CHARACTERIZATION AND REMEDIATION OF WASTEWATER FROM UNCONVENTIONAL OIL AND GAS DEVELOPMENT

by

Tiffany Michelle Liden

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Supervising Committee:
Dr. Kevin A. Schug, Supervising Professor
Saiful Chowdhury
Krishnan Rajeshwar
Frank Foss Jr.

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Abstract

Characterization and Remediation of Wastewater from Unconventional Oil and Gas Development

Tiffany Michelle Liden, Ph.D.

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Supervising Professor: Kevin A. Schug

Increasing energy demands from the nation and technological advancement in well development have led to the rapid expansion of unconventional oil and gas extraction. Current disposal methods for wastewater generated from the development of low porosity formations are not environmentally sustainable. The billions of gallons of highly variable, chemically-rich wastewater, referred to as produced water, is frequently sequestered in subsurface, non-productive stratum through injection wells. Cost-effective options to treat produced water are being sought as an alternative to injection wells to prevent the loss of water from the water cycle and decrease anthropologically induced seismic events. Ultimately, it has been determined that the feasibility of reusing produced water hinges on the water quality. Twenty-four unconventional development wastewater samples were evaluated from South and West Texas to characterize their variability and to assess the feasibility for direct reuse without treatment. Analytical methods were used to evaluate the samples; the results were compared to reuse thresholds. Based on published reuse guidelines, the directed reuse of produced water for subsequent well development is not a suitable option without treatment. Therefore, forward osmosis, an osmotically-driven process, was evaluated as a remediation option for produced water. Three studies were conducted using forwarded osmosis to remediate produced water from the Permian Basin. First, was a fundamental study that determined forward osmosis is a feasible remediation option for the high salinity waste stream with total dissolved solids ranging from 16,000 to 210,000 mg/L. The second study was used to determine that the decrease in flux measured during experimental trials was due to irreversible fouling on the membrane’s surface. Finally, the efficacy of pretreating the wastewater prior to remediation using forward osmosis was assessed. Throughout the studies, various analytical methods were used to validate the effectiveness of using forward osmosis as a remediation approach for of produced water.

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UNCONVENTIONAL OIL AND GAS PRODUCTION: WASTE MANAGEMENT AND THE WATER CYCLE

Tiffany Liden, Billy G. Clark, Zacariah L. Hildenbrand, Kevin A. Schug, Chapter Two - Unconventional Oil and Gas Production: Waste Management and the Water Cycle, Editor(s): Kevin A. Schug, Zacariah L. Hildenbrand, Advances in Chemical Pollution, Environmental Management and Protection, Elsevier, Volume 1, 2017, Pages 17-45, ISBN 9780128128022, https://doi.org/10.1016/bs.apmp.2017.08.012.[1]

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Unconventional Oil and Gas Production: Waste Management and the Water Cycle

Tiffany Liden[1], BG Clark[2], Zacariah L. Hildenbrand[3,4], Kevin A. Schug[1,3]*

AUTHOR INFORMATION:

1. Department of Chemistry and Biochemistry, The University of Texas at Arlington, 700 Planetarium Place, Arlington, TX 76019, USA
2. Solaris Water Midstream, LLC, 9811 Maple Avenue, Suite 450, Dallas, TX 75219
3. Affiliate of Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, USA
4. Inform Environmental, LLC, 6060 N. Central Expressway, Suite 500, Dallas, TX 75206

Correspondence should be addressed to: 700 Planetarium Pl.; Box 19065; Arlington, TX 76019-0065 (email) kschug@uta.edu; Tel.: +1-817-272-3541; Fax: +1-817-272-3808

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1.1 Abstract

Approximately 81% of the nation’s energy demands are supported by hydrocarbons, largely in part to the relatively recent exploration of oil and gas from unconventional shale energy reserves. The extraction of shale energy requires technological ingenuity, such as hydraulic fracturing and horizontal drilling, and significant freshwater resources to successfully recover the previously sequestered hydrocarbons from low porosity formations. As unconventional oil and gas development continues to expand to meet the growing energy demands, it becomes increasingly more important to understand the potential environmental implications and to practice proper environmental stewardship. For example, concerns over water usage and the related consequences have dramatically increased due to the demand for water used in hydraulic fracturing, the increased volumes of wastewater being produced, and the need to dispose of or reuse the wastewater without compromising the surface and subsurface environments. As such, this chapter will cover the lifecycle of water in oil and gas development (conventional and unconventional), including water use and waste production in the drilling, stimulation, and production phases; the current waste management strategies and challenges within the various treatment modalities; and the widespread implications of the varying forms of waste management.

