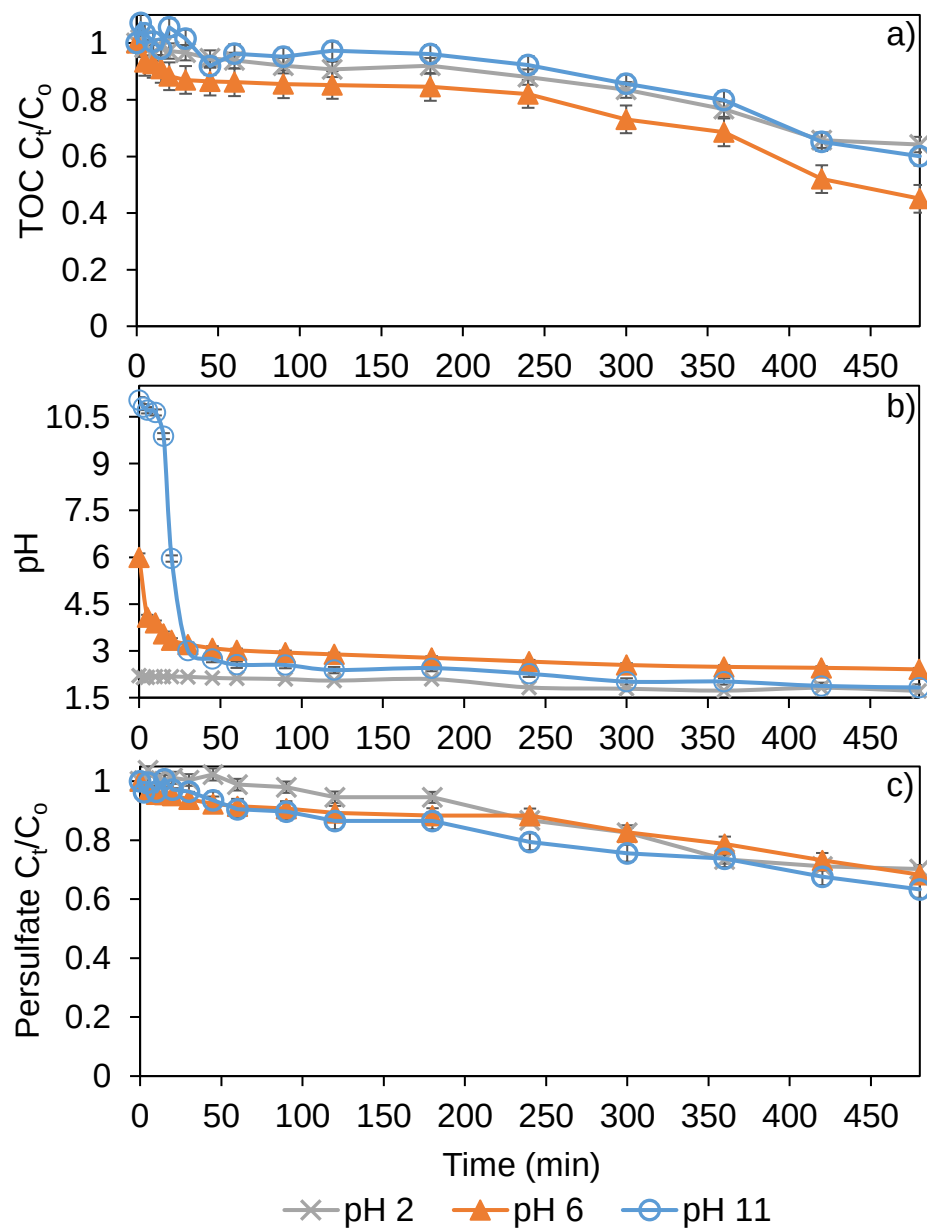


Figure 3-13. Decrease in TOC, pH, and persulfate concentration during 2-BE degradation in solutions with varying initial pH (55°C, initial dose of 21 mmol L⁻¹ persulfate). Initial pHs are 2, 6, and 11.

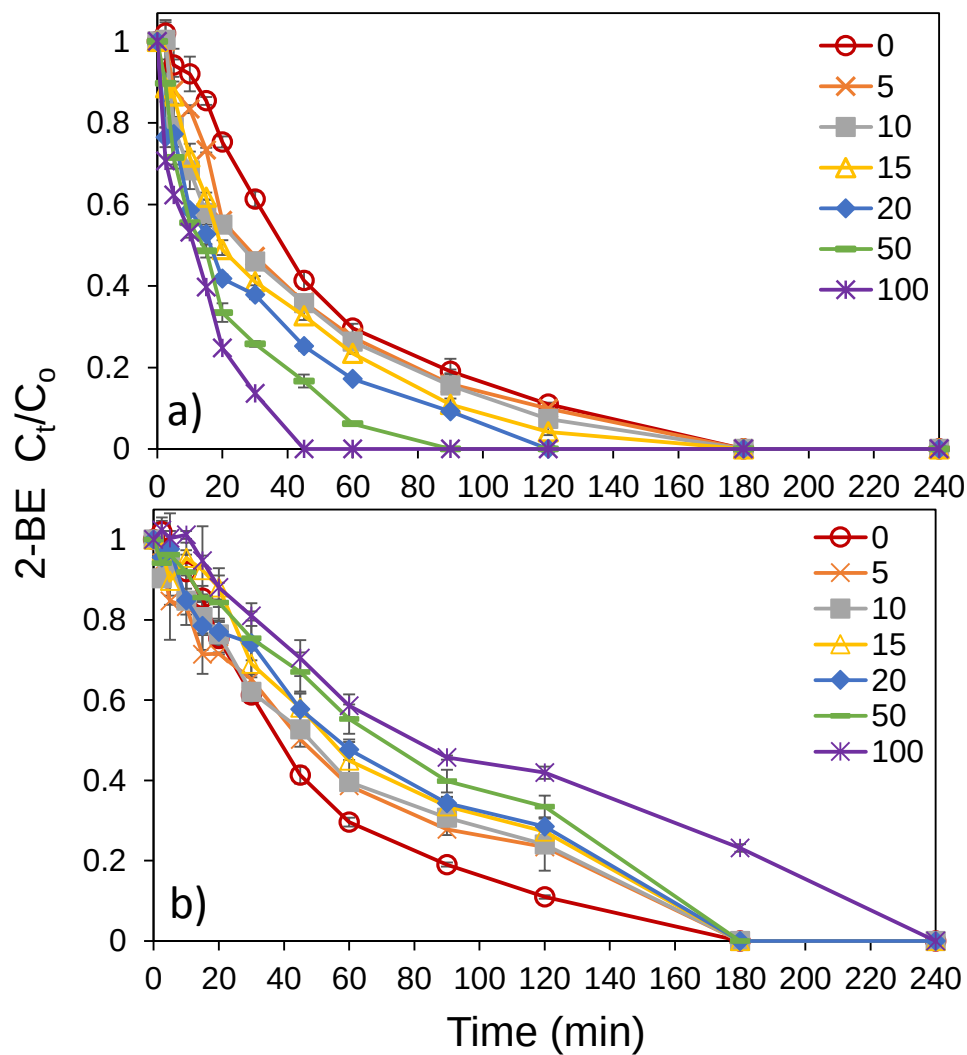


Figure 3-14. Degradation of 2-BE in solutions with (a) Fe(II) and (b) shale rock (55°C, initial dose of 21 mmol L⁻¹ persulfate, initial pH 2, initial 2-BE concentration 120 mg L⁻¹). Legends indicate the mg L⁻¹ concentration of Fe (II). Data below the limit of detection (0.957 mg L⁻¹ 2-BE) were not used to calculate the rate constants reported in the text. Error bars represent standard error.

Table 3-4. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at varying Fe(II) concentrations (55°C , 21 mmol L⁻¹ sodium persulfate, initial pH 6).

[Fe] (mg L⁻¹)	k (s⁻¹)	Half-life (h)
0	3.061x10 ⁻⁴	0.629
5	3.360x10 ⁻⁴	0.573
10	3.680x10 ⁻⁴	0.523
15	4.354x10 ⁻⁴	0.442
20	4.790x10 ⁻⁴	0.402
50	7.525x10 ⁻⁴	0.256
100	1.130x10 ⁻³	0.170

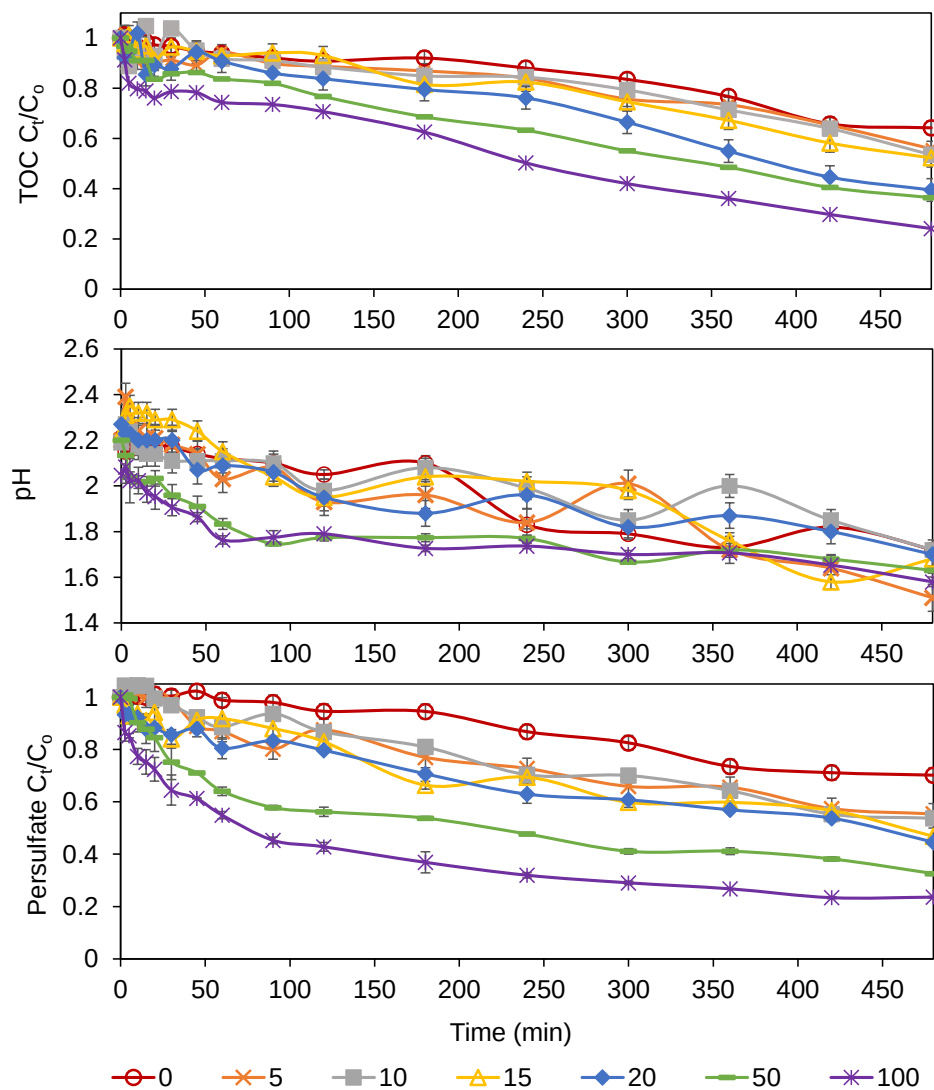


Figure 3-15. Decrease in TOC, pH, and persulfate concentration during 2-BE degradation in solutions with varying Fe(II) concentration (55°C, initial dose of 21 mmol L⁻¹ persulfate, initial pH 2). Legend indicates the mg L⁻¹ concentration Fe(II).

Figure 3-14 (b) displays the degradation of 2-BE when different concentrations of shale are in solution at pH 2 (55°C, 21 mmol L⁻¹ persulfate). The concentration of shale added provides an iron concentration (0, 5, 10, 15, 20, 50, and 100 mg L⁻¹) comparable to the amounts tested in Figure 3-14 (a). As shale concentration increases, the degradation of 2-BE slows down. Table 3-5 summarizes the $k_{obs,2-BE}$ and half-life values for these reactions. Unlike Fe(II)-activation, increasing the iron concentration using shale did not lead to increasing $k_{obs,2-BE}$ values. When 18.86 mg L⁻¹ of shale (5 mg L⁻¹ Fe(II)) is added, complete 2-BE degradation is achieved after 180 minutes and the $k_{obs,2-BE}$ value is $2.477 \times 10^{-4} \text{ s}^{-1}$. At the highest shale concentration tested, 373.6 mg L⁻¹, (100 mg L⁻¹ Fe(II)) complete 2-BE degradation is achieved at 240 minutes and the $k_{obs,2-BE}$ value is $1.268 \times 10^{-4} \text{ s}^{-1}$. As the shale concentration increases, the $k_{obs,2-BE}$ value decreases.

Figure 3-16 shows persulfate profiles for the reactions with shale. At all shale concentrations, the persulfate concentration continues to decrease after complete degradation of 2-BE, as shown in Figure 3-16. As shale concentration increases, the pseudo-first-order reaction rate constant decreases, despite the increasing iron concentration in the shale. In the field, pyrite dissolution and oxidation depends on dissolved oxygen content [130] and may vary compared to batch experiments. The decreasing pseudo-first-order reaction rate constant is due to the dissolution of other minerals in the shale, especially carbonates. Figure 3-17 displays SEM images of the shale taken with a high definition back scatter detector (HDBSD), which allows for compositional and crystallographic information. Though the brighter spots in this image correspond to heavier elements, many were determined to be pyrite deposits. As displayed, the minerals in the shale used in this study are heterogeneously distributed throughout. When the shale is added to water or persulfate begins to react with the shale, these minerals dissolve into solution. The slower observed 2-BE degradation is due to the dissolution of these minerals, especially minerals like dolomite and calcite, which contain carbonate and can quench persulfate reactions [109]. Figure 3-18 displays the XRD pattern of the shale before and after the experiment. By comparing the XRD patterns before and after the experiment, observations may be made in how the reactions impacted the shale mineralogy. The two main minerals that were depleted from the shale are dolomite and calcite.

Carbonate speciation is dependent on pH, as shown in Reaction 3-6 and Reaction 3-7. In hydraulic fracturing conditions, such as those tested in this study, the pH of the injected fluids is as low as 2. Figure 3-16 displays the change in pH over the course of the reactions with shale rock. In this study, the initial pH is 2 and does not change much over the course of the experiment. The amount of shale used is not enough to raise the pH, so the carbonates in solution are in the form of carbonic acid, H₂CO₃. The sulfate radical reacts with carbonic acid according to Reaction 3-8 [114] and the hydroxyl radical according to Reaction 3-9 [115]. The reaction occurs rapidly, consuming radicals in solution and preventing degradation of 2-BE. The carbonate radical produced in Reaction 8 and 9 may oxidize the remaining organics produced from 2-BE or inorganics from the shale, which would produce a carbonate anion [131].

Persulfate may also react with other metals in the shale. Figure 3-19 displays the major, minor, and trace metal dissolution into solution as 120 mg L⁻¹ 2-BE and 21 mmol L⁻¹ persulfate react with 373.6 mg L⁻¹ shale (100 mg L⁻¹ Fe(II)) in solution. As shown in Figure 3-19, numerous metals increase in concentration as the reaction proceeds. Most

Table 3-5. Pseudo first order reaction rate constants and half-lives for 2-BE experiments at varying Fe(II) concentrations (55°C , 21 mmol L⁻¹ sodium persulfate, initial pH 6).

[Shale] (mg L⁻¹)	[Fe] (mg L⁻¹)	k (s⁻¹)	Half-life (h)
0	0	3.061*10 ⁻⁴	0.629
18.68	5	2.477*10 ⁻⁴	0.777
37.36	10	2.367*10 ⁻⁴	0.813
56.04	15	2.016*10 ⁻⁴	0.955
74.72	20	1.876*10 ⁻⁴	1.03
188.6	50	1.485*10 ⁻⁴	1.29
373.6	100	1.268*10 ⁻⁴	1.52

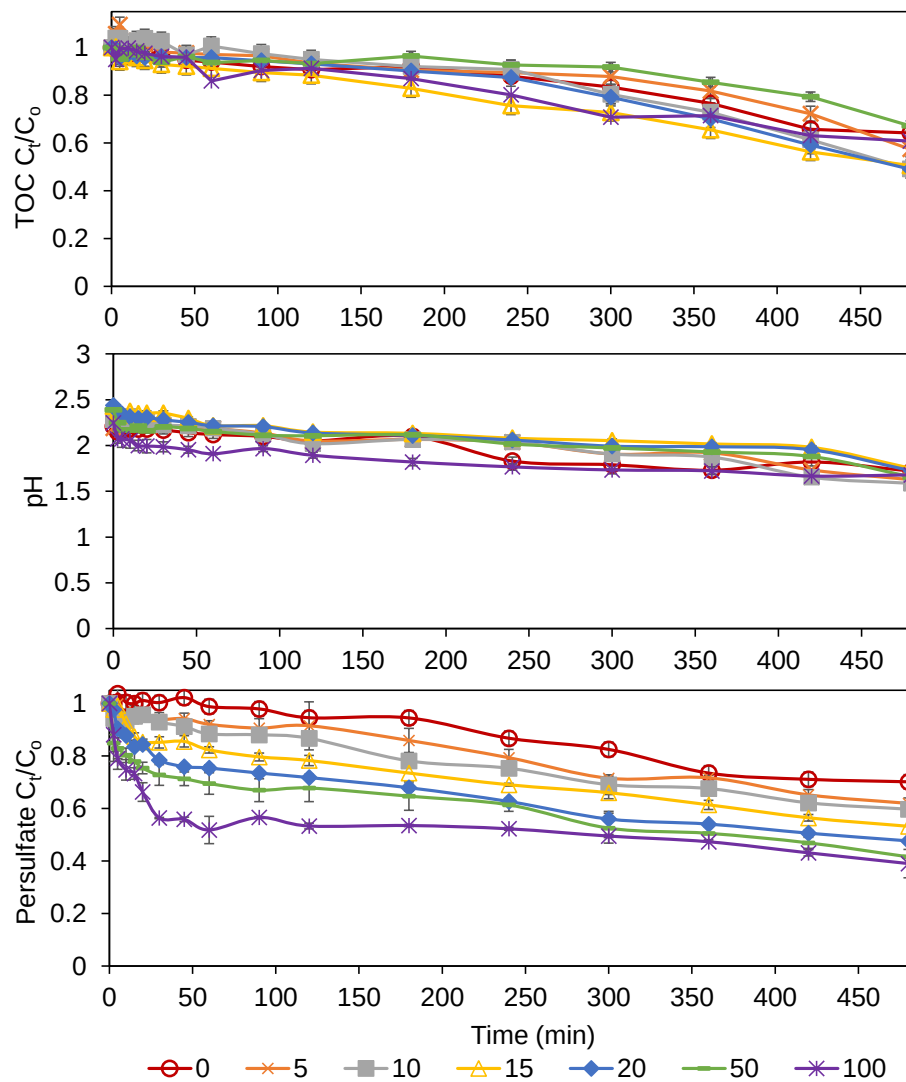


Figure 3-16. Decrease in TOC, pH, and persulfate concentration during 2-BE degradation in solutions with varying shale concentration (55°C, initial dose of 21 mmol L⁻¹ persulfate, initial pH 2). Legend indicates the mg L⁻¹ concentration Fe(II).

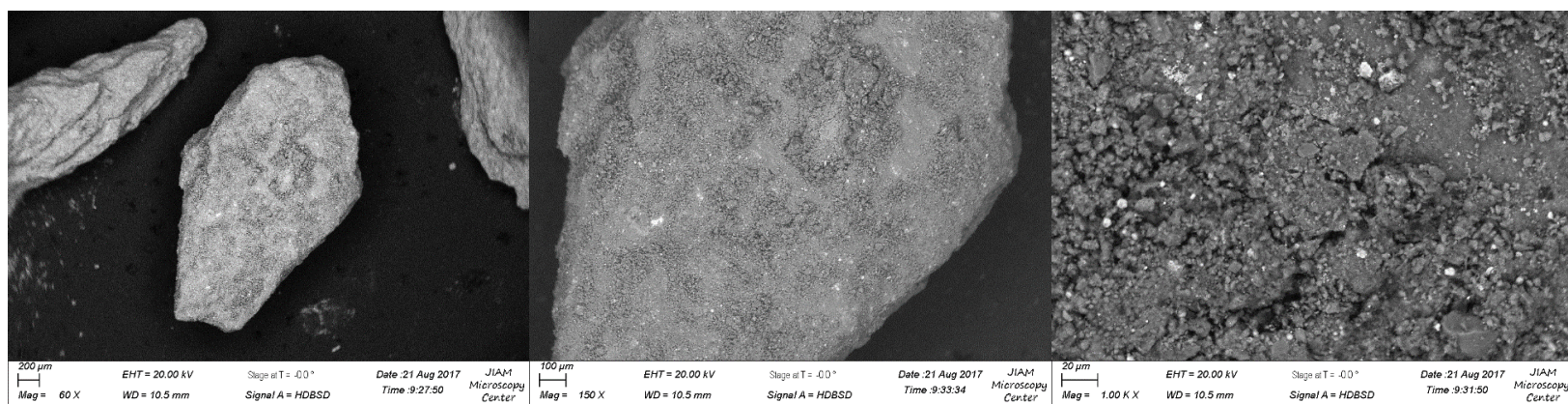


Figure 3-17. Unreacted WV7 shale rock SEM image.

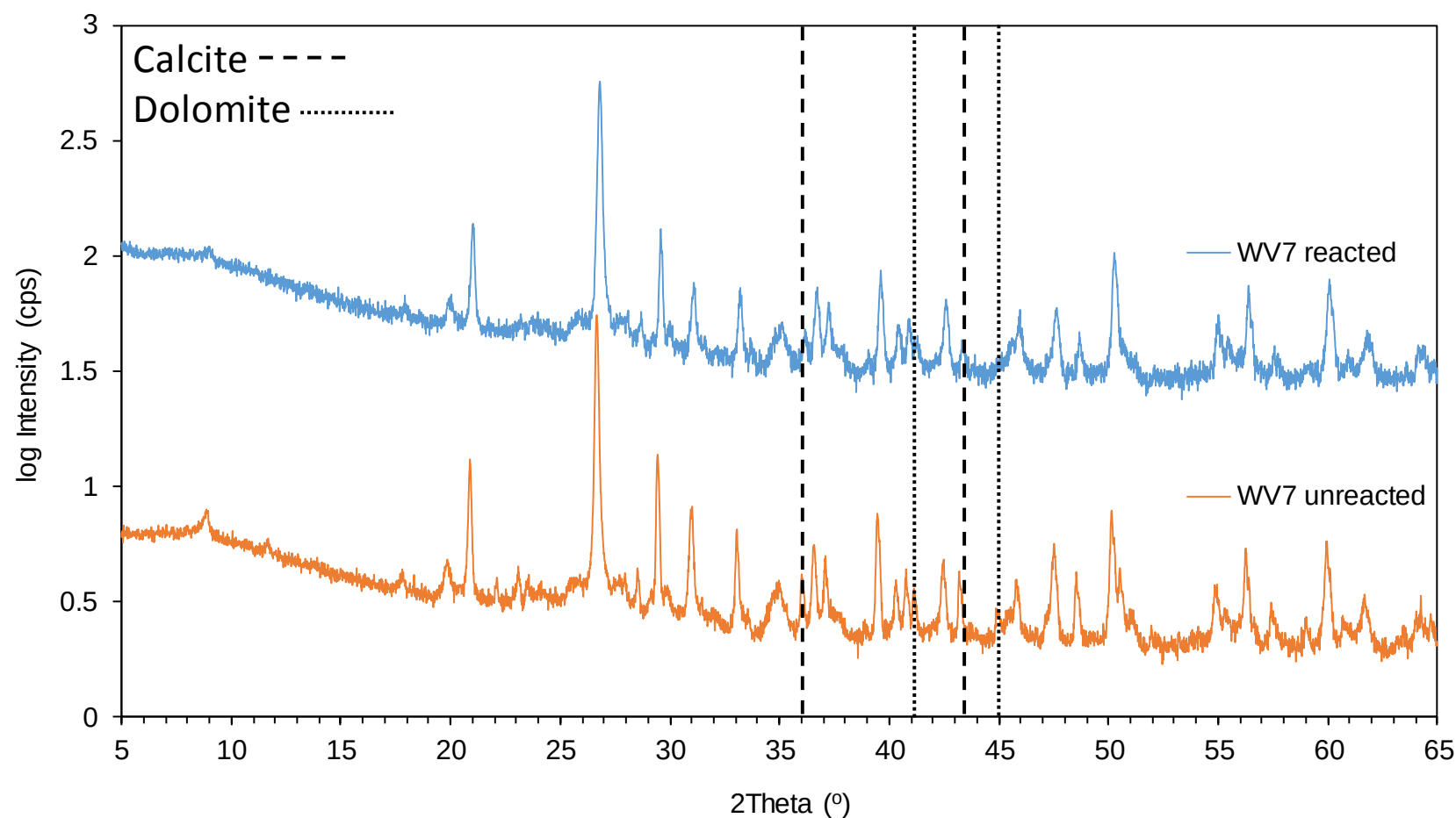


Figure 3-18. XRD pattern of unreacted (bottom) and reacted (top) shale (55°C, initial dose of 21 mmol L⁻¹ persulfate, initial pH 2, initial 2-BE concentration 120 mg L⁻¹). Reacted shale was collected after the entire experiment was completed and filtered out of solution. The y-axis has been modified by taking log of intensity and stacking the plots in order to make the graphic clearer. Vertical lines show where minerals are depleted in the diffractogram of the reacted shale in comparison to the unreacted shale. Calcite and dolomite were the two minerals determined to be depleted from the shale.