1.2 Introduction

Water and energy exhibit an interwoven relationship where both resources are essential needs in today's expanding society. Water is required to produce energy and energy is necessary to make water available for use. With an ever-increasing population, the draw on both resources is also expanding rapidly. As of 2014, the global human population reached 7 billion and it is predicted to expand beyond 9 billion by the end of the century.[1] According to an ongoing study being conducted by Global Footprint Network, it would require 1.6 planets to continue to provide the resources to sustain current usage and absorb the waste.[2] Moreover, approximately one-fifth, or 1.3 billion people, of those on the planet still do not have reliable electricity.[1] Without energy there is no economic advancement, so as innovation increases to meet the energy demands of today, consideration for the effects of resource consumption, as well as management of the corresponding waste, need to be taken into account.

Currently, the American economy relies heavily on oil and natural gas to meet the growing domestic energy requirements.[3] Approximately 81% of the nation's energy demands are supported by hydrocarbons, also known as fossil fuels.[4] Transportation accounted for 71% of the 19.6 million barrels of petroleum used per day (1 barrel= 42 gal) in 2016, followed by industrial use consuming 23%, and the final 6% is allocated for residential, commercial, and power plants.[5] Renewable sources provided 19% of the necessary energy. Biomass, organic material from plants and animals which contains stored energy from the sun,[6] accounted for 47% of the renewable energy being generated.[5] The remainder stems from a combination of wind, solar, and hydroelectric.

To articulate the life cycle of water in oil and gas development, one must understand fossils in their natural state. Fossil fuels are formed from a continuum of increasing molecular weights (# of carbons atoms) which is shown in figure 1 along with the type of fossil fuel each weight range represents). Oil and gas are entrained in subsurface reservoirs under high temperatures and pressures.[7] As they are brought to the surface, the pressures and temperatures decrease, which results in phase changes. Natural gas, the most volatile component, can be found in formations "associated" or dissolved in oil. The production of natural gas from formations not dissolved in oil is classified as "non-associated." The composition of the raw natural gas extracted from producing wells depends on the type, depth, and location of the underground deposit and the geology of the area.[8] Pure natural gas, primarily methane, comes to the surface mixed with condensates or natural gas liquids (NGLs). These molecules are in a gaseous state at underground pressures, but become liquid (condense) at normal atmospheric pressure.

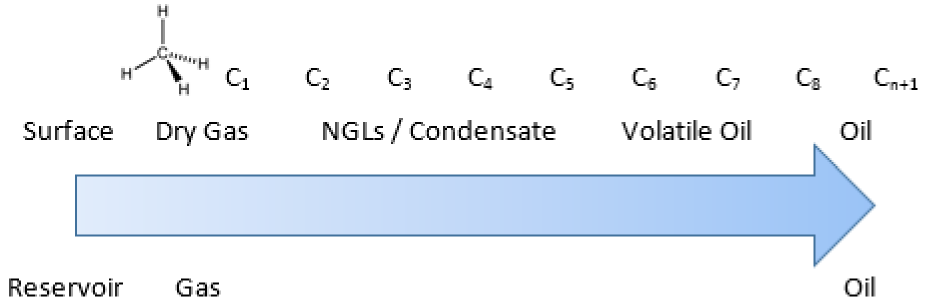


Figure 1. Schematic showing different fossil fuels with arrow indicating direction of increase of molecular weight. Adapted from [7] supplemental information.[7]

Oil and gas are acquired through the practices of conventional and unconventional exploration and production in petroliferous strata (rock containing petroleum). Historically, oil and gas resources were found primarily entrained in reservoirs within sand and limestone formations. These pockets of hydrocarbons, termed as conventional resources, are subsurface strata that are porous enough to allow the oil, gas, and natural formation water to migrate to the wellhead with minimal aid (Figure 2).[3,9] In contrast, unconventional oil and gas resources are found in low porosity, tight-sands, and shale formations, which require more advanced technologies and processes to achieve hydrocarbon extraction. These technologies primarily include horizontal drilling and hydraulic stimulation.

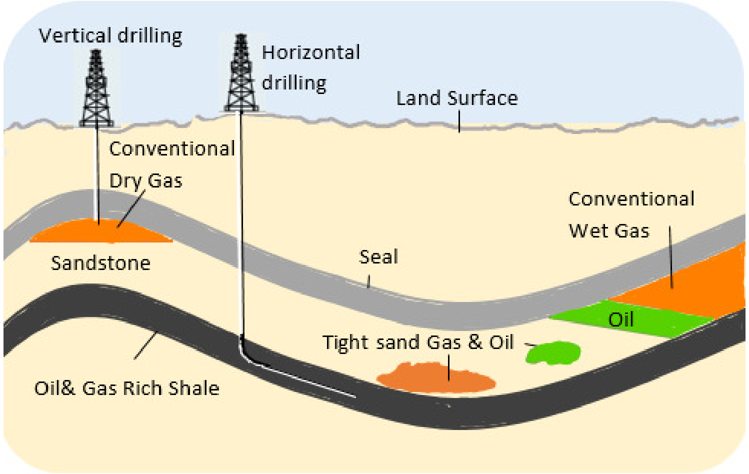


Figure 2. Schematic geology of natural gas resources. Modified from USGS.[10]

Historically, drilling for oil and gas was through vertical wellbores that extended through strata containing oil and gas. The well bore was lined with steel casing and allowed the oil and gas to flow into the pipe and then be pumped to the surface. Drilling progressed as completion techniques were developed to enhance the recovery of oil and gas. These techniques are referred to as well stimulation and are optimized for each target formation.[7] Well stimulation has been around for more than a century; however, hydraulic fracturing has garnered the most notoriety as it is the most common form of well stimulation used today.[9,11,12] The production well is stimulated by pumping large volumes of prepared stimulation fluid and proppant (typically sand) into the well bore at a high rate and pressure to fracture the formation.[12–15] A variety of water-based stimulations additives exist, such as gel, slick water,[16] and polymers, depending on the geology of the formation. Fissures fill with fluid and proppant under high pressure, creating fractures in the target zone. While both hydraulic fracturing and horizontal drilling were both well-established practices with proven track records, the pairing of the two techniques allowed oil and gas operators to extract hydrocarbons across multiple basins previously thought to be impractical or uneconomical.[12,17] The combination triggered extensive growth of unconventional oil and gas development (UD).[18]

In 2000, approximately 26,000 unconventional production wells accounted for 7% of domestic natural gas production.[19] By 2007, this metric had risen to 46% and in 2015, two-thirds of the American natural gas output came from approximately 300,000 hydraulically-fractured production wells.[12,19,20] From 2011-2014, UD operations spanned the lower 48 states, but 92% of domestic oil and gas production growth was derived from unconventional resources in seven key oil and gas basins: Bakken (North Dakota and Montana), Niobrara (Colorado), Marcellus and Utica (Pennsylvania, Ohio and West Virginia), Haynesville (Louisiana and East Texas), Eagle Ford (South Texas), and the Permian Basin (West Texas and Southeast New Mexico) (Figure 3).[21]

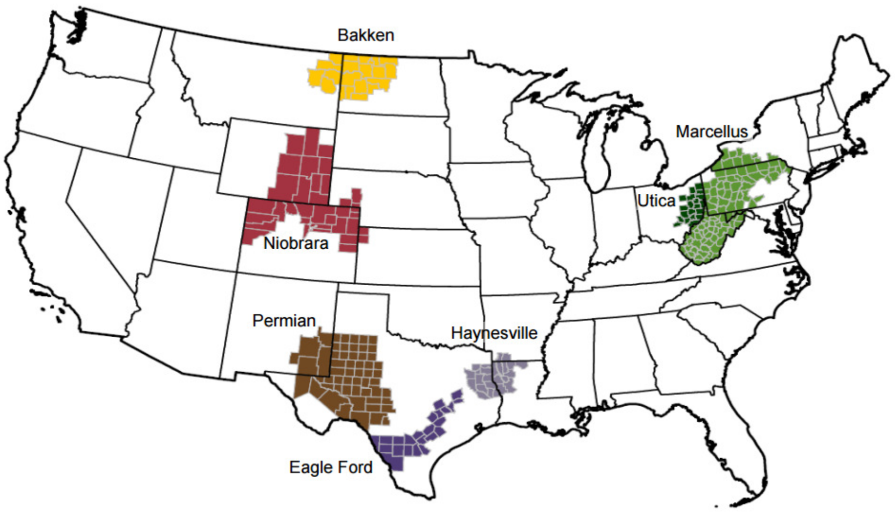


Figure 3. Seven regions in the US that accounted for 92 % of domestic oil and gas production from 2011-2014.[21] Reprinted from EIA Drilling Productivity Report April 2017.