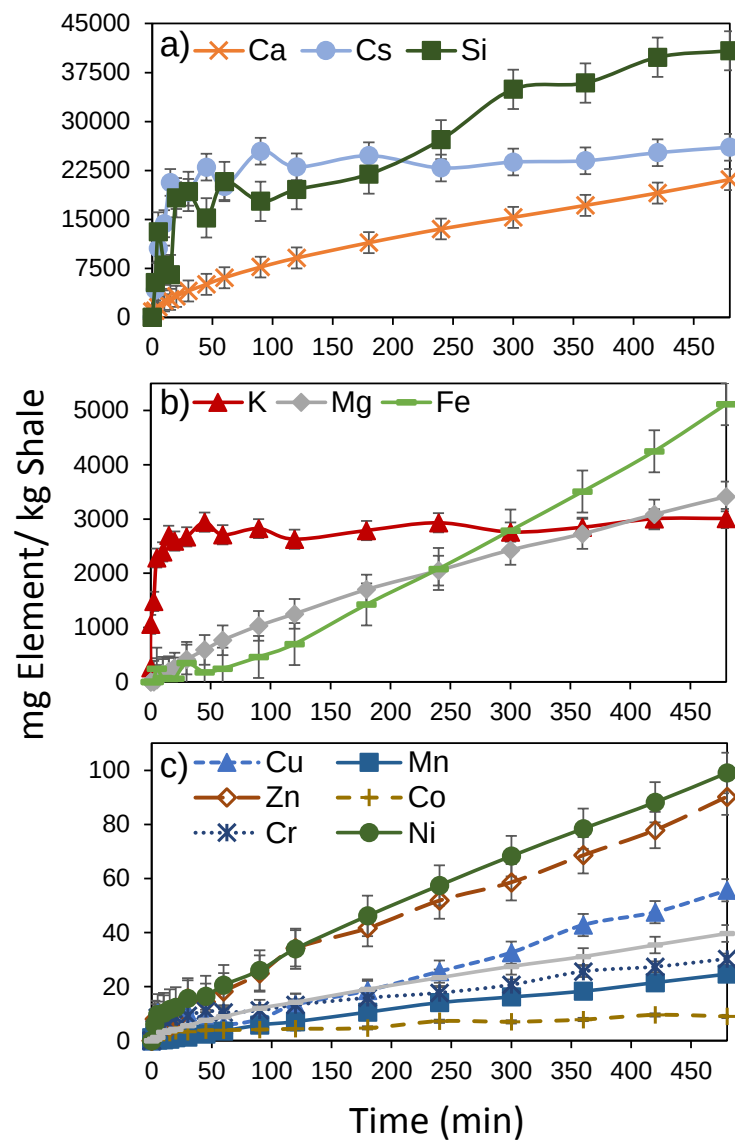


Figure 3-19. Dissolution of (a) major, (b) minor, and (c) trace metals from the shale rock over the course of 2-BE degradation activated by 21 mmol L⁻¹ persulfate (initial pH 2).

metals constantly increase in concentration over the course of the reaction. Two metals, potassium and cesium, reach a maximum concentration after 90 minutes. While no cesium containing minerals were detected using XRD, cesium has been previously detected in flowback fluids [132] and typically occurs in pollucite, which is associated with minerals that naturally occur in shale [133], such as quartz and muscovite. Scaling metals, including calcium and magnesium, continually increase over the course of the reaction as displayed in Figure 3-19. The calcium and magnesium likely come from the dolomite and calcite that are depleted from the shale as previously discussed.

In the field, the metal concentration detected in flowback and produced waters will depend on the amount of shale that the fluids contact. This study shows that metals will precipitate into the fluids with minimal agitation. As soon as the shale was added to solution, metals began to precipitate. The exact metal concentrations in the field will vary depending on the shale play, the chemical supplier, and other factors. Additionally, 2-BE degradation was shown to slow in the presence of shale, which is likely due to the shale carbonate content. Further studies are needed to understand how individual additives contribute to the precipitation of metals from shale and how extreme pressures impact metal leaching.

Conclusion

In summary, the hydraulic fracturing spill indicator compound 2-BE may degrade readily downhole in the presence of activated persulfate. Conclusions from this study were:

- The persulfate anion may directly oxidize 2-BE at room temperature.
- As expected, increasing temperature sped up 2-BE degradation by persulfate activation due to the production of sulfate radicals.
- pH did not impact 2-BE degradation greatly.
- Increasing iron concentration increased the degradation rate of 2-BE; however, increasing the iron concentration using shale rock decrease the degradation rate.
- Metals continuously precipitate into solution during the oxidation reaction between 2-BE and persulfate. Further investigation is needed to understand how persulfate is impacting the dissolution of the minerals in the shale.

CHAPTER 4
CHARACTERIZATION OF SHALE PARTICULATES AND RESULTING
CHANGES IN WASTEWATER QUALITY DUE TO INTERACTION WITH
HYDRAULIC FRACTURING ADDITIVES

Abstract

Hydraulic fracturing companies use water mixed with a myriad of chemical additives to produce natural gas. During the hydraulic fracturing process, the fluids contact shale rock, which may result in altered shale properties and fluid composition. This study investigates shale deterioration and dissolution caused by typical fracturing additives, including HCl, persulfate, and five organic additives (enzyme breaker LEB-10X, gelling agent WGA, friction reducer FRS, surface tension reducer Revert Flow, and biocide BXL). Changes in shale physical and chemical properties were measured using laser-based particle size analysis (PSA), SEM, XRD, and BET (surface area). PSA measurements showed untreated shale was susceptible to breakage at intense mixing speeds and the optimal mixing speed was 2800 rpm. Chemically treated shales did not exhibit statistically different D_{10} , D_{30} , or D_{60} particle sizes than those treated with water alone after 8 days of treatment. However, the inorganic treatments (persulfate and HCl) significantly impacted the shale rock mineralogy. Additionally, the resulting effect of the shale/fluid interactions on water quality was established using inductively coupled plasma optical emission spectrometry (ICP-OES), pH, and persulfate concentration measurements of the solutions. The influence of fluid contact time was also investigated using the most extreme additives, hydrochloric acid and persulfate.

Introduction

The Energy Information Administration (EIA) predicts that the US will become a net energy exporter by 2026, and natural gas generated electricity will increase by 30 to 40% until 2040 [1]. Hydraulic fracturing, or “fracing,” and horizontal drilling allow the US to meet natural gas demands. The process itself requires drilling a wellbore in shale rock containing natural gas, pumping fluids down the wellbore, pressurizing the well, and collecting the natural gas at the surface of the well. Fluid injection requires 2-10 million gallons of water and approximately 200,000-L of chemical additives per well fractured [19, 36].

Fracing companies use chemical additives for various purposes [17, 26, 27, 37]. Typical chemicals include surfactants, acids, biocides, friction reducers, viscosity reducers, gelling agents, and breaking agents [16, 17, 36]. Acids and breaking agents are used to degrade gelling agents and clean the wellbore. Two different types of breaking agents may be used: enzyme breakers that target gelling agents at specific sites, or delayed breakers that non-selectively degrade organic material. After injection, the additives contact the shale at high temperatures and pressures.

Exposure to fluids may alter the physical characteristics of the contacted shale and impact well productivity. Once a wellbore is drilled and prepared, it is perforated using explosions from a blasting gun, which creates fissures in the shale rock and produces small shale particles. As these small particles are exposed to fluids and high mixing speeds when returning to the well surface, the particle sizes may decrease due to changes in the physical characteristics of the shale brought on by exposure to the harsh chemicals. The generated fines are likely to aggregate and plug the pores, which may reduce fracture conductivity (a measure of how easily fluids flow through a fracture) and gas production [134].

Reactions between the shale and the fluids may also change the shales' chemical characteristics. Previous studies investigating the impact of synthetic fracturing fluids containing various inorganic species and slightly acidic pH on shale found that carbonate and gypsum precipitate from the shale rock [33]. However, no observations were made for persulfate and organic additives, which may cause further precipitation and demineralization of chemical species, including heavy metals that can be toxic to aquatic life in excess concentrations [72]. As shale constituents and organic additives react with persulfate, more toxic and environmentally threatening pollutants may leach into the water; therefore, establishing these interactions is imperative to understanding the environmental consequences caused by fracturing practices [33].

After injection, a portion of the fluids return to the surface as flowback (first two weeks after stimulation) and produced waters (after two weeks), which contain naturally occurring materials from the shale formation [20, 135]. These fluids have a high total dissolved solids (TDS) content ranging from 66,000 to greater than 261,000 mg L⁻¹ [7]. Disposal methods for these waste fluids varies between shale plays [136], with typical methods including fluid injection into disposal wells, transport to off-site water treatment facilities, or dilution with fresh water for reuse in another fracture. These disposal methods may result in fracturing fluid spills [137]. Exposure to spilled fluids may cause reproductive, neurological, gastrointestinal, and dermatological problems and even death in wildlife living near well-sites [138]. Failure to address environmental and ecosystem concerns has caused the public to question whether the benefits of natural gas production outweighs the perceived risks [3].

The purpose of this study is to determine the extent of shale deterioration and dissolution caused by typical chemical additives used in fracturing, including hydrochloric acid (HCl), persulfate, and five organic additives. The influence of the fluids on physical characteristics – shale particle size and topology – are presented. Dissolution of heavy metals was measured to understand how chemical contact with shale influences wastewater quality. Finally, the influence of contact time between the fluids and the shale is presented.

Materials and Methods

Shale rock

WV6 shale rock (depth = 7440.3 – 7440.5 m) was obtained from the West Virginia Geological Survey (Morgantown, WV 26508, USA). X-ray diffraction patterns of the shale rock were collected using a Panalytical Empyrean X-Ray Diffractometer (XRD) with copper to determine the bulk mineralogy prior to exposure to experimental treatments. The resulting diffraction pattern is shown in the Appendix Figures A2 and A3 and ICP verification in Figure 4-1. Details of shale digestion for ICP verification are later described. Table 4-1 shows the mineralogy of the untreated shale, which contained quartz, albite, calcite, dolomite, muscovite, pyrite, lavendulan, and gypsum, determined using XRD and verified with ICP.

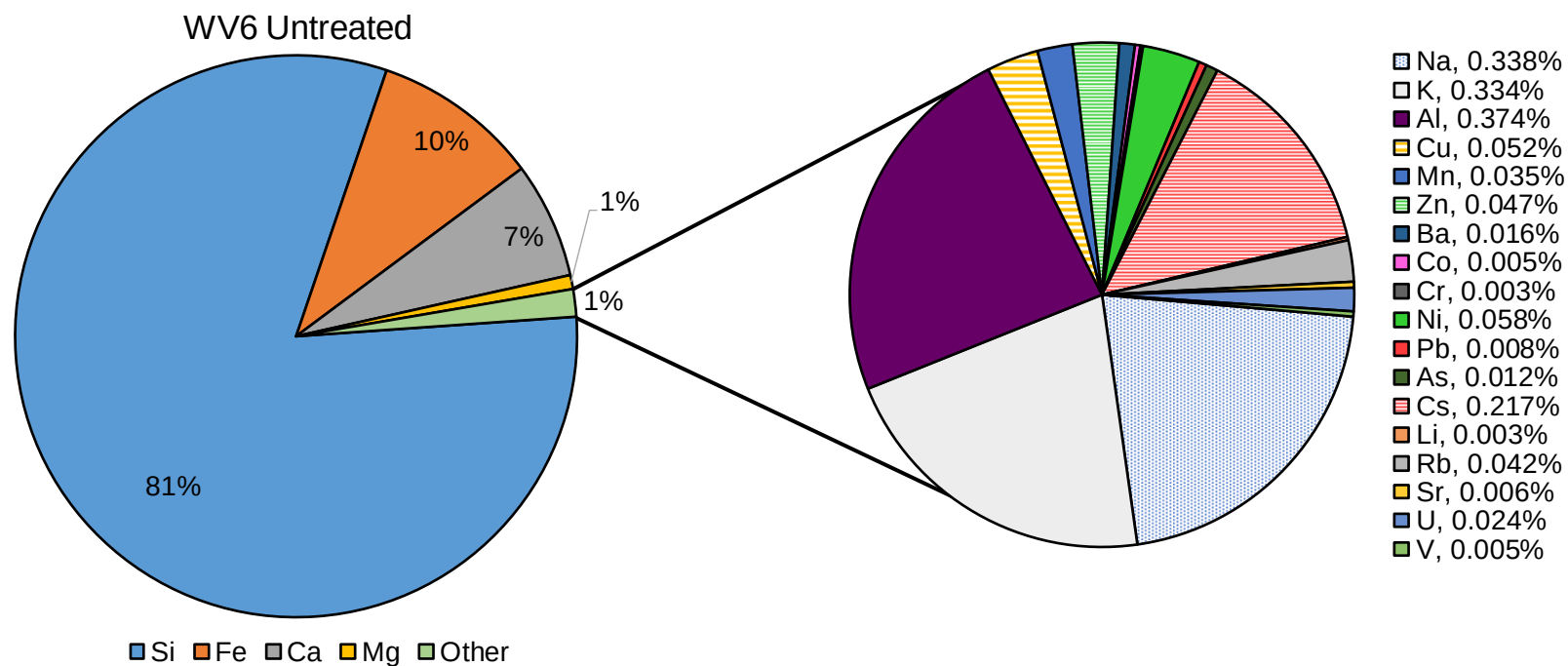


Figure 4-1. Metals detected in supernatant of untreated shale digestion using digestion and ICP. Results were used to verify XRD data. The major ion detected was Si, which comes from the major mineral quartz. The element with the second highest concentration was Fe, which comes from the pyrite in the shale. The third most concentrated element, Ca, in the shale could have come from several different minerals, including calcite, dolomite, gypsum, and lavendulan.

Table 4-1. Mineralogy of Untreated WV6 shale determined using XRD and verified with ICP using shale digestion

Mineral Name		Chemical Formula	Approximate Designation
Albite		$\text{NaAlSi}_3\text{O}_8$	Trace
Calcite		CaCO_3	Minor
Dolomite		$\text{CaMg}(\text{CO}_3)_2$	Trace
Gypsum		$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Minor
Lavendulan		$\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl} \cdot 5\text{H}_2\text{O}$	Trace
Muscovite -2M1, ammonian		$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ with NH_4^+	Minor
		$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ with Mg,	
Muscovite -2M1		Fe	Minor
Pyrite		FeS_2	Minor
Quartz		SiO_2	Major
Designation			
Major	>25%		
Minor	10-25%		
Trace	<10% clearly in sample		
Trace	<10% may not be in sample		

Chemicals

Fracing chemical additives, including FRS (friction reducer), WGA (gelling agent), LEB-10X (enzyme breaking agent), BXL (biocide) and Revert Flow (viscosity reducer), were obtained from Weatherford International (Houston, TX, USA). HCl (35-38%), TraceMetal™ grade nitric acid, sodium persulfate (>98%), sodium bicarbonate (>99%), potassium iodide (>99%), and SPEX CertiPrep™ calibration standard 2 without mercury (5% nitric acid) were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). Solutions were prepared in deionized (DI) water produced using a Milli-Q Plus water purification system (Darmstadt, Germany).

Chemical additive solutions

Treatment conditions used in this study included water, 0.07% by volume HCl (concentration used by fracing companies) [28, 139], 21 mmol L⁻¹ sodium persulfate, 0.07% HCl combined with 21 mmol L⁻¹ sodium persulfate, and five organic fracing chemical additives, including FRS (friction reducer), WGA (gelling agent), LEB-10X (enzyme breaking agent), BXL (biocide) and Revert Flow (viscosity reducer). All solutions, except for persulfate, were prepared 24 hours prior to starting the experiment to ensure well mixed conditions. Persulfate solutions were prepared within an hour before beginning experiments to minimize prior reactions. Solutions containing organic additives were diluted to concentrations typically used by fracing companies as indicated by the chemical supplier. The following amounts were added to separate 500-mL volumes of DI-water: 250-μL FRS, 1.505-g WGA, 12.5-μL LEB-10X, 1000-μL BXL, and 500-μL Revert Flow.

Experimental procedure

Shale was crushed with a mortar and pestle and sieved using No. 10 and 16 sized meshes. A 27-g sample of the crushed and sieved shale was split into 54 samples using a riffler to prevent sampling bias and ensure each sample had approximately the same initial size distribution. Each sample weighed approximately 0.5-g prior to treatment. Amber jars containing 100-mL of the 9 treatment solutions in triplicate (27 total jars) were set in an 80°C oven overnight. After 24 hours, 27 of the shale samples were added to the treatment solutions. Treatments using persulfate were spiked with a concentrated solution of sodium persulfate to achieve a final sodium persulfate concentration of 21 mmol L⁻¹. Sodium persulfate concentration used in fracturing depends on formation conditions and site location; concentrations between 0.125 mmol L⁻¹ and 47 mmol L⁻¹ are reported [34, 68-70]. Amber jars containing shale were incubated in the 80°C oven for 8 days. After 8 days, 20-mL aliquots of the supernatant were taken and immediately frozen to stop any reactions, especially those with persulfate. The shale samples were frozen until measurements on the solid shale samples were performed. To determine the relationship between contact-time with critical chemical additives, the experimental procedure was repeated in triplicate for 1 and 14 incubation days at 80°C. The critical chemical additives were determined to be water, 0.07% hydrochloric acid, 21 mmol L⁻¹ sodium persulfate, and 0.07% hydrochloric acid and 21 mmol L⁻¹ sodium persulfate combined.

Particle size, shape, and porosity analysis

Particle size distribution was measured using a laser-based Mastersizer 3000 Particle Size Analyzer (PSA) (Malvern Instruments Ltd., Worcestershire, UK) equipped with a wet-

dispersion unit. The PSA used can measure particle size distribution in real-time [140], allowing particle size changes to be observed with instrument mixing speed. The entire 100-mL sample suspensions containing 0.5-g shale and the treatment solutions were poured into the PSA mixing tank and diluted with 500-mL DI-water, as is the typical procedure for PSA to ensure particles reach the detector. Particle size measurements were obtained at 2800-rpm mixing speed, the optimal mixing speed for measuring shale particles (further details are explained in the results and discussion section). Optimal mixing speed is the stirrer speed where minimal particle breakage occurs while all particles are maintained in suspension. The minimum and maximum particle sizes measured were 0.005- μm and 2200- μm , respectively.

PSA measurements are based in part on the optical properties of the solids and the dispersing medium of the suspension. Refractive index of the shale suspension was measured using a refractometer (Ametek AR-9, Reichert technologies). The resulting suspension refractive index was not significantly different than that of water (1.333).

Particle shapes were observed using a Zeiss scanning electron microscope (SEM) (model EVO-MA15) equipped with an Energy-dispersive X-ray (EDS) detector (Bruker, model X Flash 6130). A Quantachrome Autosorb-1-c gas sorption instrument was used to measure shale particle surface area. Brunner-Emmett-Teller (BET) surface areas were determined using N_2 adsorption at 77 K. Samples with weights between 30 and 50-mg were outgassed at 150°C with Helium. N_2 adsorption isotherms were obtained in relative pressures ($P_{\text{actual}}/P_{\text{saturation}}$) between 10^{-6} and 0.99.

Inorganic metal identification in liquid samples

Liquid samples were analyzed for inorganic composition using ICP-OES (iCAP 7000 Series, ThermoFisher Scientific, Waltham, MA USA 02451) and compared to standards made from a stock solution containing 10 mg L^{-1} of Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Pb, Rb, Se, Sr, Tl, U, V, and Zn. Calibration curves were created by performing serial dilutions of a standard stock solution with 5% trace metal grade nitric acid. Initial samples were taken prior to adding shale to each solution. XRD results of the untreated shale were verified by digesting the shale in 1-part nitric acid to 2-parts HCl and analyzing the supernatant using ICP-OES.

Liquid samples pH and persulfate measurements

Solution pH was measured using a Fisher Scientific Accumet XL600 benchtop meter (Pittsburgh, PA 15275, USA). Persulfate anion concentrations were determined using a modified spectrophotometric/iodometric method [34, 124]. A solution containing excess potassium iodide and sodium bicarbonate were prepared in DI-water. 2.5-mL aliquots of this solution were added to scintillation vials. Each sample, in 20 to 100- μL volumes, was added to their own aliquot of the potassium iodide-sodium bicarbonate solution and allowed to react for 20 minutes. The resulting mixture was measured using a UV/Vis spectrophotometer (Thermo Fisher Scientific, Model Evolution 600 Madison, WI 53711, US) using a maximum wavelength of 352-nm. Persulfate concentrations were determined using a calibration curve made with potassium iodide-sodium bicarbonate standards containing known sodium persulfate concentrations.

Statistical analysis

Statistical analysis was performed using SAS JMP Pro software, version 12.0.1 (Cary, NC 27516). One-way analysis of variance (ANOVA) paired with a post-hoc Tukey-Kramer honest significant difference (HSD) test was used ($\alpha = 0.05$) to determine which treatments' particle sizes differ from the control group (no treatment). Experiments were performed in triplicate and the standard error (SE) was calculated using Equation 4-1 where s is the sample standard deviation and n is the number of observations.

$$SE = \frac{s}{\sqrt{n}}$$

Equation 4-1

Results and Discussion

Impacts on shale particle physical and chemical properties

Mixing Speed Optimization for PSA Measurements

Figure 4-2 shows the relationship between mixing speed and the measured 10th percentile diameter (D_{10}), 30th percentile diameter (D_{30}), and the 60th percentile diameter (D_{60}) of five dry untreated shale replicates as mixing speed is varied at regular intervals. Mixing speed was increased from 2500 to 2800, 3000, 3200, and 3500-rpm and then decreased to 3200, 3000, 2800, and 2500-rpm. Figure 4-2 demonstrates how exposure to intense mixing impacts particle size, especially for D_{10} particles. At the lowest mixing speed (2500 rpm), the measured D_{10} particle size was 27- μm . Mixing speed was increased to 2800-rpm, and the measured D_{10} was 35- μm . The difference between D_{10} sizes at these two mixing speeds is due to larger particles settling to the bottom of the PSA dispersion unit at the lower mixing speed. The lower mixing speed was not fast enough to keep the larger particles in suspension and reach the PSA detector. As mixing speed was increased beyond 2800-rpm, the measured D_{10} continued to decrease, reaching a value of 21- μm . This observation indicates that the particles likely deteriorated (physical breakage) due to the mixing process. Thus, optimum mixing speed occurs at 2800-rpm, at which most of the particles are transported to the detector with minimal particle deterioration.

By the end of the experiment, the D_{10} particle size was as small as 8.7- μm at a mixing speed of 2500-rpm, and the particles decreased by 75% of their maximum measured size. This indicates that the untreated shale is susceptible to being broken down when exposed to intense mixing speeds and, upon intense mixing, the smallest particles become even smaller. As the particles deteriorate, generation of fine particles causes solution turbidity, colloidal particles, and suspended solids to increase. Compared to large particles, colloidal and suspended solids provide higher surface area for microbial growth to occur in aerobic and anoxic conditions [73-75]. Increasing small particles downhole as a result of exposure to fracturing fluids could provide increased locations for

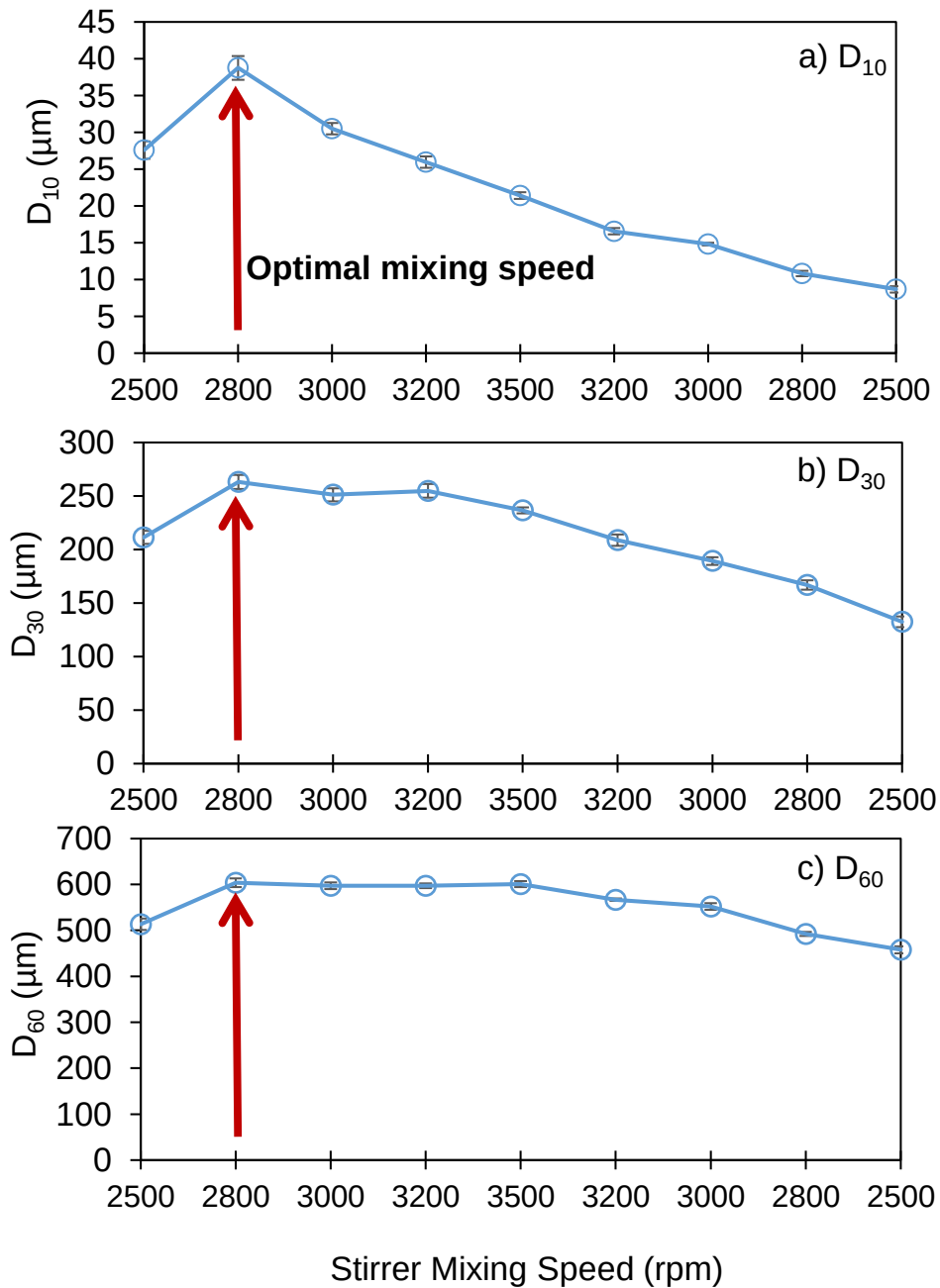


Figure 4-2. D₁₀, D₃₀, and D₆₀ particle size measurements of dry, untreated shale at different mixing speeds in the PSA (n=5). Mixing speed was increased and decreased at regular intervals from 2500 to 2800, 3000, 3200, and 3500, then back down to 3200, 3000, 2800, and 2500-rpm.

microbial growth, resulting in increased sulfide production and souring of the natural gas [77]. Additionally, shale fines of 45- μm or less in concentration of 2% reduces fracture conductivity by 24.4%; while fines concentration of just 10% can completely block a fracture [134].

Also shown in Figure 4-2, deterioration in particles is also observed in the D_{30} and D_{60} particle size. The maximum D_{30} size, 263- μm , occurs at the lowest mixing speed (2800-rpm). The D_{30} particle size then decreases with increasing mixing speed. At the maximum 2500-rpm mixing speed, the average D_{30} is 132- μm , which is a 50% decrease compared to the observed D_{30} at 2800-rpm. For D_{60} , the maximum size, 603- μm , also occurs at 2800-rpm. However, the measured sizes at 3000, 3200, and 3500-rpm are within 2% of this value. Therefore, the optimum mixing speed was determined to be 2800-rpm. This mixing speed was used to compare the D_{10} , D_{30} , and D_{60} particle sizes for each fracturing additive treatment.

Particle size changes in the treated shale

Changes in particle sizes were compared across treatments at the optimized 2800-rpm mixing speed. Figure 4-3 and Table 4-2 show the measured D_{10} , D_{30} , and D_{60} particle sizes for all treatments. One-way ANOVA with Tukey's HSD post hoc test was performed to evaluate differences in mean particle size between all 9 treatments and the control, which had not been exposed to any fluids prior to being added to the PSA. The ANOVA result indicated the mean D_{10} diameters for all treatments were significantly different from the control ($\alpha=0.05$). Of the treated shales, the highest mean D_{10} was 25.6- μm for the sodium persulfate only treatment, while the lowest initial mean D_{10} was 17.9- μm for the Revert Flow treated shale.

ANOVA was also performed to evaluate differences in D_{30} and indicated that the untreated shale was significantly different from all other treatments. However, the WGA treatment, which has a mean D_{30} of 53- μm , is also statistically different from all other treatments. As shown in Figure 4-4, WGA provides a background on the PSA measurement. When measuring WGA without shale in water, a particle size is observed due to the physical properties of the additive. WGA is a gelling agent composed of petroleum distillate [141] that is solid until mixed with water and forms flocs in solution when mixed in water. Although the samples are diluted by water when measured in the PSA, the WGA still interfered with the measurement. Disregarding WGA, the smallest measured D_{30} particle size is the shale treated with Revert Flow (168.6- μm). The largest D_{30} particle size of the treated shales is the HCl treatment. Finally, ANOVA was performed to compare the differences in the D_{60} particle size across treatments. The mean D_{60} for the untreated, persulfate, HCl, and LEB-10X were not statistically different from one another. The untreated shale was statistically different from the rest of the treatments. However, all of the treatments were not statistically different from one another as the post hoc test grouped all of the treatments in the second group. The background in WGA most likely impacted measured particle size for the D_{60} even though the results are not statistically different. Ignoring WGA, the smallest resulting D_{60} particle size is from the Revert Flow treatment.

No single inorganic or organic treatment led to a D_{10} , D_{30} , or D_{60} particle size that was statistically different from the water only treatment. This was not expected as the organic and inorganic additives used are more corrosive than water. In addition to

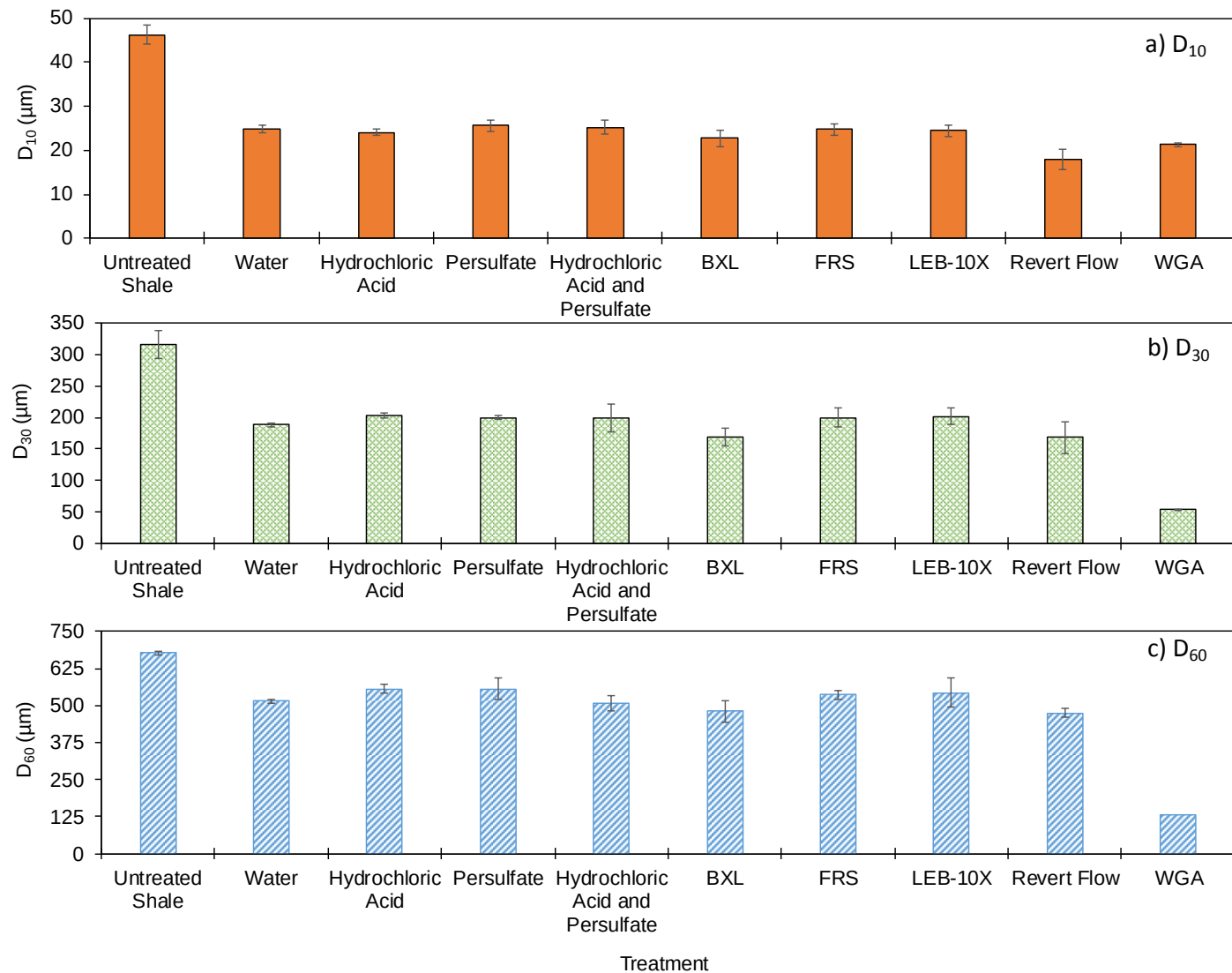


Figure 4-3. D_{10} , D_{30} , and D_{60} particle size measurements of treated shales, including water, 0.07% HCl, 21 mmol L⁻¹ persulfate, combined acid and persulfate, and the organic additives compared to untreated shale (n=3). Measurements were taken using the PSA.

Table 4-2. Average D-10, 30, and 60 particle sizes measured at 2800 rpm on the PSA (n=3).

Treatment	Average D ₁₀ (μm)	Average D ₃₀ (μm)	Average D ₆₀ (μm)
Untreated Shale	46.20	316.51	678.35
Water	24.84	188.21	514.25
Hydrochloric Acid	24.05	202.46	555.96
Persulfate	25.6	199.37	556.19
Hydrochloric Acid and Persulfate	25.22	198.93	507.64
BXL	22.74	168.87	480.87
FRS	24.71	200.05	536.22
LEB-10X	24.44	201.53	542.48
Revert Flow	17.9	168.61	475.30
WGA	21.24	53.32	131.17

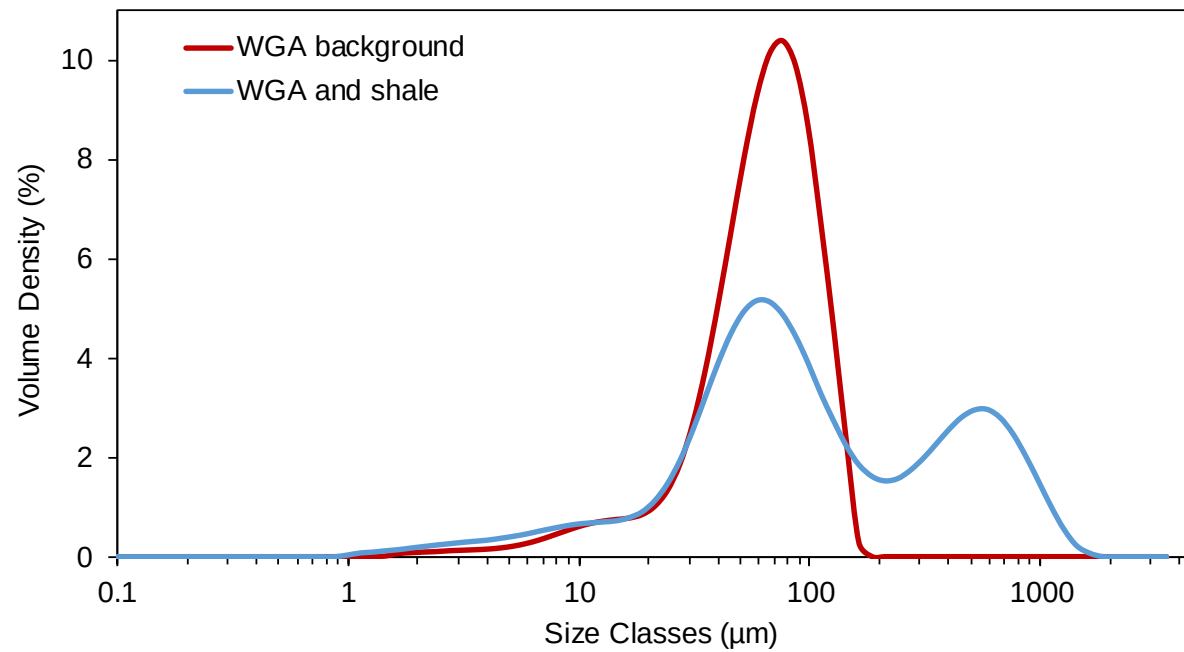


Figure 4-4. Background particle size provided by WGA on the PSA. WGA is a cellulosic solid material that provides a background on the PSA size distribution measurements.

abrasion during treatment, the water treatment was significantly different from the untreated particle size due to dissolution of major minerals in the shale, which will be discussed later in this chapter. The dissolution of minerals as the particles aged in the treatment likely weakened the shale particles, causing them to break apart.

Impact on shale minerology

Shale minerology was assessed before and after measurement in the PSA using XRD. Table 4-3 shows the shale minerology for each treatment post-mixing in the PSA. The XRD pattern of all the inorganic treatments are displayed in Figure 4-5 and organic treatments are displayed in Figure 4-6. Shale minerology did not vary before and after mixing in the PSA. The water and organic additives depleted the same minerals from the shale, including gypsum, some muscovite, and some calcite. Calcite, dolomite, gypsum, lavendulan, and some muscovite were depleted in the treatment containing 0.07% HCl. Pyrite was not observably impacted in the water, HCl, or organic additive treatments. However, pyrite was depleted in the treatments containing persulfate. Solutions were measured for persulfate concentration after the 8-day period; persulfate was below the detection limits of the method. Pyrite has previously been shown to activate persulfate due to the dissolution of Fe (II), producing strong hydroxyl radicals [142]. Fe (II) is used during *in situ* chemical oxidation (ISCO) as a persulfate activator [109]. While heat activates persulfate as shown in Reaction 1, additional activation using iron can speed up the production of strong sulfate radicals as shown in Reaction 2 [109]. The sulfate radicals subsequently react with water to form the hydroxyl radicals as shown in Reaction 3 [65]. Iron is problematic in fracing because it can clog pores and reduce production over time [17, 130].



Shale topology and mineral distribution

Figure A4 in the appendix displays the SEM images of the untreated shale. The untreated shale particles have observable surface roughness, jagged edges and are angular in shape. Figure 4-7 displays SEM images of untreated, water treated, and combined HCl/Persulfate treated shale taken with a high definition back scatter detector (HDBSD), which allows for compositional and crystallographic information. The brighter spots in the HDBSD images correspond to heavier elements; those analyzed were determined to be pyrite deposits. Minerals in the untreated shale, as shown in Figure 4-7 (a), are heterogeneously distributed. As shown in Appendix Figure A4, there is minimal surface pitting in untreated shale, which will be further discussed later in this paper using BET surface area measurements.

Table 4-3. Minerology of treated shales in comparison to untreated particles measured using XRD patterns displayed in Figure 4-5 and
Error! Reference source not found..

Sample Treatment	Albite	Calcite	Dolomite	Gypsum	Lavendulan	Muscovite -2M1, ammonian	Muscovite- 2M1	Pyrite	Quartz
Untreated	Trace	Minor	Trace	Minor	Trace	Minor	Minor	Minor	Major
Water	Trace	Minor	Trace	-	Trace	Minor	Minor	Minor	Major
BXL	Trace	Minor	Trace	-	Trace	Minor	Minor	Minor	Major
WGA	Trace	Minor	Trace	-	Trace	Minor	Minor	Minor	Major
FRS	Trace	Minor	Trace	-	Trace	Minor	Minor	Minor	Major
Revert Flow	Trace	Minor	Trace	-	Trace	Minor	Minor	Minor	Major
LEB-10X	Trace	Minor	Trace	-	Trace	Minor	Minor	Minor	Major
0.07% Hydrochloric Acid	Trace	-	-	-	Trace?	Minor	Minor	Minor	Major
21 mM Sodium Persulfate	Trace	-	-	-	Trace?	Minor	Minor	Trace	Major
0.07% Hydrochloric Acid + 21 mM Sodium Persulfate	-	-	-	-	Trace?	Minor	Minor	-	Major
Major	>25%								
Minor	10-25%								
Trace	<10% clearly in sample								
Trace?	<10% may not be in sample								

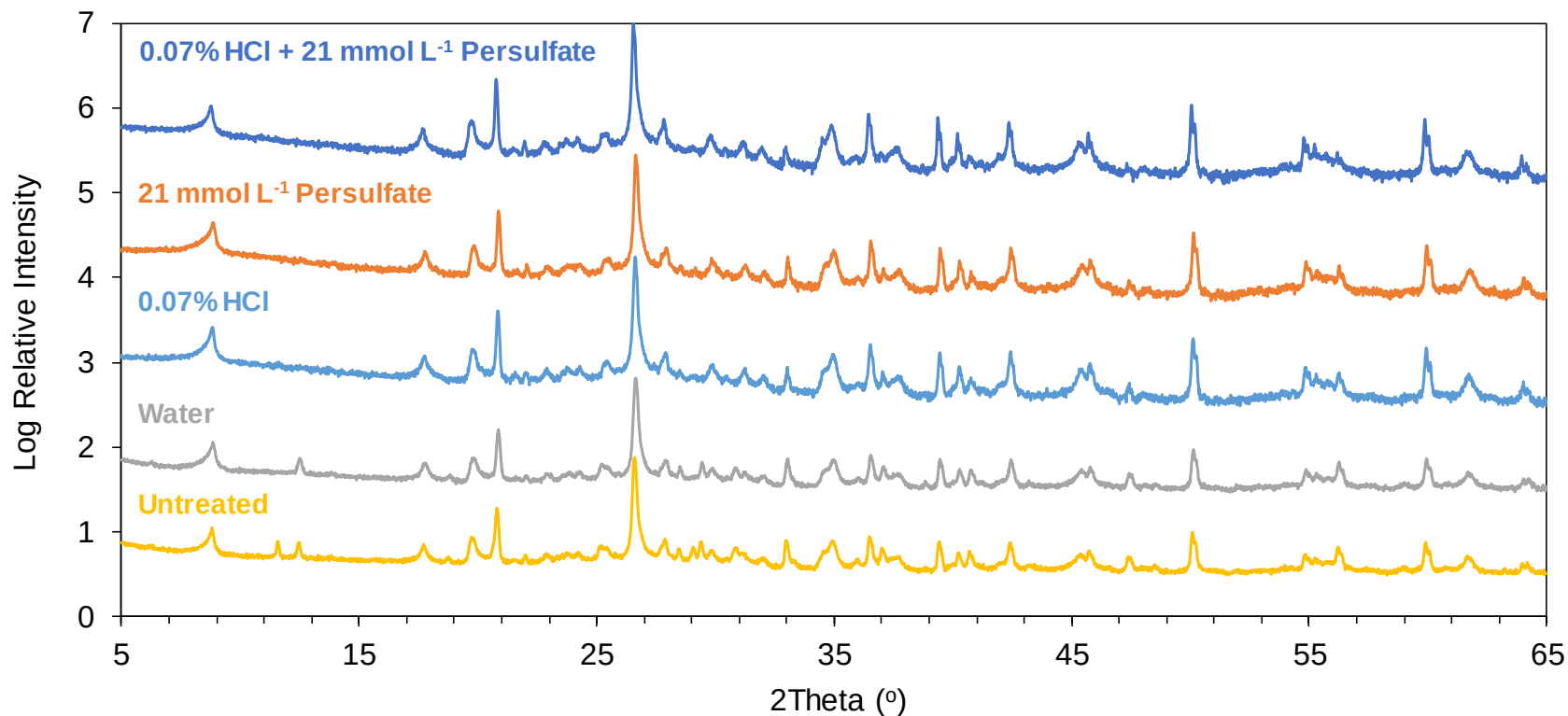


Figure 4-5. Diffraction pattern of inorganic treated shale particles in comparison to untreated shale particles obtained using XRD. Plots are log scale and the y-axis has been adjusted for ease of comparison. Hydrochloric acid depleted calcite, dolomite, gypsum, lavendulan, and some muscovite from the shale rock. Pyrite is depleted from the shale particles treated with persulfate.