The Permian Basin has been a major producer of fossil fuels for nearly a century and is one of the most prolific producing basins in the world. Currently, several major fields discovered in the Permian Basin during the 1940s are still ranked in the top 20 proven reservoirs by the United

States' Energy Information Administration.[22] In 2012, the region accounted for two-thirds of Texas crude oil production and 14% of the nation's.[23] Figure 4 represents the Permian Basin, which is 250 miles wide and 300 miles long, contains three prominent geological features: The Midland Basin; the Delaware Basin; and the Central Basin Platform (Figure 4).[24] Horizontal drilling and hydraulic fracturing have greatly improved the economic prospects of these shale formations. These technologies have increased oil production from 850,000 barrels per day (bpd) in 2007 to over 2.2 million bpd in 2012.[21,25,26]

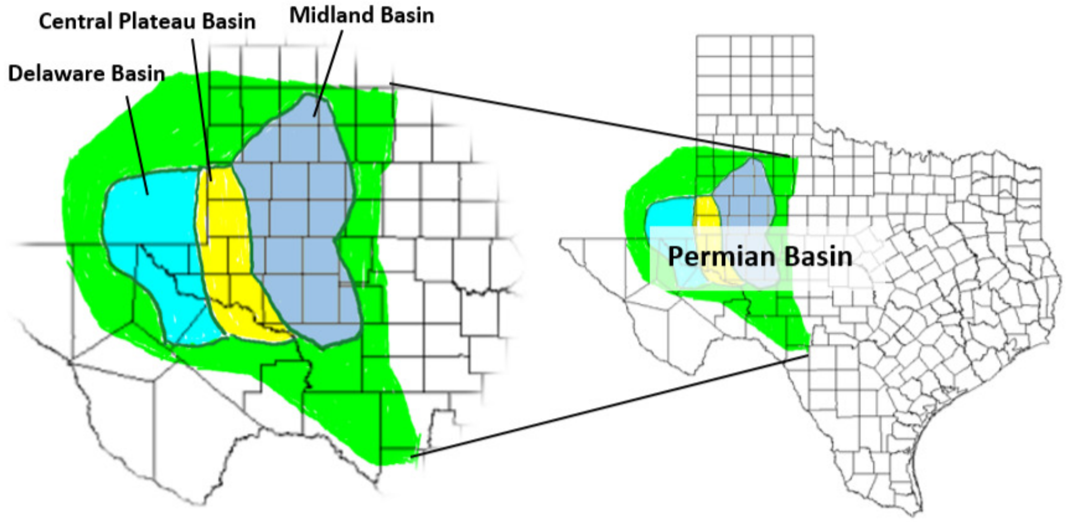


Figure 4. Three major formations of the Permian Basin.

The Permian Basin offers multiple producing layers vertically stacked on top of each other. In the early 2000s, multistage hydraulic fracturing techniques were refined to allow conventional well operators the ability to comingle production zones.[22] For examples, the Wolfcamp formation, frequently a target of multistage operations, can be found at a depth of roughly 1-3 miles throughout the Permian Basin.[24] The Sprayberry formation can be found above the Wolfcamp formation in the Midland Basin.[22] The combination of drilling both production zones (Sprayberry and Wolfcamp) has been nicknamed the "Wolfberry". "Wolfbone" is another combination play formed from drilling the Bone Springs formation and Wolfcamp in the Delaware Basin. Unconventional oil and gas operators are taking advantage of this by developing multiple production zones from a single surface site as known as pad drilling shown in figure 5.[24]