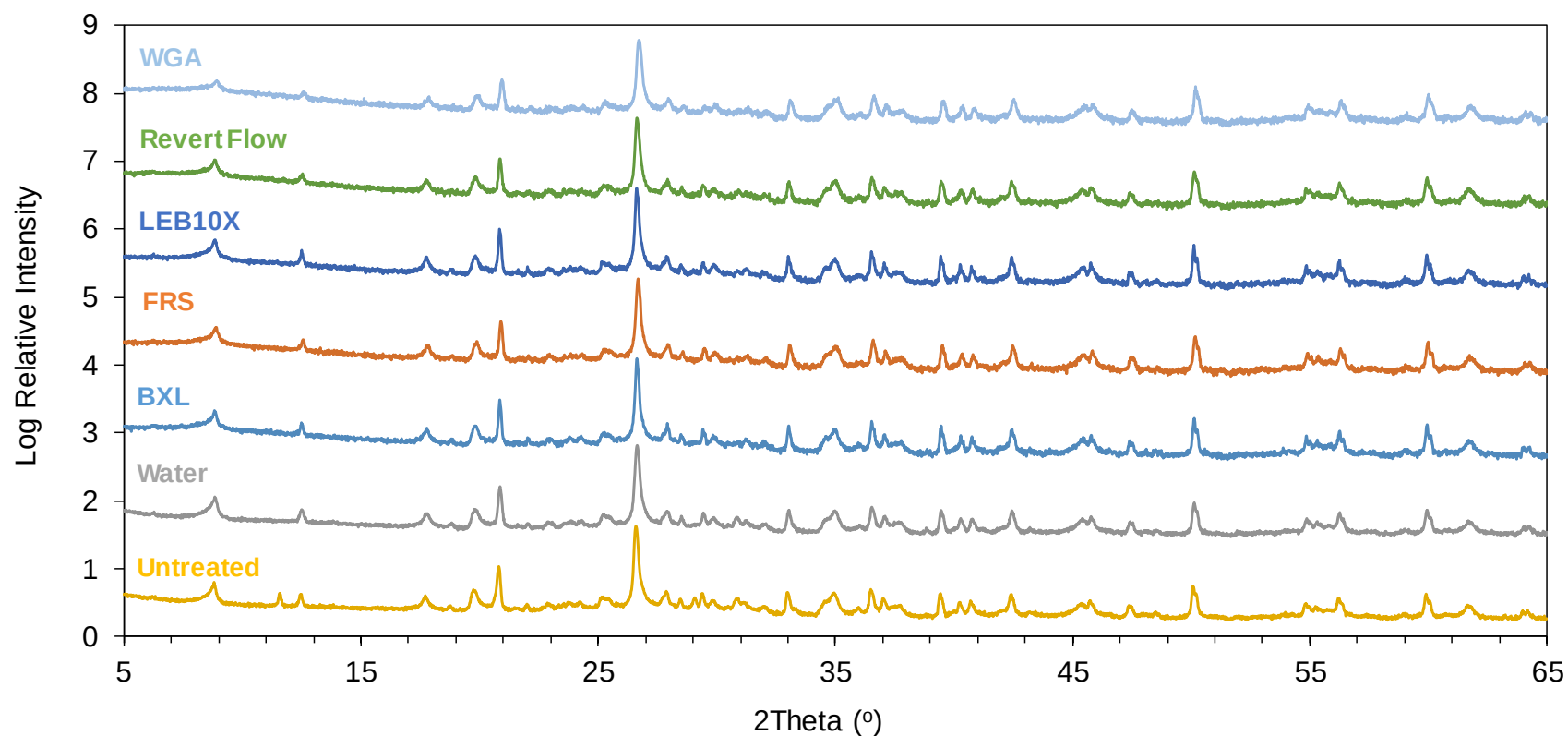


Figure 4-6. Diffraction pattern of organic treated shale particles in comparison to untreated shale particles measured using XRD. Plots are log scale and the y-axis has been adjusted for ease of comparison. Organic additives depleted the same minerals from the shale as water treatment removed, including gypsum, some muscovite, and some calcite.

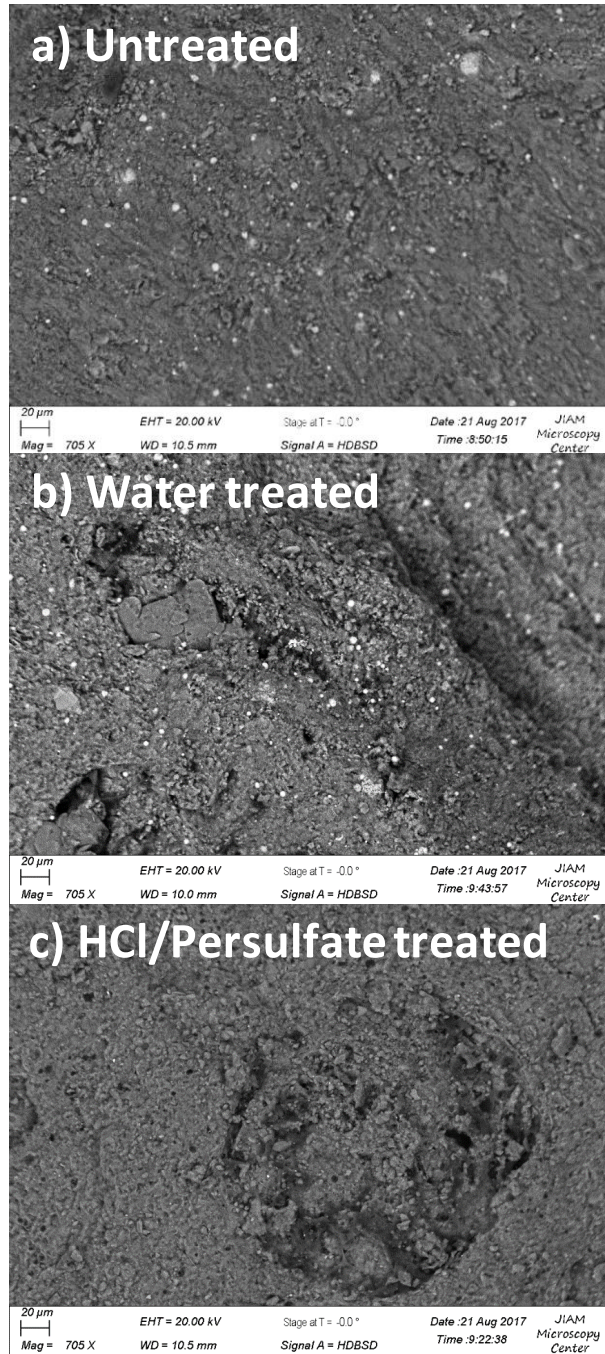


Figure 4-7. SEM images taken with HDBSD of the surface of (a) untreated, (b) water treated, and (c) combined HCl/persulfate treated shale. Bright spots in these images represent heavier elements in the surface minerals of the shale. The heavier elements are retained in untreated and water treated shale, but depleted from the HCl/persulfate treated shale.

SEM images of the water-treated shale particles before and after intense mixing in the PSA are shown in Appendix Figure A5 (a-c) and Figure A5 (d-f), respectively. Compared to untreated particles displayed in Appendix Figure A4, before mixing in the PSA, water-treated particles in Appendix Figure A5 (d-f) have rounder and less angular particle shape. Putting the shale particles in the PSA altered surface roughness. After mixing, the water-treated particles have smoother edges than before mixing. Pre-mixing, minimal surface area pitting is observed in comparison to post-mixing in the PSA for water-treated particles. As shown in Figure 4-7 (b), heavier elements are retained within the surface minerals of the water treated shale as observed by the numerous bright spots.

Appendix Figure A6, Figure A7, Figure A8, Figure A9, and Figure A10 display SEM images of the shale particles treated with organic additives after mixing in the PSA. Similarly, minimal pitting and rounded shape was observed post-mixing in the particles treated with organic additives. On the other hand, persulfate and HCl treated shales did exhibit pitting pre-mixing as shown in Appendix Figure A11 (a-c) for HCl and Appendix Figure A12 (a-c) for persulfate. Post-mixing, the persulfate treated shales retained some of the heavier elements as shown in Appendix Figure A12 (d-f); however, particles treated with HCl did not retain heavier elements as the images in Appendix Figure A12 (d-f) have no bright spots. Figure 4-7 (c) and Appendix Figure A13 displays SEM images of the shales particles treated with both HCl and persulfate. The combined treatment displays pitting and depletion of heavier elements. Depletion of elements is further supported by the ICP data presented in the next section.

Impacts on water quality

Solution pH

Figure 4-8 displays the average solution pH before and after 8 days of treatment. Generally, solution pH became more basic in treatments containing water or just organic additives after contact with the shale. In these treatments, the shale buffered the pH around 8.7. This is likely due to the dissolution of gypsum into solution, as previously discussed. In treatments with 0.07% HCl, the pH was very acidic before and after treatment. The average pH did not change greatly before and after 8 days, increasing from 1.94 to 1.97 without persulfate present. The slight rise in pH for treatments with HCl is consistent with the findings of Jew *et al* [130]. However, in all of the treatments containing sodium persulfate, solution pH became more acidic. With persulfate alone, the average pH dropped from 5.32 down to 1.84. The pH of the shales treated with sodium persulfate combined with HCl did not significantly change. The average initial pH was 1.94 and the average final pH was 1.66. Unlike the treatment with HCl alone, pH decreased with the addition of persulfate. Despite the carbonates in the shale that increased pH in all other cases, the radicals produced during heat and iron activation of persulfate (Reaction 4-1 and Reaction 4-2) quickly react with water to produce a hydrogen ion, as described in Reaction 4-3. This indicates that fracturing water chemistry varies and may change drastically depending on the additives used by fracturing companies. Solution pH in fracturing fluids will also largely depend and vary based on the amount of shale in contact with the fluid; the concentrations of shale used in this study are most likely less than those seen in the field.

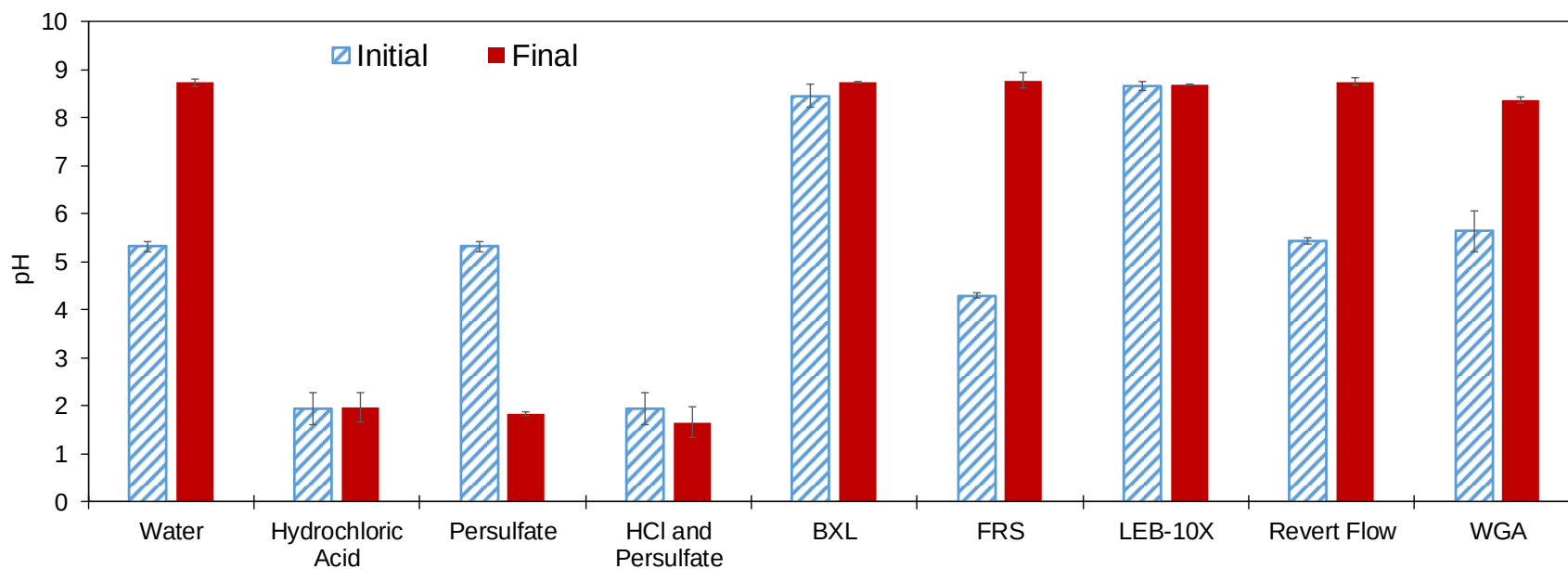


Figure 4-8. Average solution pH before and after the 8 days for each treatment (n=3). pH is buffered at 8.7 in the organic and water treatments. HCl and persulfate treated shales do not reach this buffering pH. HCl treated shale stays very acidic after the 8 days. The solution of persulfate treated shales decreased pH.

Aqueous inorganic geochemistry

Figure 4-1 shows the relative percentage of metals in the untreated shale. The untreated shale contained Si, Fe, Ca, Mg, Na, K, Al, Cu, Mn, Zn, Ba, Co, Cr, Ni, Pb, As, Cs, Li, Rb, Sr, U, and V. The major ions detected were Si, Fe, and Ca. Figure 4-9 displays the mass of individual inorganic metals leached into solution per mass of shale used in each 8-day treatment. In general, higher concentrations of the metals detected were in inorganic treatments. The major ion detected in the treatment fluid was Si, which is expected as shales are primarily composed of quartz (SiO_2). Minor metals detected in all treatments were K, Mg, and Ca and was confirmed with the XRD results of the treated shales, which previously showed gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), some muscovite ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$), and some calcite (CaCO_3) were depleted after all treatments. Higher levels of K, Mg, and Ca were detected in the inorganic treatments due to the depletion of dolomite ($\text{CaMg}(\text{CO}_3)_2$) and lavendulan ($\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl} \cdot 5\text{H}_2\text{O}$). Elements that were detected due to contact with inorganic treatments, but not the organic treatments, were Al, Fe, Co, Ni, U, and V. In the persulfate treated samples, the iron concentration was an order of magnitude higher than the HCl treated samples. This is due to the interactions between persulfate and pyrite. Previous studies involving the Marcellus shale play reported the same metals in flowback and produced waters as those detected in this study [7, 23, 41, 43, 135, 143-145]. The EPA has set Maximum Contaminant Levels (MCL) for some of these metals, including As (0.01 ppm), Ba (2 ppm), Cr (0.1 ppm), Cu (1.3 ppm), Pb (0 ppm), and U (0 ppm) [146]. Downhole, elevated concentrations of organics and metals decreases biocide efficacy [76, 77]. Furthermore, the concentration of TDS in flowback and produced water has been shown to increase as time from the initial stimulation increases [135].

Time dependence of inorganic treatments

Inorganic additives, including water, 0.07% HCl, 21 mmol L^{-1} persulfate, and combined HCl/persulfate, were selected as the extreme cases to investigate the impact of contact time on shale physical and chemical characteristics. Figure 4-10 shows the change in particle size over the course of 14 days in water, HCl, persulfate, and HCl/persulfate combined. For D_{10} , D_{30} , and D_{60} particle sizes in all treatments, the largest change occurred after just 24 hours of treatment. The D_{10} , D_{30} , and D_{60} did not change after day 1 for the water-treated particles. For the inorganic treatments, the D_{30} and D_{60} did not change; however, the D_{10} decreased steadily over the 14 days. For all inorganic treatments, particle size decreased by 35% (46- μm to 30- μm) between day 0 and 1. The average particle size decreased to 25- μm by day 8 and did not decrease further at day 14. Total surface area was also measured for the day 14 samples. The total specific surface area for the untreated, water, HCl, persulfate, and combined HCl/persulfate treated shale particles after mixing in the PSA was 12.6, 27.5, 43.4, 33.4, and 41.0 m^2/g , respectively. The total specific surface area of the water-treated shale nearly doubled over the 14 days. Treatment with HCl led to the largest specific surface area. On day 14, the D_{10} , D_{30} , and D_{60} particle sizes for HCl, persulfate, and combined HCl/persulfate are within 5% of one another. Particle size between treatments does not change, while the total surface area increases. This indicates that in treatments with higher total specific surface area, minerals are being stripped from the shale particles surface resulting in an

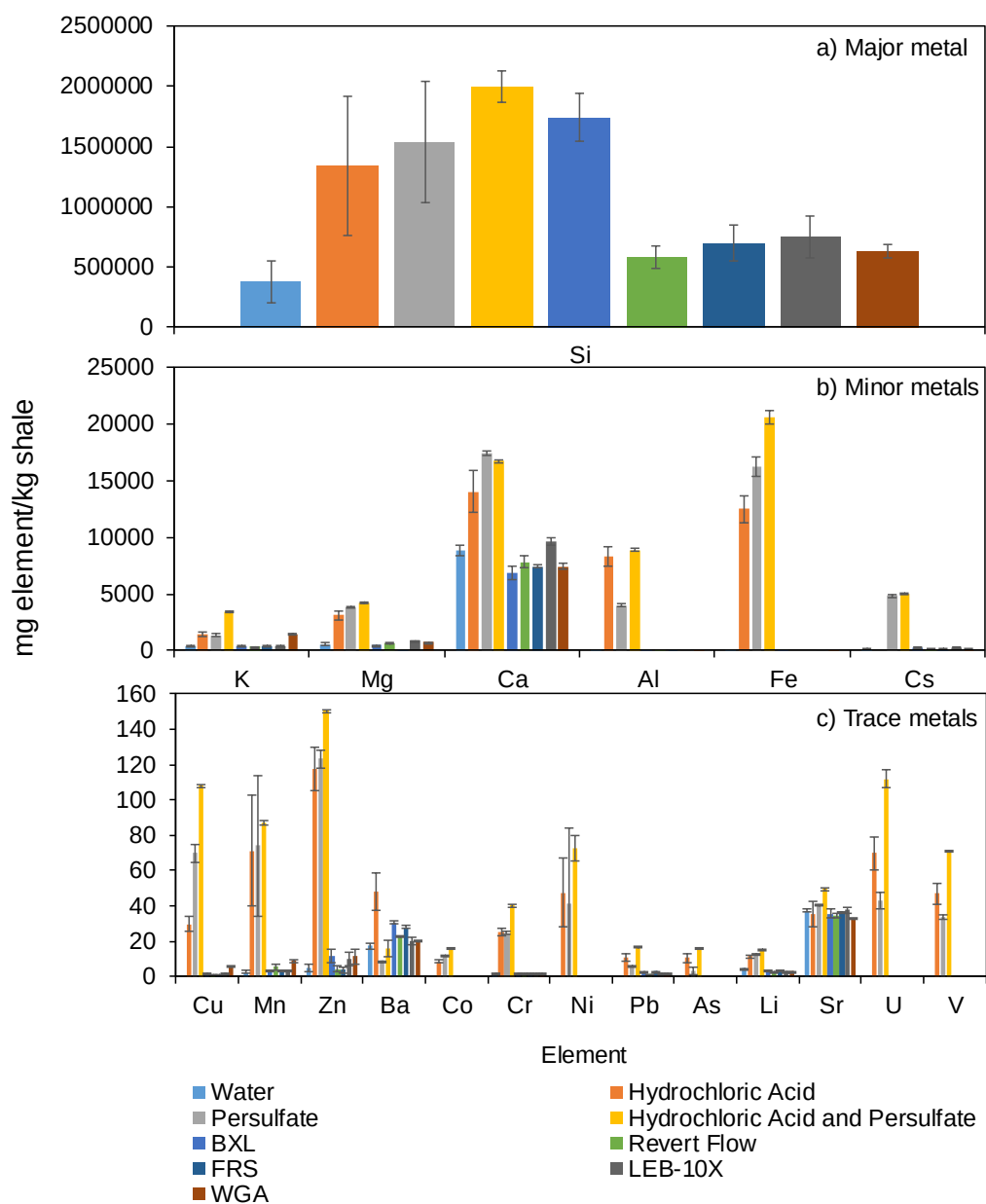


Figure 4-9. Mass of individual inorganic metals leached into solution per mass of shale used in each treatment. The major metal, Si, is displayed in (a), minor metals are displayed in (b), and trace metals are shown in (c). Concentrations of each metal in the supernatant solutions were analyzed using ICP.

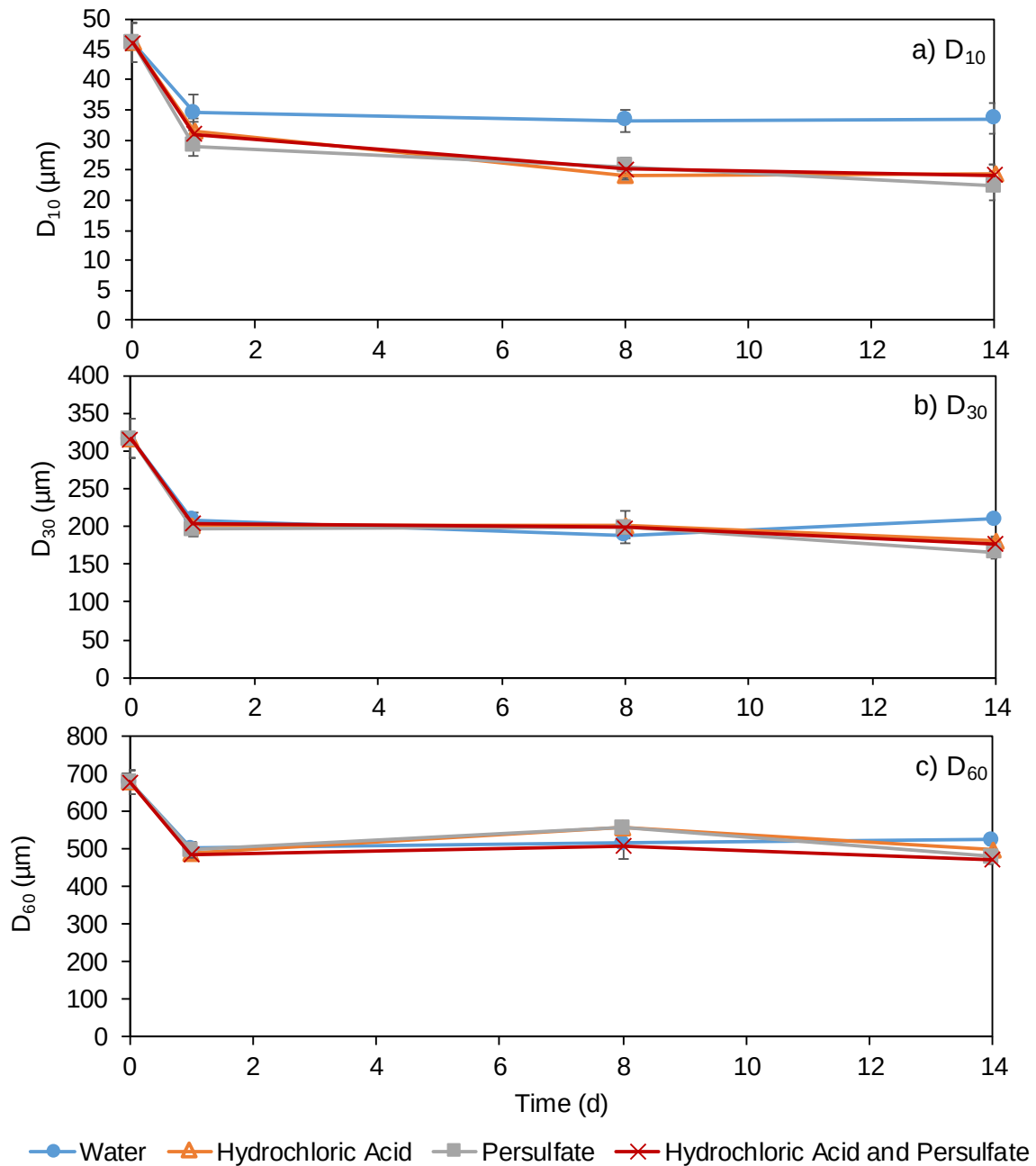


Figure 4-10. Change in D-10, 30, and 60 particle size in each tested inorganic treatment over the course of 14 days. Each sample slurry was measured using the PSA. Error bars represent standard error (n=3).

increased surface area. Dissolution of these minerals with respect to contact time will be further investigated later in this paper. Figure 4-11 displays the pH profile for each treatment and Figure 4-12 displays the concentration of persulfate remaining in solution. After 8 days, the pH of the water solution stabilizes at pH 8.7. In the treatments containing persulfate, the persulfate is completely consumed within the first 24 hours of the treatment. However, the pH continues to decrease after the first day. The persulfate treated shale solution has an initial pH of 5.45 and decreases to 1.8 by day 8. Treatments containing HCl stay very acidic over the course of the treatment, decreasing from 2 to 1.52 in the treatment with just HCl and from 2 to 1.3 in the combined persulfate/HCl treatment. The acid dissolves the minerals in the shale, but there are insufficient carbonates in the shale added to buffer the pH.

Figure 4-13, Figure 4-14, and Figure 4-15 show the dissolution of major, minor and trace metals, respectively, over the course of 14 days. The concentration of major ions, K, Mg, Si, Fe, Al, and Ca, ranges between 0 and 5×10^6 mg-metal/kg-shale. For all major ions, the concentrations are much greater in HCl, persulfate, and combined HCl/persulfate than in water over the course of the 14 days. No Fe or Al was detected in the water treatment. In the HCl and persulfate treatments, all of the major ions, besides Ca, continually dissolve over the course of 14 days. The concentration of Ca reaches a maximum after the first day in all treatments, except for the case of persulfate alone. Ca dissolution is due to the gypsum in the shale particles, which is depleted when the shale contacts water, as previously discussed. Higher concentrations of Ca are detected in the treatments with persulfate and HCl because these treatments also dissolve calcite and dolomite. The concentration of minor ions, Cs, Mn, V, Zn, Cu, and U, are between 0 and 8,000 mg-metal/kg-shale. In the water treatment, no U or V was detected over the course of 14 days and much smaller concentrations of Cs, Mn, Zn, and Cu were detected in comparison to the other treatments. Cs was only detected in solution of the treatments containing persulfate. The concentration of trace ions, Ba, Cr, Pb, Sr, Co, Ni, As, and Li, ranges between 0 and 110 mg-metal/kg-shale. No Ni or As was detected in the water treatment. In general, for major, minor, and trace metals, the highest concentrations are detected in the combined HCl/persulfate treatment, with the exception of Ba. For Ba, the concentration is much higher in the treatment with just HCl. As persulfate reacts and sulfate radicals form, the radicals eventually become sulfate (Reaction 3). In the treatments containing persulfate, Ba may be precipitating out as BaSO_4 salt; therefore, the concentration detected in the supernatant is lower. The continual dissolution of metals indicates that longer contact between the shale and fluids containing persulfate and hydrochloric additives downhole will result in greater concentrations of TDS. As the time fluids spend downhole increases, the quality of water will continually diminish.

Conclusion

This study investigated the decomposition of shale rock due to interactions with typical additives used by fracing companies, including water, hydrochloric acid, persulfate, and 5 organic additives, including LEB10X, WGA, BXL, FRS, and Revert Flow. Changes in shale physical and chemical properties were observed using laser-based PSA, SEM, and

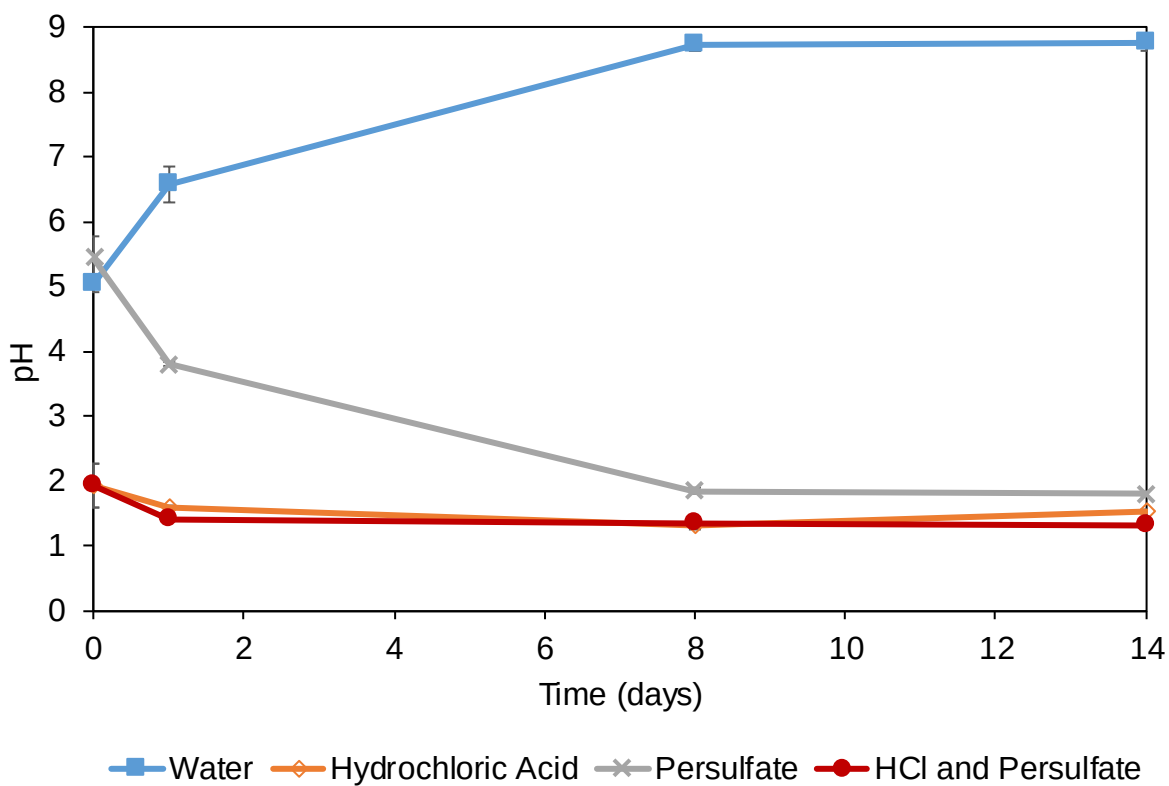


Figure 4-11. Average pH profiles in each tested inorganic treatment over the course of 14 days. Error bars represent standard error (n=3).

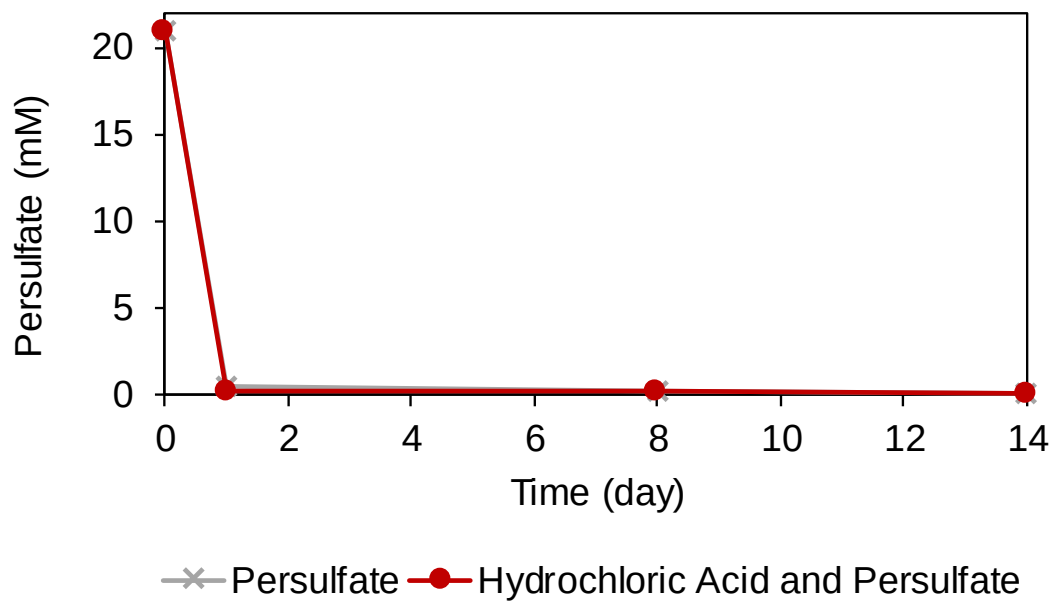


Figure 4-12. Average persulfate concentration in each treatment containing persulfate over the course of 14 days. By day 1, the remaining persulfate concentration was near the detection limits of the method used. Standard error was small, but error bars are displayed and represent standard error (n=3).

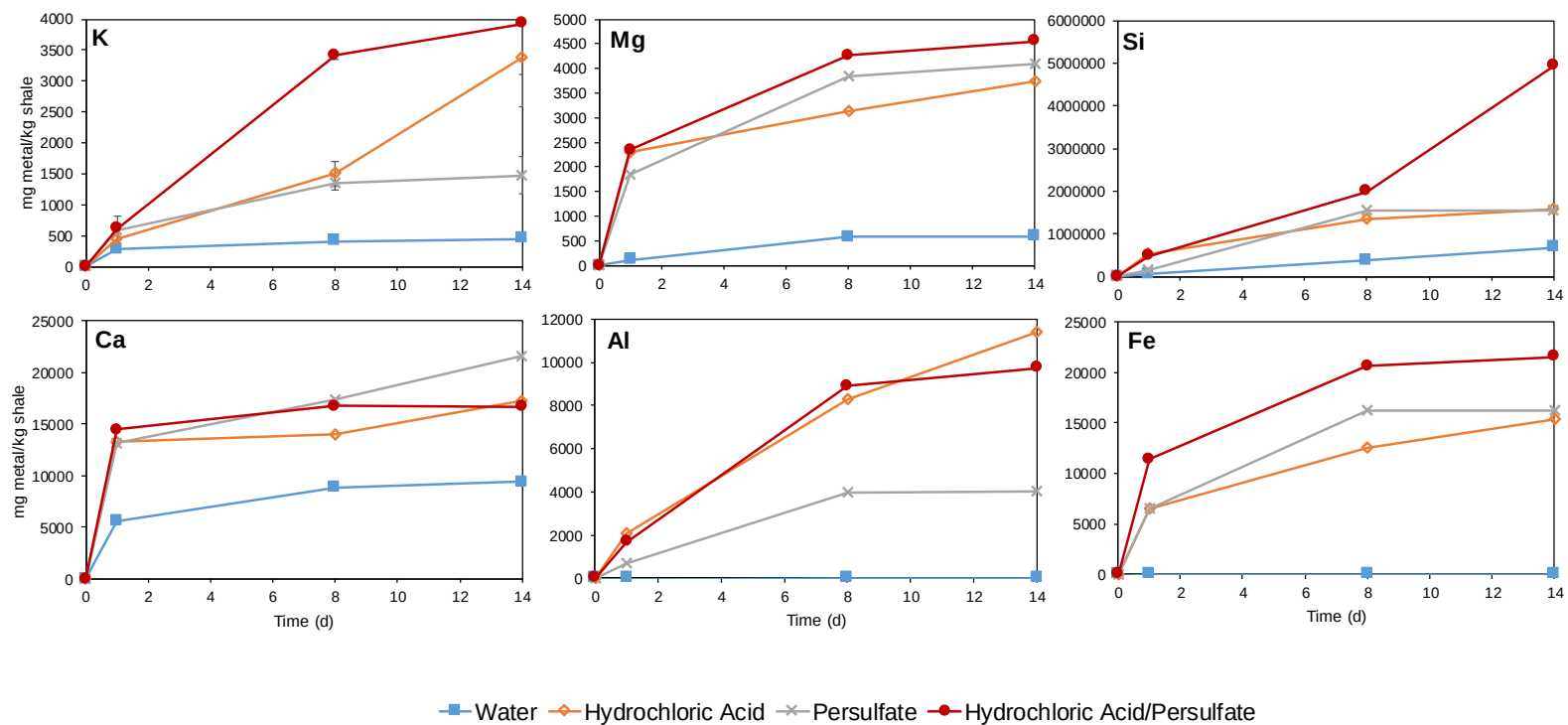


Figure 4-13. Dissolution of major ions over the course of 14 days as measured using ICP.

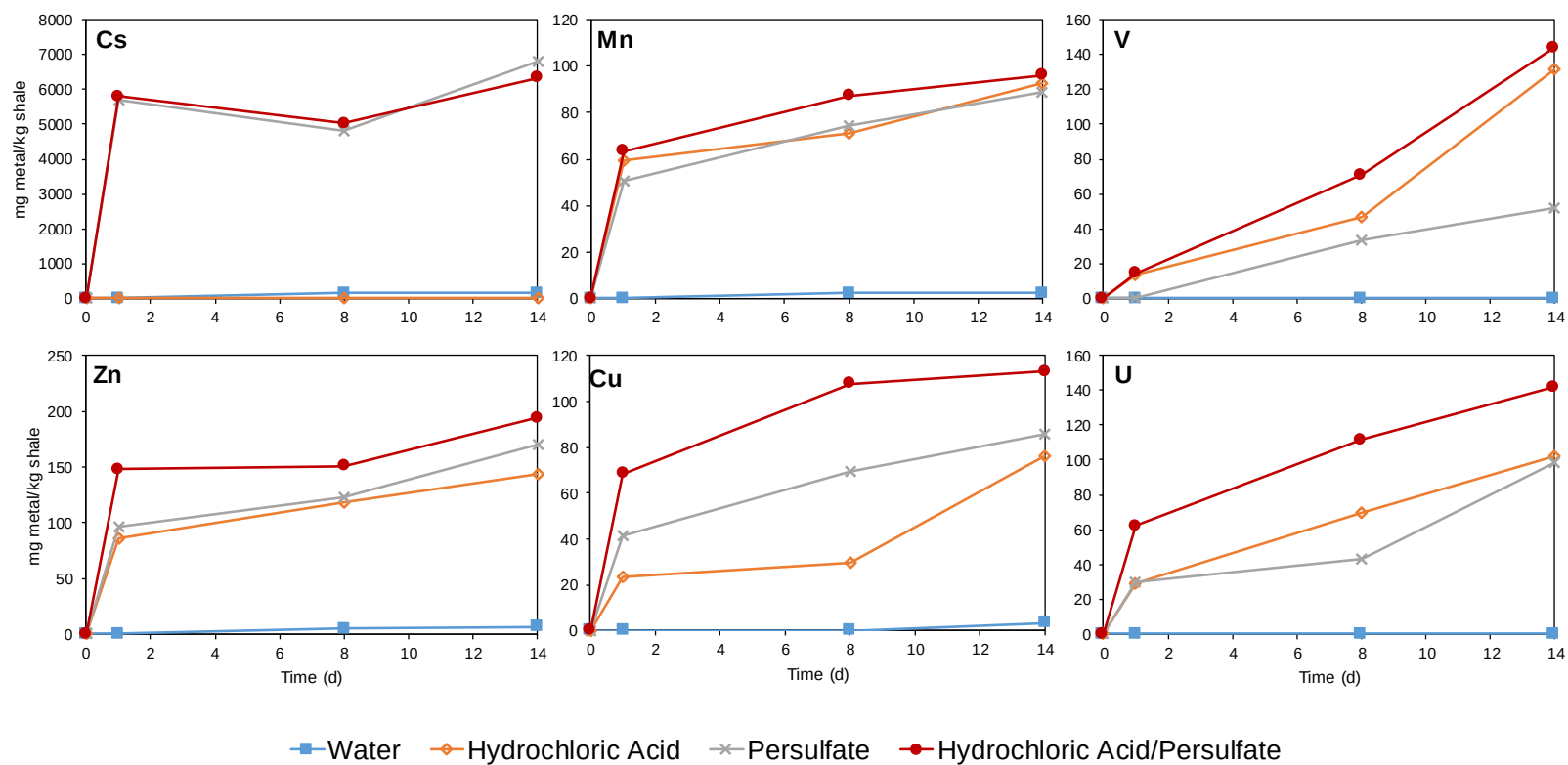


Figure 4-14. Dissolution of minor ions over the course of 14 days as measured using ICP.

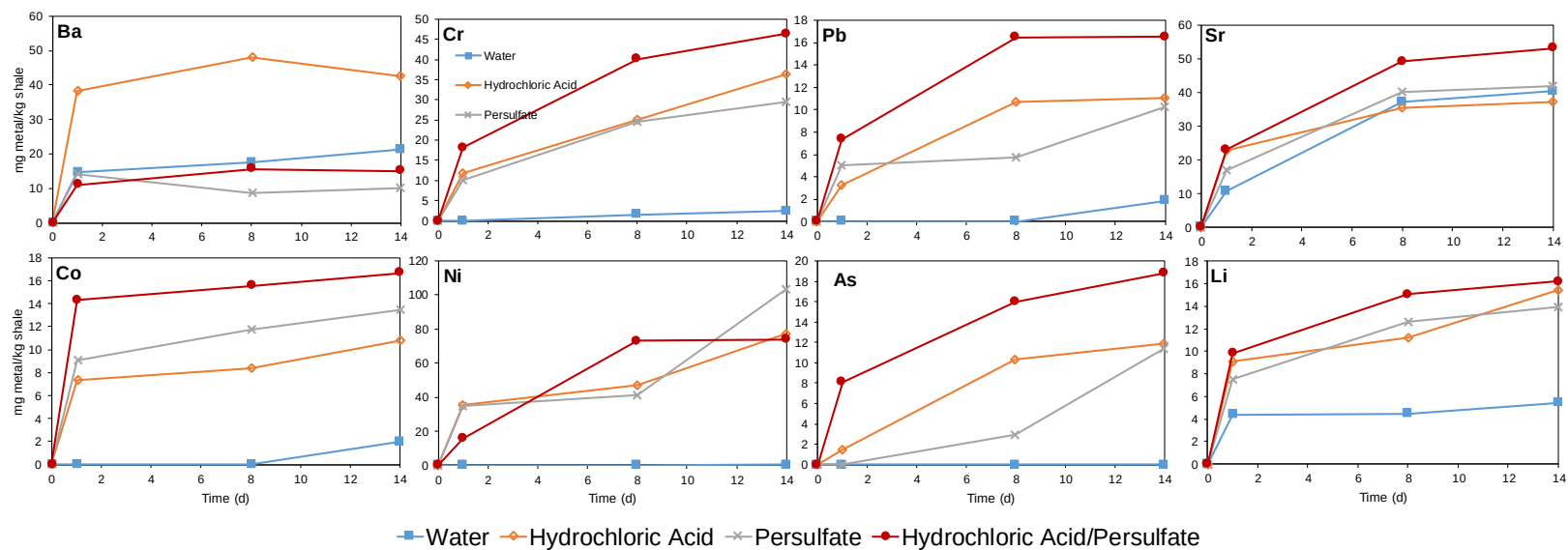


Figure 4-15. Dissolution of trace ions over the course of 14 days as measured using ICP.

XRD. As the shale constituents dissolved into the water, the impact of the interactions on water quality were examined by measuring pH, persulfate concentration, and metal concentration using ICP. For laser-based PSA measurements of untreated shale, the optimal stirrer mixing speed was determined and measurements of treated shale particles were performed at 2800-rpm. After 2800-rpm, particulates deteriorated due to the intense mixing speeds. For particles treated with the additives, the measured D_{10} , D_{30} , and D_{60} sizes were not statistically different from treatment with water alone. However, XRD results showed that more mineral types were stripped from the shale when treated with inorganic additives (persulfate and hydrochloric acid) in comparison to treatment with water. Pyrite was only depleted from the shale when persulfate was used. SEM imaging showed that there was increased pitting in particles treated with inorganic additives due to the removal of heavier elements, which was supported by the ICP analysis of the supernatant solution. Finally, the impact of solution contact time was investigated. Contact time did not impact particle size after 24 hours; however, most metals detected using ICP, some of which are regulated by the EPA, continued to dissolve into solution over the course of 14 days. BET surface area was analyzed on day 14 and surface area for all tested treatments increased in comparison to the untreated particles, while treatment with hydrochloric acid led to the highest specific surface area. Higher surface area can lead to microbial growth in aerobic and anoxic conditions [73-75], increasing sulfide production and causing natural gas souring [77].

The results of this study provide more information on how fracturing fluids change over the course of a fracture due to interaction with shale rock. By understanding which additives cause deterioration and dissolution of minerals in shale particles, fracturing companies and wastewater treatment plants can be better equipped to handle and transport the fluids. Future studies should model the geochemical interactions and investigate the impacts of extreme pressure on the reactions between inorganic additives and shale particulates.

CHAPTER 5

CONCLUSION

The research contained in this dissertation addressed water quality issues related to hydraulic fracturing, namely migration and transformation of additives and shale rock. Transformation studies are more useful in assessing the environmental threat that hydraulic fracturing fluids pose because the fluids that return to the well surface are not the same as the fluids injected. The most common cause for environmental pollution by hydraulic fracturing fluids is post-fracture spills during transportation of the fluids to treatment facilities [137]. In most cases, the spilled fluids have already transformed downhole. The post-fracture fluids are potentially more harmful and could pose severe human health and environmental risks.

This dissertation fills a knowledge gap by addressing the migration and transformation of hydraulic fracturing fluids and the impact of chemical use on the shale formations. In the second chapter, the absorption of two contaminants with surfactant and non-surfactant properties to GAC and shale rock was investigated. The major findings in this chapter were related to the potential migration of hydraulic fracturing fluids. 2-BE, the surfactant compound, and 3-furaldehyde, the non-surfactant, did not adsorb to shale rock, which indicates that these compounds may potentially migrate through the shale formation into surrounding water bodies. In the third chapter, the transformation of 2-BE in the presence of the oxidizing breaking agent persulfate was examined. 2-BE is used as an indicator compound for hydraulic fracturing spills, but the studies in Chapter 3 showed that 2-BE has a very short half-life when reacted with persulfate. Moreover, the excess persulfate causes dissolution of heavy metals from shale rock. In the fourth chapter, the interactions between shale rock and additives are studied. While the observed decrease in particle size may be attributed to interaction with water alone, interaction with each additive caused depletion of minerals from the surface of the shale. The depletion of minerals was more significant in the shales treated with inorganic additives than with organic additives.

Overall, the results of this dissertation provide more information about what the fluids contain post-fracture and the potential for chemical additive migration. Using this information, hydraulic fracturing companies may be more knowledgeable about the potential contents when spills occur or when sending the wastewater to treatment plants. Future studies should investigate the influence of extreme pressure on the adsorption of additives onto shale in the hydraulic fracturing environment, the reactions between 2-BE and persulfate, and the interactions between additives and shale particulates. Future studies should also investigate removal of constituents from the transformed fluids so that the fluids can be reused on-site for another fracture. This would alleviate fresh water requirements and prevent the transportation of fluids off-site.

REFERENCES

- [1] Annual Energy Outlook 2017 with Projections to 2050, in: U.S.E.I. Administration (Ed.), U.S. Department of Energy, Washington, DC, 2017.
- [2] A. Watterson, W. Dinan, The U.K.'s "Dash for Gas", *NEW SOLUTIONS: A Journal of Environmental and Occupational Health Policy* 0 1048291117698175.
- [3] M. Thomas, N. Pidgeon, D. Evensen, T. Partridge, A. Hasell, C. Enders, B.H. Harthorn, M. Bradshaw, Public perceptions of hydraulic fracturing for shale gas and oil in the United States and Canada, *WIREs Climate Change* (2016).
- [4] D.M. Kargbo, R.G. Wilhelm, D.J. Campbell, Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities, *Environmental Science & Technology* 44 (2010) 5679-5684.
- [5] R.D. Vidic, S.L. Brantley, J.M. Vandenbossche, D. Yoxtheimer, J.D. Abad, Impact of Shale Gas Development on Regional Water Quality, *Science* 340 (2013).
- [6] D. Rahm, Regulating hydraulic fracturing in shale gas plays: The case of Texas, *Energy Policy* 39 (2011) 2974-2981.
- [7] K.B. Gregory, R.D. Vidic, D.A. Dzombak, Water management challenges associated with the production of shale gas by hydraulic fracturing, *Elements* 7 (2011) 181.
- [8] F.R. Spellman, Environmental impacts of hydraulic fracturing, CRC Press 2012.
- [9] Q. Wang, X. Chen, A.N. Jha, H. Rogers, Natural gas from shale formation – The evolution, evidences and challenges of shale gas revolution in United States, *Renewable and Sustainable Energy Reviews* 30 (2014) 1-28.
- [10] R.A. Kerr, Natural Gas From Shale Bursts Onto the Scene, *Science* 328 (2010) 1624-1626.
- [11] B.R. Scanlon, R.C. Reedy, J.P. Nicot, Comparison of Water Use for Hydraulic Fracturing for Unconventional Oil and Gas versus Conventional Oil, *Environmental Science & Technology* 48 (2014) 12386-12393.
- [12] R.G. Newell, B.C. Prest, A. Vissing, Trophy hunting vs. manufacturing energy: The price-responsiveness of shale gas, National Bureau of Economic Research, 2016.
- [13] D.S. Lee, J.D. Herman, D. Elsworth, H.T. Kim, H.S. Lee, A critical evaluation of unconventional gas recovery from the marcellus shale, northeastern United States, *KSCE Journal of Civil Engineering* 15 (2011) 679.
- [14] API, Hydraulic Fracturing Operations - Well Construction and Integrity Guidelines, in: A.P. Institute (Ed.) Washington, DC, 2009.
- [15] D.J. Soeder, S. Sharma, N. Pekney, L. Hopkinson, R. Dilmore, B. Kutchko, B. Stewart, K. Carter, A. Hakala, R. Capo, An approach for assessing engineering risk from shale gas wells in the United States, *International Journal of Coal Geology* 126 (2014) 4-19.
- [16] W.T. Stringfellow, M.K. Camarillo, J.K. Domen, W.L. Sandelin, C. Varadharajan, P.D. Jordan, M.T. Reagan, H. Cooley, M.G. Heberger, J.T. Birkholzer, Identifying chemicals of concern in hydraulic fracturing fluids used for oil production, *Environmental Pollution* 220 (2017) 413-420.
- [17] W.T. Stringfellow, J.K. Domen, M.K. Camarillo, W.L. Sandelin, S. Borglin, Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing, *Journal of Hazardous Materials* 275 (2014) 37-54.
- [18] G.E. King, Hydraulic fracturing 101: what every representative, environmentalist, regulator, reporter, investor, university researcher, neighbor, and engineer should

- know about hydraulic fracturing risk, *Journal of Petroleum Technology* 64 (2012) 34-42.
- [19] H. Boudet, C. Clarke, D. Bugden, E. Maibach, C. Roser-Renouf, A. Leiserowitz, "Fracking" controversy and communication: Using national survey data to understand public perceptions of hydraulic fracturing, *Energy Policy* 65 (2014) 57-67.
 - [20] C.E. Clark, A.J. Burnham, C.B. Harto, R.M. Horner, INTRODUCTION: The Technology and Policy of Hydraulic Fracturing and Potential Environmental Impacts of Shale Gas Development, *Environmental Practice* 14 (2012) 249-261.
 - [21] S.G. Osborn, A. Vengosh, N.R. Warner, R.B. Jackson, Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing, *proceedings of the National Academy of Sciences* 108 (2011) 8172-8176.
 - [22] A. Vengosh, R.B. Jackson, N. Warner, T.H. Darrah, A. Kondash, A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States, *Environmental science & technology* 48 (2014) 8334-8348.
 - [23] V. Marcon, C. Joseph, K.E. Carter, S.W. Hedges, C.L. Lopano, G.D. Guthrie, J.A. Hakala, Experimental insights into geochemical changes in hydraulically fractured Marcellus Shale, *Applied Geochemistry* 76 (2017) 36-50.
 - [24] T.A. Blewett, P.L. Delompré, Y. He, E.J. Folkerts, S.L. Flynn, D.S. Alessi, G.G. Goss, Sublethal and Reproductive Effects of Acute and Chronic Exposure to Flowback and Produced Water from Hydraulic Fracturing on the Water Flea *Daphnia magna*, *Environmental Science & Technology* 51 (2017) 3032-3039.
 - [25] U.S. EPA, Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources (External Review Draft), in: U.S. EPA (Ed.) Washington, DC, 2015.
 - [26] H.A. Waxman, E.J. Markey, D. DeGette, Chemicals used in hydraulic fracturing, United States House of Representatives Committee on Energy and Commerce Minority Staff (2011).
 - [27] E.G. Elliott, A.S. Ettinger, B.P. Leaderer, M.B. Bracken, N.C. Deziel, A systematic evaluation of chemicals in hydraulic-fracturing fluids and wastewater for reproductive and developmental toxicity, *J Expos Sci Environ Epidemiol* 27 (2016) 90-99.
 - [28] E.E. Yost, J. Stanek, R.S. DeWoskin, L.D. Burgoon, Overview of Chronic Oral Toxicity Values for Chemicals Present in Hydraulic Fracturing Fluids, Flowback, and Produced Waters, *Environmental Science & Technology* 50 (2016) 4788-4797.
 - [29] R. Michalski, A. Ficek, Environmental pollution by chemical substances used in the shale gas extraction—a review, *Desalination and Water Treatment* 57 (2016) 1336-1343.
 - [30] E.E. Yost, J. Stanek, L.D. Burgoon, A decision analysis framework for estimating the potential hazards for drinking water resources of chemicals used in hydraulic fracturing fluids, *Science of The Total Environment* (2016).
 - [31] M.C. McLaughlin, T. Borch, J. Blotevogel, Spills of Hydraulic Fracturing Chemicals on Agricultural Topsoil: Biodegradation, Sorption, and Co-contaminant Interactions, *Environmental Science & Technology* 50 (2016) 6071-6078.

- [32] G.A. Kahrilas, J. Blotevogel, E.R. Corrin, T. Borch, Downhole Transformation of the Hydraulic Fracturing Fluid Biocide Glutaraldehyde: Implications for Flowback and Produced Water Quality, *Environmental Science & Technology* 50 (2016) 11414-11423.
- [33] M. Dieterich, B. Kutchko, A. Goodman, Characterization of Marcellus Shale and Huntersville Chert before and after exposure to hydraulic fracturing fluid via feature relocation using field-emission scanning electron microscopy, *Fuel* 182 (2016) 227-235.
- [34] K.E. Manz, K.E. Carter, Investigating the effects of heat activated persulfate on the degradation of furfural, a component of hydraulic fracturing fluid chemical additives, *Chemical Engineering Journal* 327 (2017) 1021-1032.
- [35] FracFocus.org, What Chemicals Are Used.
- [36] R.W. Howarth, A. Ingraffea, T. Engelder, Natural gas: Should fracking stop?, *Nature* 477 (2011) 271-275.
- [37] C.D. Kassotis, D.E. Tillitt, J.W. Davis, A.M. Hormann, S.C. Nagel, Estrogen and Androgen Receptor Activities of Hydraulic Fracturing Chemicals and Surface and Ground Water in a Drilling-Dense Region, *Endocrinology* 155 (2014) 897-907.
- [38] C.R. Tyler, S. Jobling, J.P. Sumpter, Endocrine Disruption in Wildlife: A Critical Review of the Evidence, *Critical Reviews in Toxicology* 28 (1998) 319-361.
- [39] R.L. Cooper, R.J. Kavlock, Endocrine disruptors and reproductive development: a weight-of-evidence overview, *Journal of Endocrinology* 152 (1997) 159-166.
- [40] Y. He, E.J. Folkerts, Y. Zhang, J.W. Martin, D.S. Alessi, G.G. Goss, Effects on Biotransformation, Oxidative Stress, and Endocrine Disruption in Rainbow Trout (*Oncorhynchus mykiss*) Exposed to Hydraulic Fracturing Flowback and Produced Water, *Environmental Science & Technology* 51 (2017) 940-947.
- [41] K.E. Manz, K.E. Carter, Extraction and recovery of 2-butoxyethanol from aqueous phases containing high saline concentration, *Analytical Chemistry Research* 9 (2016) 1-7.
- [42] U.S. EPA, Study of the potential impact of hydraulic fracturing on drinking water resources: progress report, in: U.S.E.P. Agency (Ed.) Washington, D.C., 2012.
- [43] K.J. Ferrar, D.R. Michanowicz, C.L. Christen, N. Mulcahy, S.L. Malone, R.K. Sharma, Assessment of effluent contaminants from three facilities discharging Marcellus Shale wastewater to surface waters in Pennsylvania, *Environmental science & technology* 47 (2013) 3472-3481.
- [44] N. Ito, T. Fujiyama, Y. Udagawa, A Study of Local Structure Formation in Binary Solutions of 2-Butoxyethanol and Water by Rayleigh Scattering and Raman Spectra, *Bulletin of the Chemical Society of Japan* 56 (1983) 379-385.
- [45] F. Quirion, L. Magid, M. Drifford, Aggregation and critical behavior of 2-butoxyethanol in water, *Langmuir*; (USA) 6 (1990).
- [46] J.D. Rogers, T.L. Burke, S.G. Osborn, J.N. Ryan, A Framework for Identifying Organic Compounds of Concern in Hydraulic Fracturing Fluids Based on Their Mobility and Persistence in Groundwater, *Environmental Science & Technology Letters* 2 (2015) 158-164.
- [47] F.N. Peters, Industrial Uses of Furans, *Industrial & Engineering Chemistry* 31 (1939) 178-180.

- [48] L. Xin-tong, Application of the demulsification technique in petroleum refining, *Journal of Jilin Institute of Chemical Technology* 1 (2011) 010.
- [49] H.E. Hoydonckx, W.M. Van Rhijn, W. Van Rhijn, D.E. De Vos, P.A. Jacobs, *Furfural and Derivatives*, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA2000.
- [50] M. Zoveidavianpoor, A. Gharibi, Application of polymers for coating of proppant in hydraulic fracturing of subterranean formations: A comprehensive review, *Journal of Natural Gas Science and Engineering* 24 (2015) 197-209.
- [51] F. Liang, M. Sayed, G.A. Al-Muntasheri, F.F. Chang, L. Li, A comprehensive review on proppant technologies, *Petroleum* 2 (2016) 26-39.
- [52] G.T. Llewellyn, F. Dorman, J.L. Westland, D. Yoxtheimer, P. Grieve, T. Sowers, E. Humston-Fulmer, S.L. Brantley, Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development, *Proceedings of the National Academy of Sciences* 112 (2015) 6325-6330.
- [53] N.H. Proctor, J.P. Hughes, G.J. Hathaway, *Proctor and Hughes' chemical hazards of the workplace*, John Wiley & Sons2004.
- [54] Cal/OSHA, Title 8, California Code of Regulations, § 5155, Table AC-1, Permissible Exposure Limits for Chemical Contaminants. , California Division of Occupational Safety and Health (Cal/OSHA). , 2007.
- [55] OSHA, Occupational Safety and Health Guideline for Furfural, in: U.O.S.a.H.A. (OSHA) (Ed.)Washington, DC, 1996.
- [56] EPA, Toxicological Review of Ethylene Glycol Monobutyl Ether (EGBE)(CAS No. 111-76-2), in: I.R.I.S.I. U.S. Environmental Protection Agency (Ed.), 2010.
- [57] N.P. Cheremisinoff, A. Davletshin, *Hydraulic Fracturing Operations: Handbook of Environmental Management Practices*, John Wiley & Sons2015.
- [58] D.T. Birdsell, H. Rajaram, D. Dempsey, H.S. Viswanathan, Hydraulic fracturing fluid migration in the subsurface: A review and expanded modeling results, *Water Resources Research* 51 (2015) 7159-7188.
- [59] A.K. Sahu, V.C. Srivastava, I.D. Mall, D.H. Lataye, Adsorption of furfural from aqueous solution onto activated carbon: Kinetic, equilibrium and thermodynamic study, *Separation Science and Technology* 43 (2008) 1239-1259.
- [60] A.H. Sulaymon, K.W. Ahmed, Competitive Adsorption of Furfural and Phenolic Compounds onto Activated Carbon in Fixed Bed Column, *Environmental Science & Technology* 42 (2008) 392-397.
- [61] S. Lucas, M.J. Cocero, C. Zetzl, G. Brunner, Adsorption isotherms for ethylacetate and furfural on activated carbon from supercritical carbon dioxide, *Fluid Phase Equilibria* 219 (2004) 171-179.
- [62] R. Ranjan, S. Thust, C.E. Gounaris, M. Woo, C.A. Floudas, M.v. Keitz, K.J. Valentas, J. Wei, M. Tsapatsis, Adsorption of fermentation inhibitors from lignocellulosic biomass hydrolyzates for improved ethanol yield and value-added product recovery, *Microporous and Mesoporous Materials* 122 (2009) 143-148.
- [63] P. Gupta, A. Nanoti, M. Garg, A. Goswami, The removal of furfural from water by adsorption with polymeric resins, *Separation Science and Technology* 36 (2001) 2835-2844.
- [64] M. Anbia, N. Mohammadi, A nanoporous adsorbent for removal of furfural from aqueous solutions, *Desalination* 249 (2009) 150-153.

- [65] R.H. Waldemer, P.G. Tratnyek, R.L. Johnson, J.T. Nurmi, Oxidation of chlorinated ethenes by heat-activated persulfate: kinetics and products, *Environmental Science & Technology* 41 (2007) 1010-1015.
- [66] I.M. Kolthoff, I.K. Miller, The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium¹, *Journal of the American Chemical Society* 73 (1951) 3055-3059.
- [67] A.O. Aliu, J. Guo, S. Wang, Hydraulic Fracture Fluid For Gas Reservoirs in Petroleum Engineering Applications Using Sodium Carboxy Methyl Cellulose as Gelling Agent, *Journal of Natural Gas Science and Engineering*.
- [68] J. Cooper, L. Stamford, A. Azapagic, Environmental Impacts of Shale Gas in the UK: Current Situation and Future Scenarios, *Energy Technology* 2 (2014) 1012-1026.
- [69] R.C. Navarrete, H.L. Dearing, V.G. Constien, K.M. Marsaglia, J.M. Seheult, P.E. Rodgers, Experiments in Fluid Loss and Formation Damage with Xanthan-Based Fluids While Drilling, *Society of Petroleum Engineers*.
- [70] P.J. Edwards, L.L. Tracy, W.K. Wilson, Chloride concentration gradients in tank-stored hydraulic fracturing fluids following flowback, in: *USDA (Ed.), US. Forest Service, Newton Square, PA, 2011*.
- [71] J.R. Smith, *Hydraulic Fracturing for Natural Gas Extraction: Research and Regulatory Impacts*, (2015).
- [72] EPA, *Federal Register* 56 (110): 26460-26564 (1991). 1987.
- [73] H.-P. Grossart, T. Kiørboe, K. Tang, H. Ploug, Bacterial colonization of particles: growth and interactions, *Applied and Environmental Microbiology* 69 (2003) 3500-3509.
- [74] L. Tijhuis, M. Van Loosdrecht, J. Heijnen, Formation and growth of heterotrophic aerobic biofilms on small suspended particles in airlift reactors, *Biotechnology and bioengineering* 44 (1994) 595-608.
- [75] S.G. Wakeham, Lipid biomarkers for heterotrophic alteration of suspended particulate organic matter in oxygenated and anoxic water columns of the ocean, *Deep Sea Research Part I: Oceanographic Research Papers* 42 (1995) 1749-1771.
- [76] C.G. Struchtemeyer, M.D. Morrison, M.S. Elshahed, A critical assessment of the efficacy of biocides used during the hydraulic fracturing process in shale natural gas wells, *International Biodeterioration & Biodegradation* 71 (2012) 15-21.
- [77] A. Murali Mohan, A. Hartsock, K.J. Bibby, R.W. Hammack, R.D. Vidic, K.B. Gregory, Microbial Community Changes in Hydraulic Fracturing Fluids and Produced Water from Shale Gas Extraction, *Environmental Science & Technology* 47 (2013) 13141-13150.
- [78] F. Monlau, C. Sambusiti, A. Barakat, M. Quéméneur, E. Trably, J.P. Steyer, H. Carrère, Do furanic and phenolic compounds of lignocellulosic and algae biomass hydrolyzate inhibit anaerobic mixed cultures? A comprehensive review, *Biotechnology Advances* 32 (2014) 934-951.
- [79] C.E. Ramirez, S.R. Batchu, P.R. Gardinali, High sensitivity liquid chromatography tandem mass spectrometric methods for the analysis of dioctyl sulfosuccinate in different stages of an oil spill response monitoring effort, *Analytical and bioanalytical chemistry* 405 (2013) 4167-4175.

- [80] F. Johnson, How many food additives are rodent carcinogens?, *Environmental and molecular mutagenesis* 39 (2002) 69-80.
- [81] R. Kroes, A. Renwick, V. Feron, C. Galli, M. Gibney, H. Greim, R. Guy, J. Lhuguenot, J. Van de Sandt, Application of the threshold of toxicological concern (TTC) to the safety evaluation of cosmetic ingredients, *Food and Chemical Toxicology* 45 (2007) 2533-2562.
- [82] R. Smith, Review of glycol ether and glycol ether ester solvents used in the coating industry, *Environmental health perspectives* 57 (1984) 1.
- [83] K.E. Carter, J. Farrell, Removal of perfluorooctane and perfluorobutane sulfonate from water via carbon adsorption and ion exchange, *Separation Science and Technology* 45 (2010) 762-767.
- [84] M.E. Curtis, R.J. Ambrose, C.H. Sondergeld, C.S. Rai, Investigation of the relationship between organic porosity and thermal maturity in the Marcellus Shale, *North American Unconventional Gas Conference and Exhibition*, Society of Petroleum Engineers, 2011.
- [85] M. Milner, R. McLin, J. Petriello, Imaging texture and porosity in mudstones and shales: Comparison of secondary and ion-milled backscatter SEM methods, *Canadian Unconventional Resources and International Petroleum Conference*, Society of Petroleum Engineers, 2010.
- [86] M. Martinez, M. Torres, C. Guzman, D. Maestri, Preparation and characteristics of activated carbon from olive stones and walnut shells, *Industrial crops and products* 23 (2006) 23-28.
- [87] K.E. Manz, K.E. Carter, Extraction and recovery of 2-butoxyethanol from aqueous phases containing high saline concentration, *Analytical Chemistry Research* 9 (2016) 1-7.
- [88] S.J. Randtke, C.P. Jepsen, Effects of salts on activated carbon adsorption of fulvic acids, *Journal (American Water Works Association)* 74 (1982) 84-93.
- [89] F. Elizalde, J. Gracia, M. Costas, Effect of aggregates in bulk and surface properties: surface tension, foam stability, and heat capacities for 2-butoxyethanol + water, *The Journal of Physical Chemistry* 92 (1988) 3565-3568.
- [90] A. Acton, *Polynucleotide Ligases - Advances in Research and Application*, ScholarlyEditions, Atlanta, GA, 2013.
- [91] P.A. Kralchevsky, K.D. Danov, G. Broze, A. Mehreteab, Thermodynamics of Ionic Surfactant Adsorption with Account for the Counterion Binding: Effect of Salts of Various Valency, *Langmuir* 15 (1999) 2351-2365.
- [92] J.C. Crittenden, R.R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, *MWH's Water Treatment: Principles and Design*, John Wiley & Sons 2012.
- [93] M.M. Clark, *Transport modeling for environmental engineers and scientists*, John Wiley & Sons 2011.
- [94] N. Ayawei, A.N. Ebelegi, D. Wankasi, Modelling and Interpretation of Adsorption Isotherms, *Journal of Chemistry* 2017 (2017).
- [95] M. Belhachemi, F. Addoun, Comparative adsorption isotherms and modeling of methylene blue onto activated carbons, *Applied Water Science* 1 (2011) 111-117.
- [96] Y.-S. Ho, Selection of optimum sorption isotherm, *Carbon* 42 (2004) 2115-2116.

- [97] O. Redlich, D.L. Peterson, A Useful Adsorption Isotherm, *The Journal of Physical Chemistry* 63 (1959) 1024-1024.
- [98] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, *Chemical Engineering Journal* 156 (2010) 2-10.
- [99] G.D. Arrigo, R. Giordano, J. Teixeira, Small angle neutron scattering of aqueous solutions of 2-butoxyethanol and nonionic surfactants, *Physica Scripta* 1992 (1992) 248.
- [100] G. Roux, G. Perron, J.E. Desnoyers, Model systems for hydrophobic interactions: Volumes and heat capacities of n -alkoxyethanols in water, *Journal of Solution Chemistry* 7 (1978) 639-654.
- [101] G. Douhéret, A. Pal, M.I. Davis, Ultrasonic speeds and isentropic functions of (a 2-alkoxyethanol + water) at 298.15 K, *The Journal of Chemical Thermodynamics* 22 (1990) 99-108.
- [102] H. Chen, K.E. Carter, Water usage for natural gas production through hydraulic fracturing in the United States from 2008 to 2014, *Journal of environmental management* 170 (2016) 152-159.
- [103] E.M. Thurman, I. Ferrer, J. Blotvogel, T. Borch, Analysis of hydraulic fracturing flowback and produced waters using accurate mass: identification of ethoxylated surfactants, *Analytical chemistry* 86 (2014) 9653-9661.
- [104] K.E. Manz, G. Haerr, J. Lucchesi, K.E. Carter, Adsorption of hydraulic fracturing fluid components 2-butoxyethanol and furfural onto granular activated carbon and shale rock, *Chemosphere* 164 (2016) 585-592.
- [105] J.D. Rogers, I. Ferrer, S.S. Tummings, A.R. Bielefeldt, J.N. Ryan, Inhibition of Biodegradation of Hydraulic Fracturing Compounds by Glutaraldehyde: Groundwater Column and Microcosm Experiments, *Environmental Science & Technology* 51 (2017) 10251-10261.
- [106] D.C. DiGiulio, R.B. Jackson, Impact to Underground Sources of Drinking Water and Domestic Wells from Production Well Stimulation and Completion Practices in the Pavillion, Wyoming, Field, *Environmental Science & Technology* 50 (2016) 4524-4536.
- [107] N. Gaillard, A. Thomas, C. Favero, Novel Associative Acrylamide-based Polymers for Proppant Transport in Hydraulic Fracturing Fluids, *Society of Petroleum Engineers*.
- [108] A.N. Paukert Vankeuren, J.A. Hakala, K. Jarvis, J.E. Moore, Mineral Reactions in Shale Gas Reservoirs: Barite Scale Formation from Reusing Produced Water As Hydraulic Fracturing Fluid, *Environmental Science & Technology* 51 (2017) 9391-9402.
- [109] A. Tsitonaki, B. Petri, M. Crimi, H. Mosbæk, R.L. Siegrist, P.L. Bjerg, In Situ Chemical Oxidation of Contaminated Soil and Groundwater Using Persulfate: A Review, *Critical Reviews in Environmental Science and Technology* 40 (2010) 55-91.
- [110] D.A. House, Kinetics and Mechanism of Oxidations by Peroxydisulfate, *Chemical Reviews* 62 (1962) 185-203.
- [111] H. Herrmann, A. Reese, R. Zellner, Time-resolved UV/VIS diode array absorption spectroscopy of SO_x^- ($x=3, 4, 5$) radical anions in aqueous solution, *Journal of Molecular Structure* 348 (1995) 183-186.

- [112] D. Zhao, X. Liao, X. Yan, S.G. Huling, T. Chai, H. Tao, Effect and mechanism of persulfate activated by different methods for PAHs removal in soil, *Journal of Hazardous Materials* 254–255 (2013) 228-235.
- [113] C. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Persulfate oxidation for in situ remediation of TCE. I. Activated by ferrous ion with and without a persulfate–thiosulfate redox couple, *Chemosphere* 55 (2004) 1213-1223.
- [114] J. Criquet, N.K.V. Leitner, Degradation of acetic acid with sulfate radical generated by persulfate ions photolysis, *Chemosphere* 77 (2009) 194-200.
- [115] G. Czapski, S.V. Lymar, H.A. Schwarz, Acidity of the Carbonate Radical, *The Journal of Physical Chemistry A* 103 (1999) 3447-3450.
- [116] D.B. Medinas, G. Cerchiaro, D.F. Trindade, O. Augusto, The carbonate radical and related oxidants derived from bicarbonate buffer, *IUBMB Life* 59 (2007) 255-262.
- [117] C. Liang, Z.-S. Wang, N. Mohanty, Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20 °C, *Science of The Total Environment* 370 (2006) 271-277.
- [118] B.G. Petri, R.J. Watts, A. Tsitonaki, M. Crimi, N.R. Thomson, A.L. Teel, Fundamentals of ISCO Using Persulfate, in: L.R. Siegrist, M. Crimi, J.T. Simpkin (Eds.) *In Situ Chemical Oxidation for Groundwater Remediation*, Springer New York, New York, NY, 2011, pp. 147-191.
- [119] K.E. Manz, K.E. Carter, Investigating the effects of heat activated persulfate on the degradation of furfural, a component of hydraulic fracturing fluid chemical additives, *Chemical Engineering Journal* 327 (2017) 1021-1032.
- [120] L. Torres, O.P. Yadav, E. Khan, A review on risk assessment techniques for hydraulic fracturing water and produced water management implemented in onshore unconventional oil and gas production, *Science of The Total Environment* 539 (2016) 478-493.
- [121] D. Kekacs, M. McHugh, P.J. Mouser, Temporal and Thermal Changes in Density and Viscosity of Marcellus Shale Produced Waters, *Journal of Environmental Engineering* 141 (2015).
- [122] I. Ferrer, E.M. Thurman, Chemical constituents and analytical approaches for hydraulic fracturing waters, *Trends in Environmental Analytical Chemistry* 5 (2015) 18-25.
- [123] P.J. Mouser, M. Borton, T.H. Darrah, A. Hartsock, K.C. Wrighton, Hydraulic fracturing offers view of microbial life in the deep terrestrial subsurface, *FEMS Microbiology Ecology* 92 (2016) fiw166-fiw166.
- [124] C. Liang, C.-F. Huang, N. Mohanty, R.M. Kurakalva, A rapid spectrophotometric determination of persulfate anion in ISCO, *Chemosphere* 73 (2008) 1540-1543.
- [125] I. Kolthoff, E. Carr, Volumetric determination of persulfate in presence of organic substances, *Analytical chemistry* 25 (1953) 298-301.
- [126] C. Minero, V. Maurino, L. Campanella, C. Morgja, E. Pelizzetti, Photodegradation of 2-ethoxy- and 2-butoxyethanol in the presence of semiconductor particles or organic conducting polymer, *Environmental Technology Letters* 10 (1989) 301-310.

- [127] C. Liang, H.-W. Su, Identification of Sulfate and Hydroxyl Radicals in Thermally Activated Persulfate, *Industrial & Engineering Chemistry Research* 48 (2009) 5558-5562.
- [128] J. Ma, H. Li, L. Chi, H. Chen, C. Chen, Changes in activation energy and kinetics of heat-activated persulfate oxidation of phenol in response to changes in pH and temperature, *Chemosphere* 189 (2017) 86-93.
- [129] I.M. Kolthoff, A.I. Medalia, H.P. Raaen, The Reaction between Ferrous Iron and Peroxides. IV. Reaction with Potassium Persulfate^{1a}, *Journal of the American Chemical Society* 73 (1951) 1733-1739.
- [130] A.D. Jew, M.K. Dustin, A.L. Harrison, C.M. Joe-Wong, D.L. Thomas, K. Maher, G.E. Brown, J.R. Bargar, Impact of Organics and Carbonates on the Oxidation and Precipitation of Iron during Hydraulic Fracturing of Shale, *Energy & Fuels* 31 (2017) 3643-3658.
- [131] P. Neta, R.E. Huie, A.B. Ross, Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution, *Journal of Physical and Chemical Reference Data* 17 (1988) 1027-1284.
- [132] Y. Lester, I. Ferrer, E.M. Thurman, K.A. Sitterley, J.A. Korak, G. Aiken, K.G. Linden, Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment, *Science of the Total Environment* 512 (2015) 637-644.
- [133] W.P. Freeborn, M. Zolensky, B.E. Scheetz, S. Komarneni, G.J. McCarthy, W.B. White, Shale Rocks as Nuclear Waste Repositories: Hydrothermal Reactions with Glass, Ceramic and Spent Fuel Waste Forms, *Scientific Basis for Nuclear Waste Management*, Springer 1980, pp. 499-506.
- [134] Y.S. Zou, S.C. Zhang, J. Zhang, Experimental Method to Simulate Coal Fines Migration and Coal Fines Aggregation Prevention in the Hydraulic Fracture, *Transport in Porous Media* 101 (2014) 17-34.
- [135] L.O. Haluszczak, A.W. Rose, L.R. Kump, Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA, *Applied Geochemistry* 28 (2013) 55-61.
- [136] D.S. Alessi, A. Zolfaghari, S. Kletke, J. Gehman, D.M. Allen, G.G. Goss, Comparative analysis of hydraulic fracturing wastewater practices in unconventional shale development: Water sourcing, treatment and disposal practices, *Canadian Water Resources Journal / Revue canadienne des ressources hydriques* 42 (2017) 105-121.
- [137] L.A. Patterson, K.E. Konschnik, H. Wiseman, J. Fargione, K.O. Maloney, J. Kiesecker, J.-P. Nicot, S. Baruch-Mordo, S. Entekin, A. Trainor, J.E. Saiers, Unconventional Oil and Gas Spills: Risks, Mitigation Priorities, and State Reporting Requirements, *Environmental Science & Technology* (2017).
- [138] M. Bamberger, R.E. Oswald, Impacts of gas drilling on human and animal health, New solutions: a journal of environmental and occupational health policy 22 (2012) 51-77.
- [139] S. Burden, J. Dean, J. Koplos, C. Meza-Cuadra, A. Singer, M.E. Tuccillo, Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1, in: U.S. EPA (Ed.), 2015.

- [140] C. Jedari, A.M. Palomino, H. Cyr, E.C. Drumm, D. Boles, Grain and Floc Size Distribution Analysis of Fine Coal Refuse Slurry, the 19th International Conference on Soil Mechanics and Geotechnical Engineering, Seoul, Korea, 2017.
- [141] D. Kekacs, B.D. Drollette, M. Brooker, D.L. Plata, P.J. Mouser, Aerobic biodegradation of organic compounds in hydraulic fracturing fluids, *Biodegradation* 26 (2015) 271-287.
- [142] A.L. Teel, M. Ahmad, R.J. Watts, Persulfate activation by naturally occurring trace minerals, *Journal of Hazardous Materials* 196 (2011) 153-159.
- [143] E. Barbot, N.S. Vidic, K.B. Gregory, R.D. Vidic, Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing, *Environmental science & technology* 47 (2013) 2562-2569.
- [144] K.L. Hickenbottom, N.T. Hancock, N.R. Hutchings, E.W. Appleton, E.G. Beaudry, P. Xu, T.Y. Cath, Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations, *Desalination* 312 (2013) 60-66.
- [145] R.S. Balaba, R.B. Smart, Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater, *Chemosphere* 89 (2012) 1437-1442.
- [146] USEPA, United States Environmental Protection Agency. National Primary Drinking Water Regulations, 2017.

APPENDIX

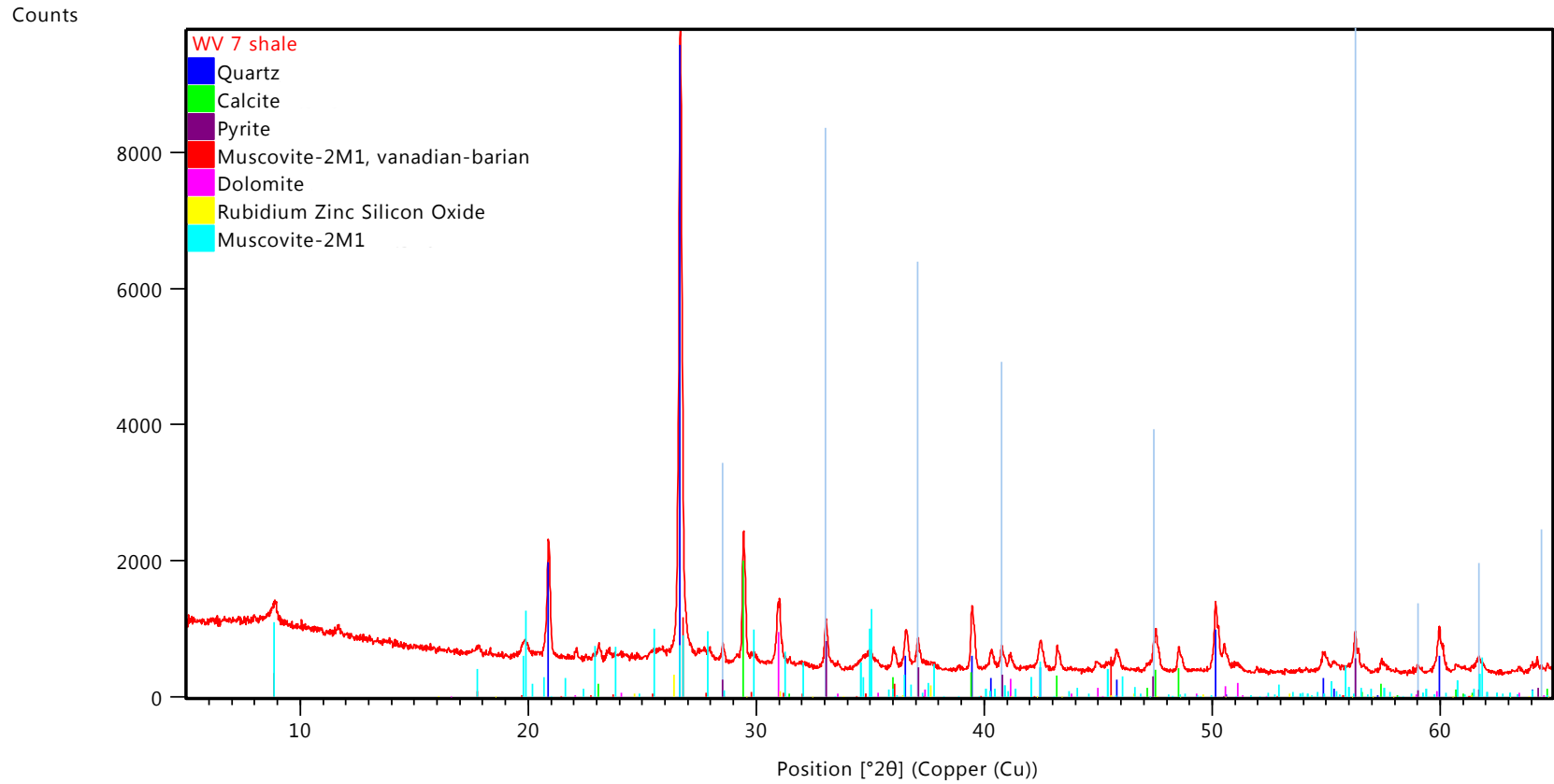


Figure A1. XRD diffractogram of unreacted WV7 shale.

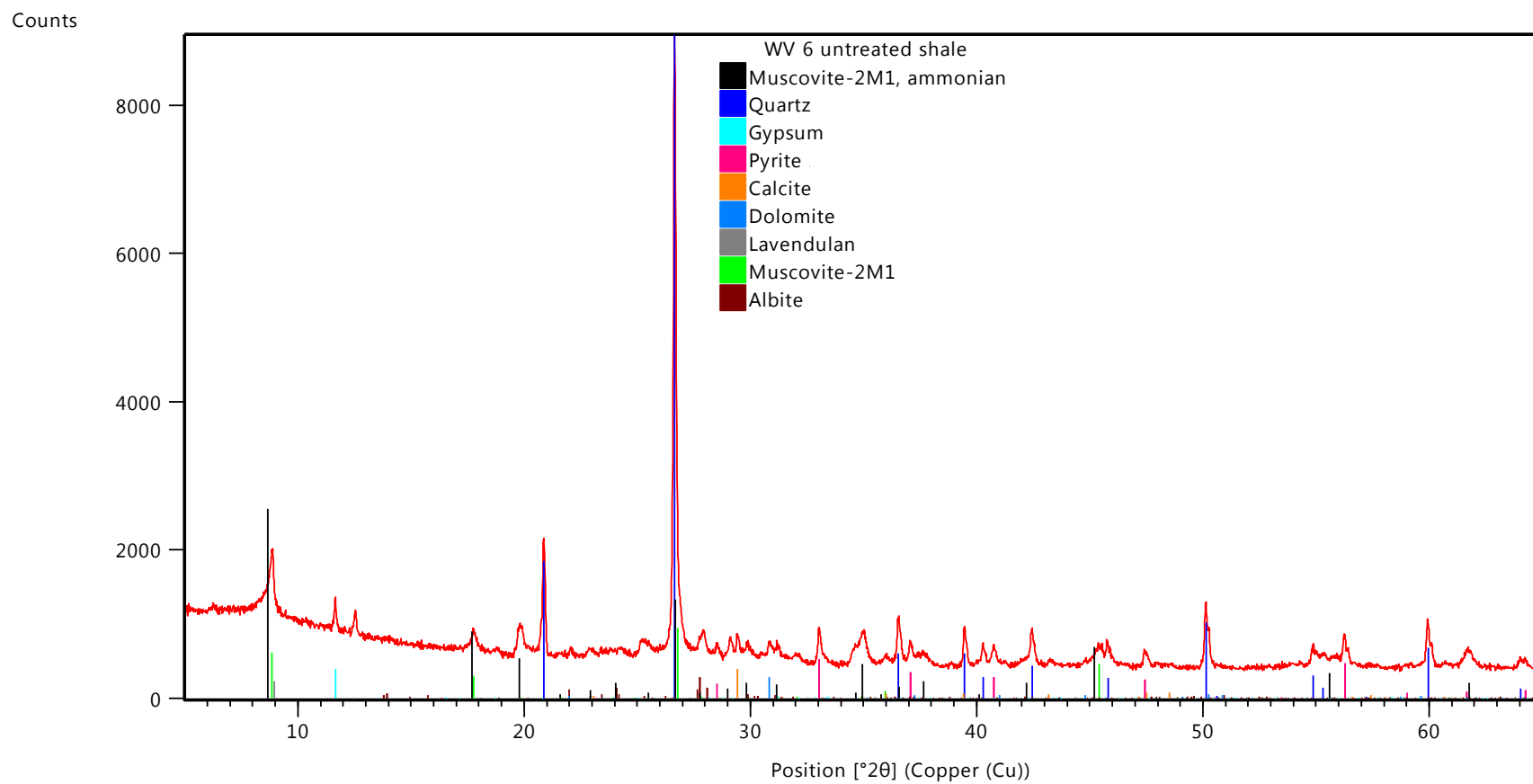


Figure A2. Diffraction pattern of untreated WV6 shale particles and mineral identification obtained using XRD. The major mineral in the shale was quartz.

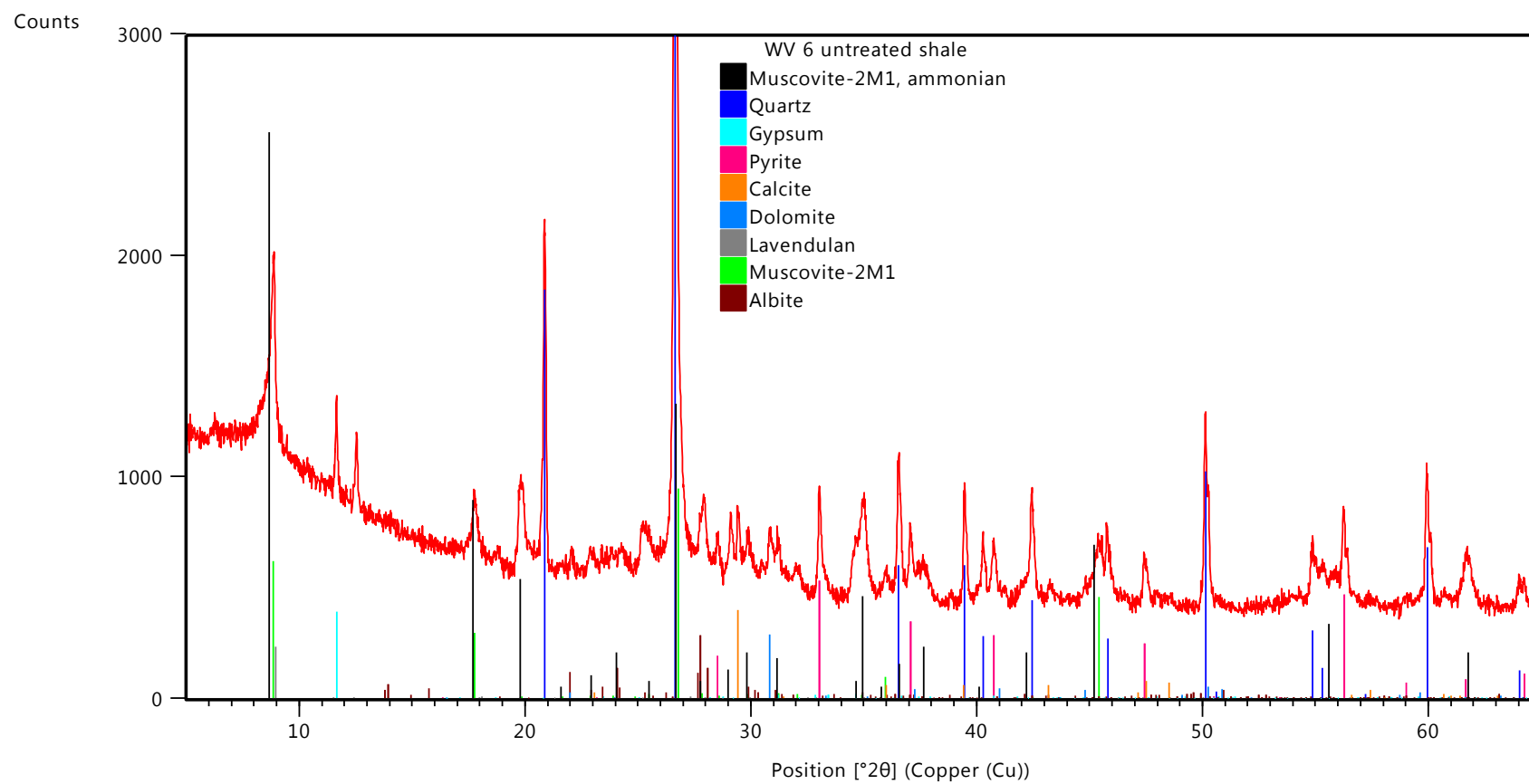


Figure A3. Zoomed in diffraction pattern displayed in Figure A2 obtained using XRD.

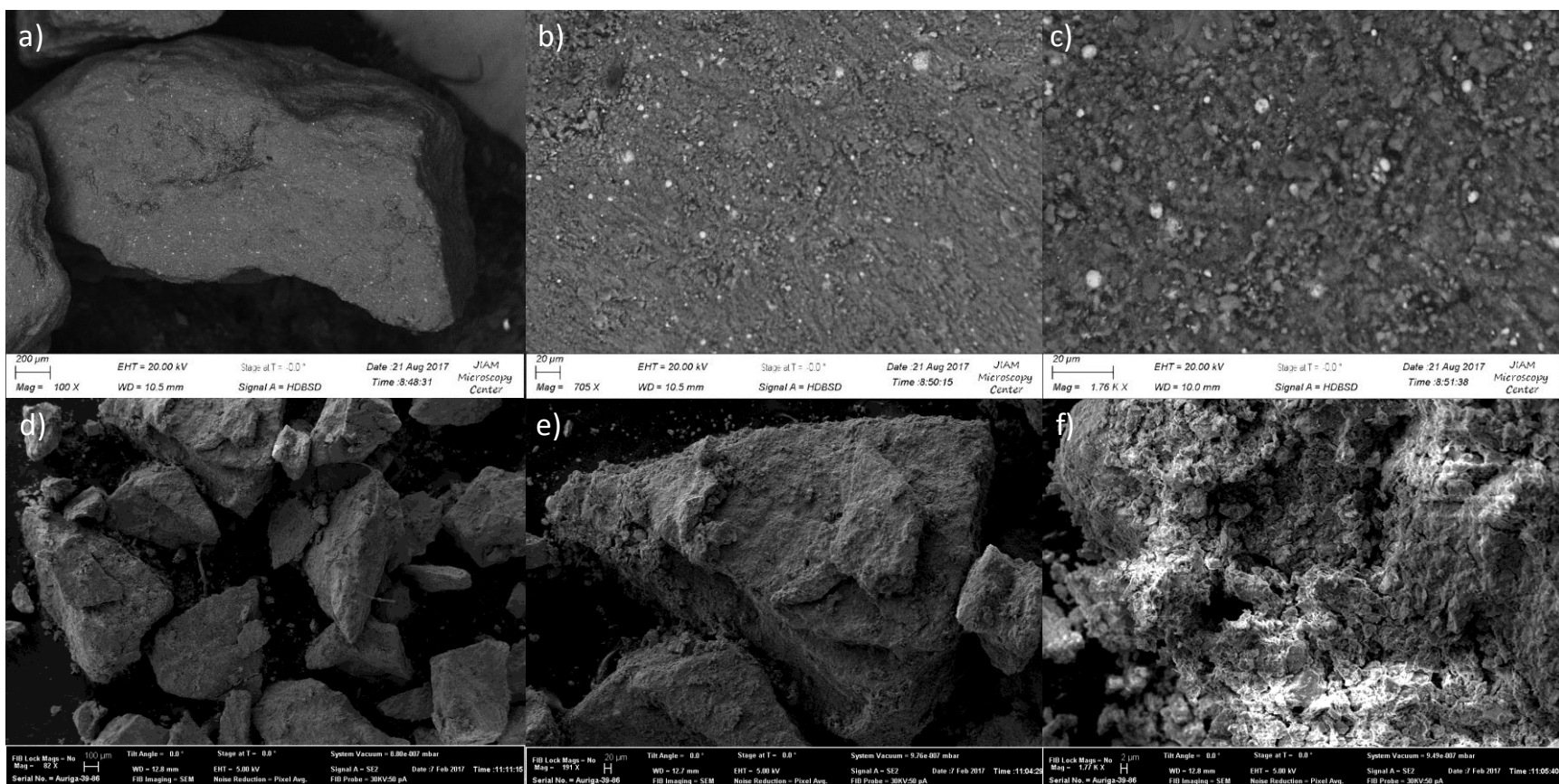


Figure A4. SEM images of untreated shale particles. Bright spots in the SEM images (b) and (c) are taken using the HDBSD. These bright spots correlate to heavier elements in the minerals of the shale.

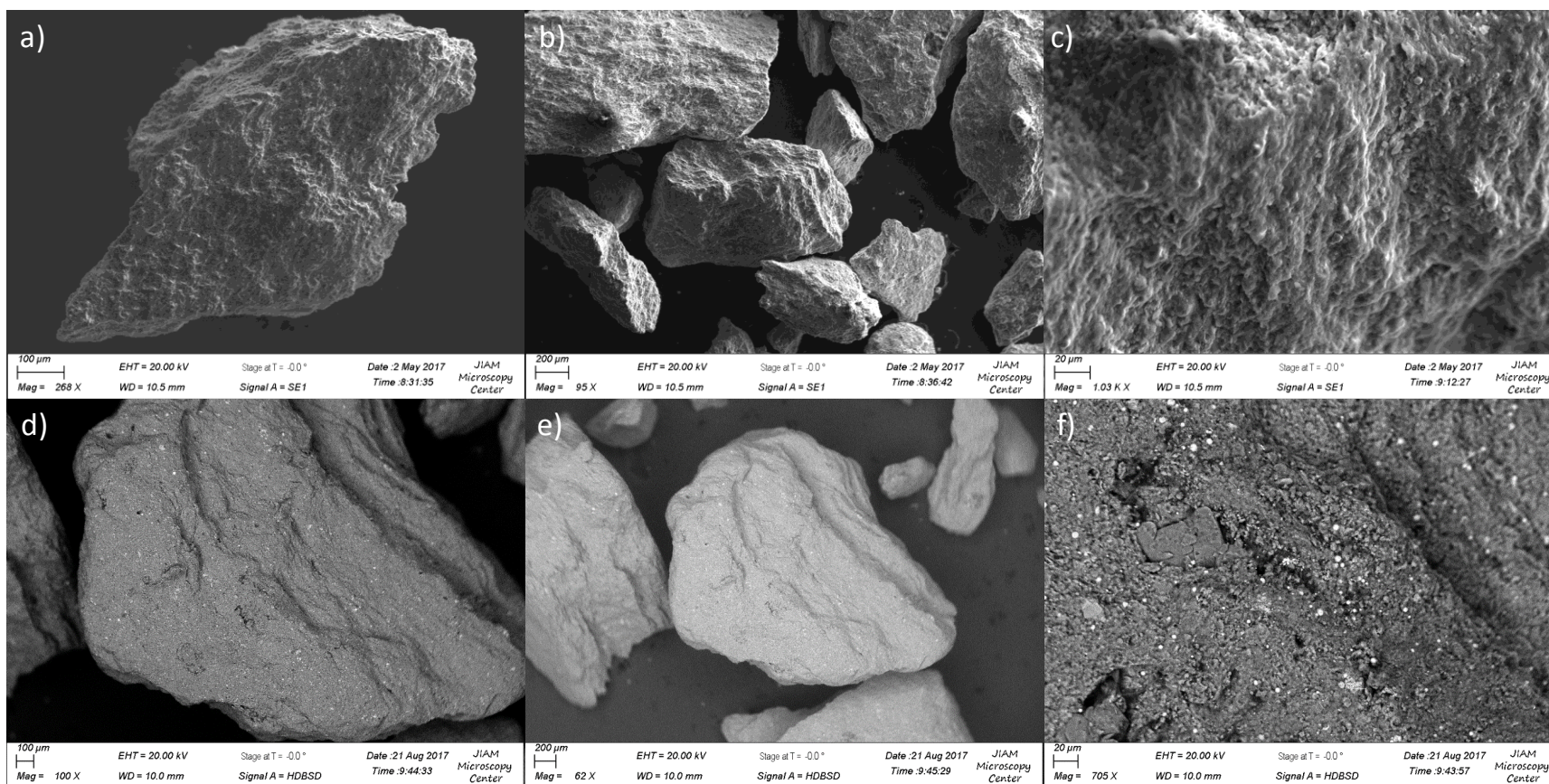


Figure A5. SEM images of water treated shale particles. Images taken before mixing in the PSA are shown in a-c. Images taken after mixing in the PSA are shown in d-f. Image (f) is taken with the HDBSD and exhibits bright spots.

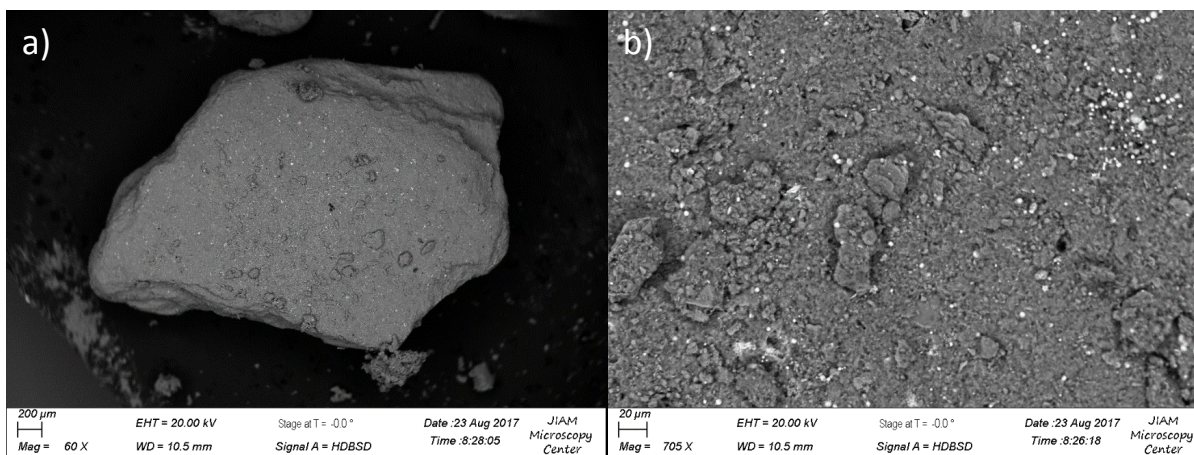


Figure A6. SEM images of BXL treated shale particles. Image (b) is taken with the HDBSD and exhibits bright spots.

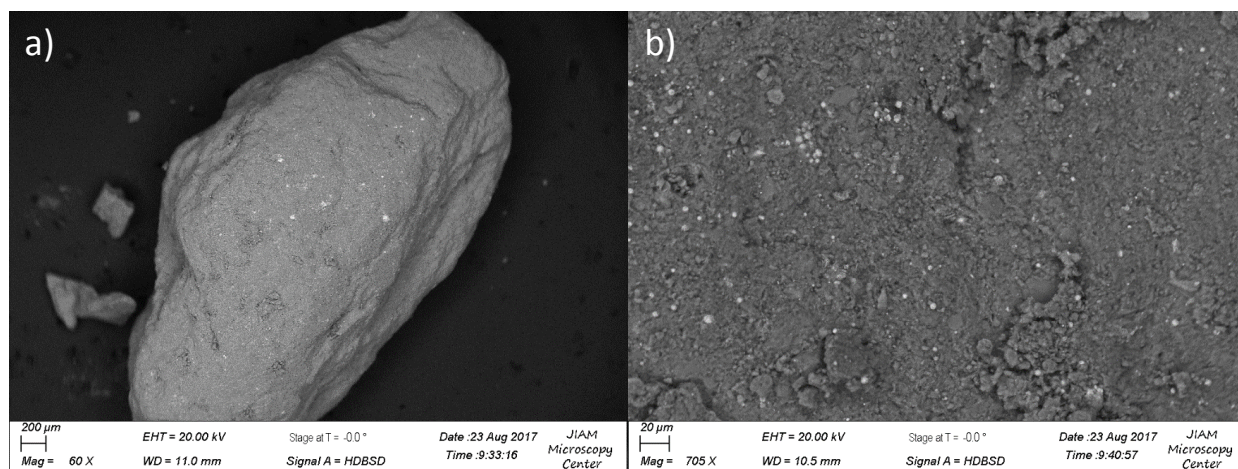


Figure A7. SEM images of FRS treated shale particles. Image (b) is taken with the HDBSD and exhibits bright spots.

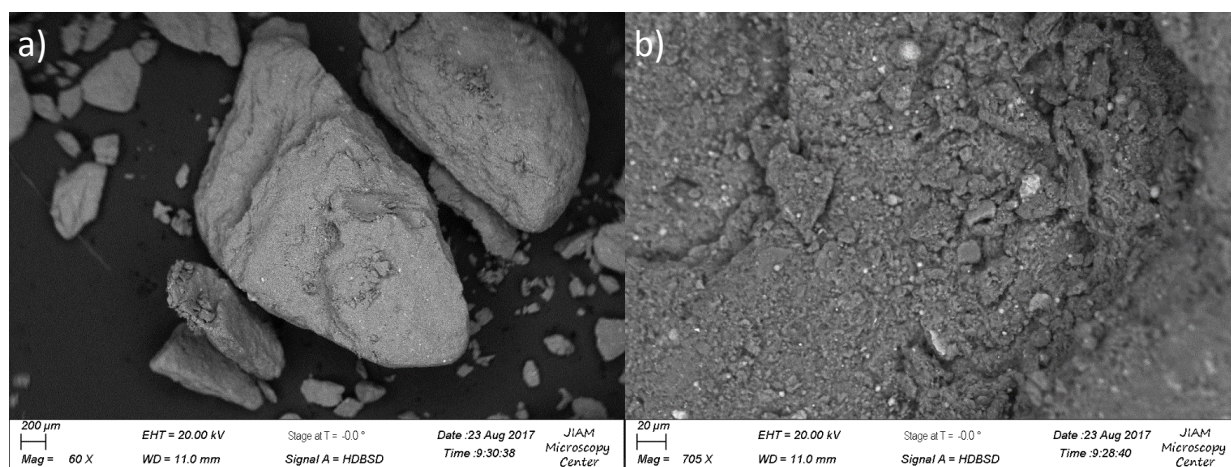


Figure A8. SEM images of LEB-10X treated shale particles. Image (b) is taken with the HDBSD and exhibits bright spots.

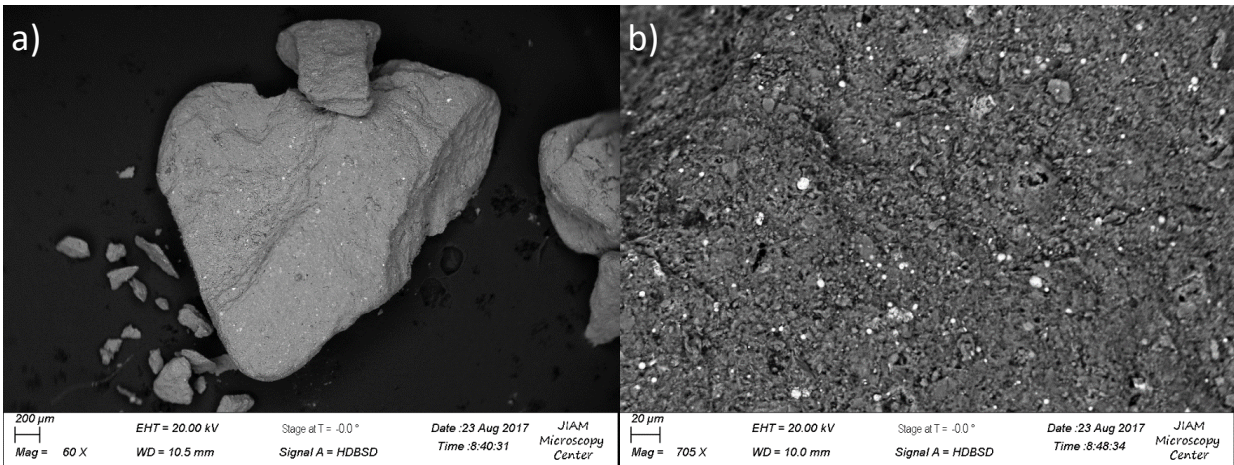


Figure A9. SEM images of Revert Flow treated shale particles. Image (b) is taken with the HDBSD and exhibits bright spots.

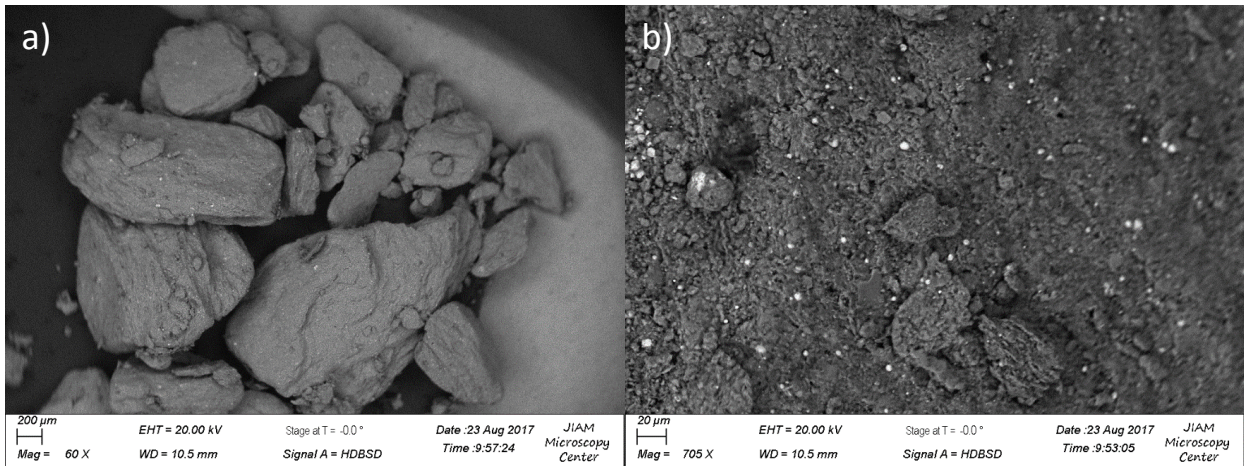


Figure A10. SEM images of WGA treated shale particles. Image (b) is taken with the HDBSD and exhibits bright spots.

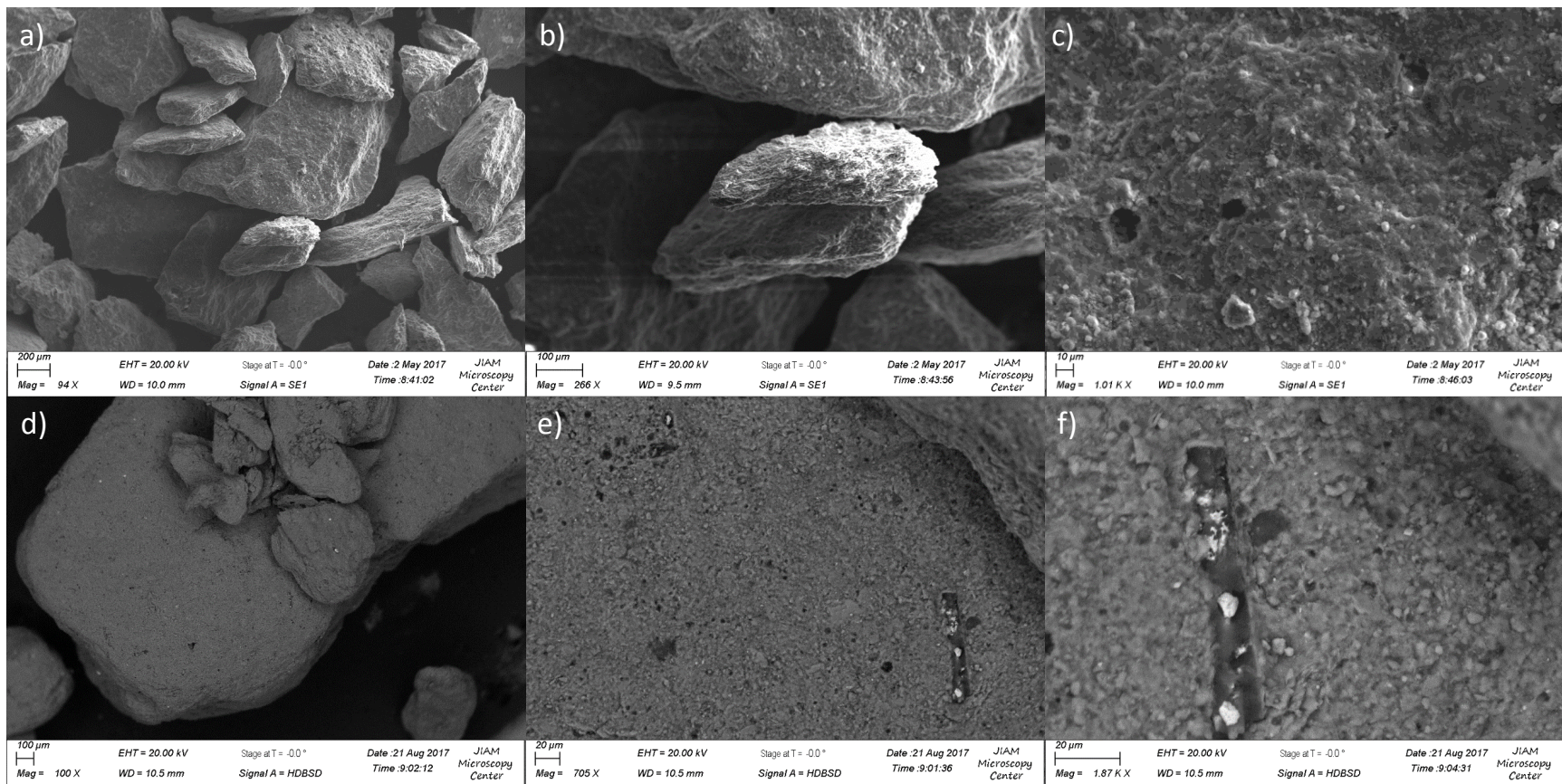


Figure A11. SEM images of hydrochloric acid treated shale particles. Images taken before mixing in the PSA are shown in a-c. Images taken after mixing in the PSA are shown in d-f. Images (e) and (f) were taken with the HDBSD and bright spots are almost completely removed from the shale, which indicates heavier elements were stripped from the shale.

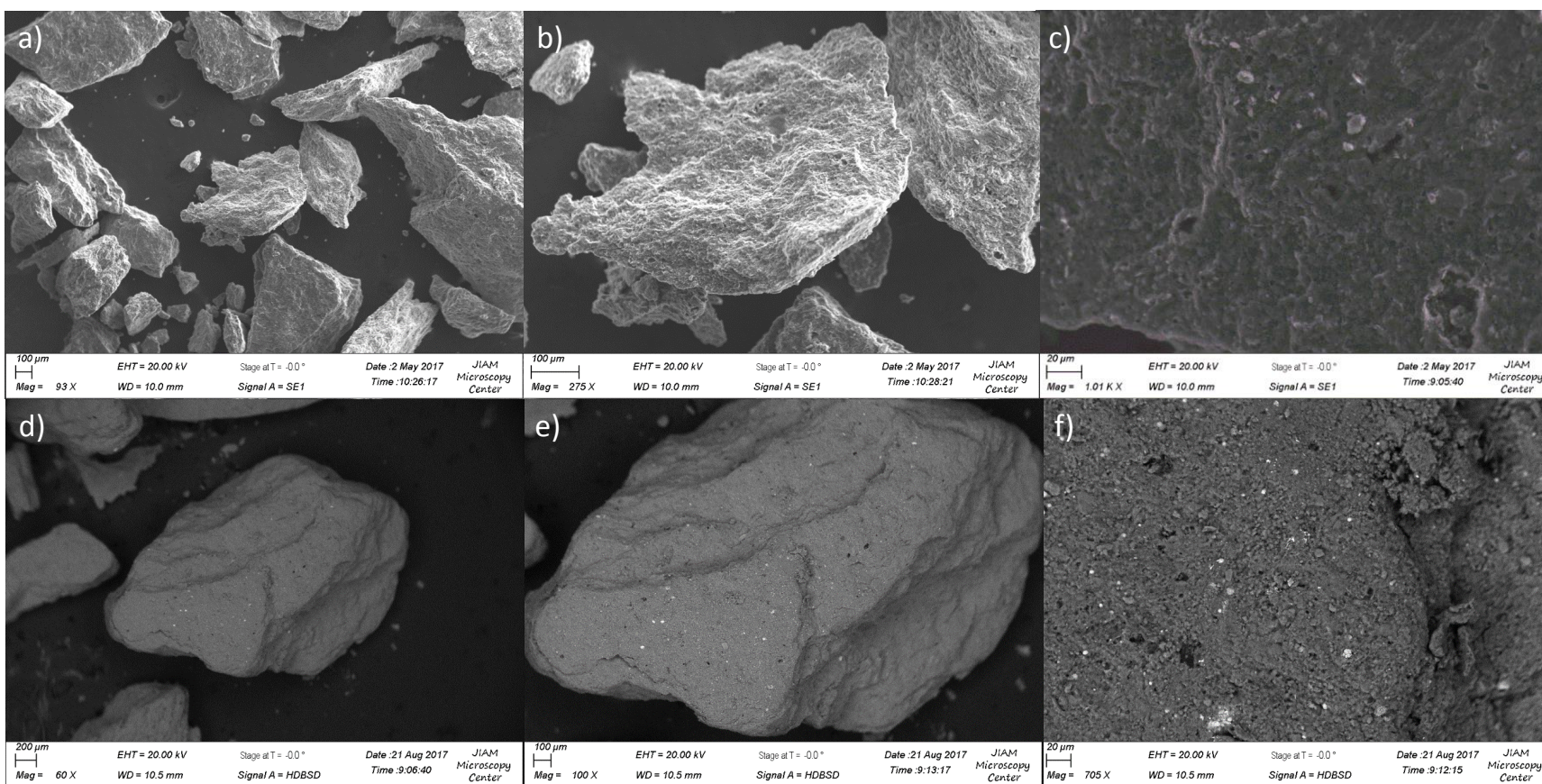


Figure A12. SEM images of persulfate treated shale particles. Images taken before mixing in the PSA are shown in a-c. Images taken after mixing in the PSA are shown in d-f.

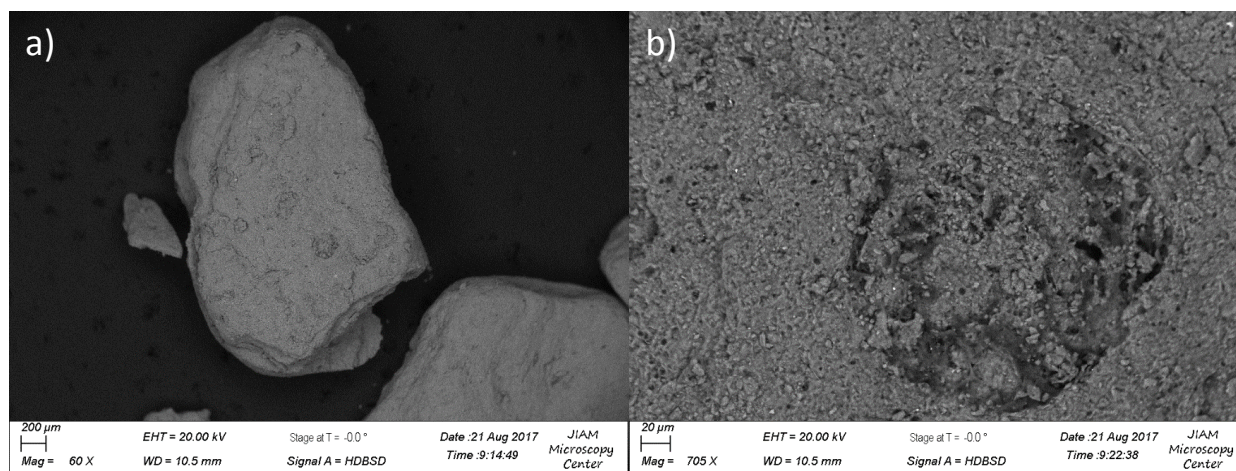


Figure A13. SEM images of combined hydrochloric acid and persulfate treated shale particles. Image (b) was taken with the HDBSD and bright spots are almost completely removed from the shale, which indicates heavier elements were stripped from the shale.

VITA

Katherine Manz earned a Bachelor's of Science degree in Chemistry from Rensselaer Polytechnic Institute (RPI) in Troy, NY in May 2013. During her time as an undergraduate, she performed research in Dr. K.V. Lakshmi's lab in the Baruch '60 Center for Biochemical Solar Energy Research. Her research focused on creating highly efficient and cost effective solar energy conversion through fundamental understanding of biological chemistry at the molecular level. For this research, she was awarded the John L. Marsh '58 RPI Summer Undergraduate Research Project Fellowship in 2011, the Arthur G. Schultz Award for Undergraduate Research in Chemistry in 2012, and an Undergraduate Research Project Fellowship for every semester from 2010 until 2013. She was also awarded the Who's Who Among Students in American Universities & Colleges at RPI. During the summer of 2012, Katherine was an undergraduate student research intern for the USDA NIFA CenUSA Bioenergy project at Iowa State University in Ames, Iowa. Her project goals were to determine the expected net energy returns from the cellulosic systems of corn stover, switchgrass, and miscanthus and to compare the amounts of recoverable energy obtained from the crop systems.

Katherine joined the University of Tennessee and Oak Ridge National Laboratory's Bredeisen Center for Interdisciplinary Research and Graduate Education in Fall 2013 to pursue her PhD in Energy Science and Engineering. While working towards this goal, she earned a Master's of Science in Environmental Engineering in Summer 2016. During graduate school at UT, Katherine worked with Dr. Kimberly Carter in the Department of Civil and Environmental Engineering on various water quality issues related to hydraulic fracturing. Katherine plans to continue her professional development with a postdoctoral research position at Brown University with Dr. Kurt Pennell.