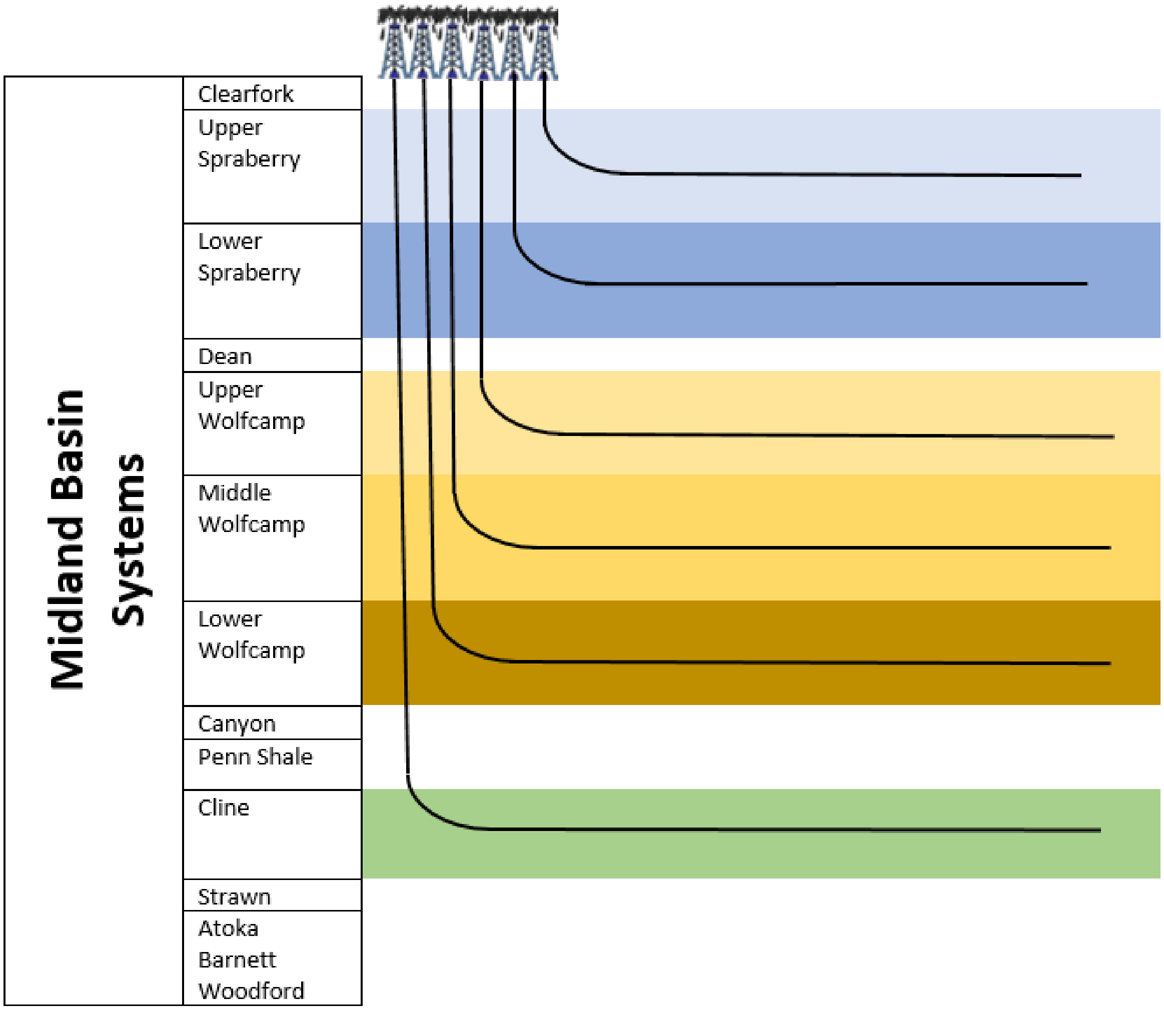


Figure 5. Examples of stacked formations found in the Midland Basin.

Despite the economic benefits of UD in recent years, hydraulic fracturing has become a controversial topic, largely in part due to concerns over contamination of groundwater,[27–31] surface water,[32,33] and air quality,[28,34,35] as well as high water usage, frequently in arid and semiarid regions,[18] and the potential inducement of seismic activity[12]. Understanding the causes of potential contamination helps to develop responsible energy extraction and environmental practices. For example, studies have shown that groundwater contamination concerns are most likely associated with faulty casing and cement issues, rather than the development process.[27,36–38] Also, mechanical inefficiencies from production pad sites have been shown by studies to have a negative impact on air quality, such as excessive venting of gas, rather than from the UD process itself.[28]

As unconventional oil and gas exploration expands, it becomes important to understand the sources of water and its usage, required volumes, water separation in the production phase, and the eventual disposal of wastewater. A mastery of the complete water cycle, which is shown in figure 6, allows for discernment of the consequence of the process, which will be expanded throughout this chapter. For instance, studies indicate that there is a direct correlation between the number of earthquakes and the volume of produced water being injected into disposal wells.[39–41] Understanding the areas of concern can facilitate the process of determining new potential areas of reuse and recycling based on the development of new technologies. The remainder of this chapter will cover the lifecycle of water in oil and gas development, including water use and waste production in the drilling, stimulation, and production phases. The current waste management strategies and challenges within the various treatment modalities will also be covered, along with the financial implications of the varying forms of waste management.

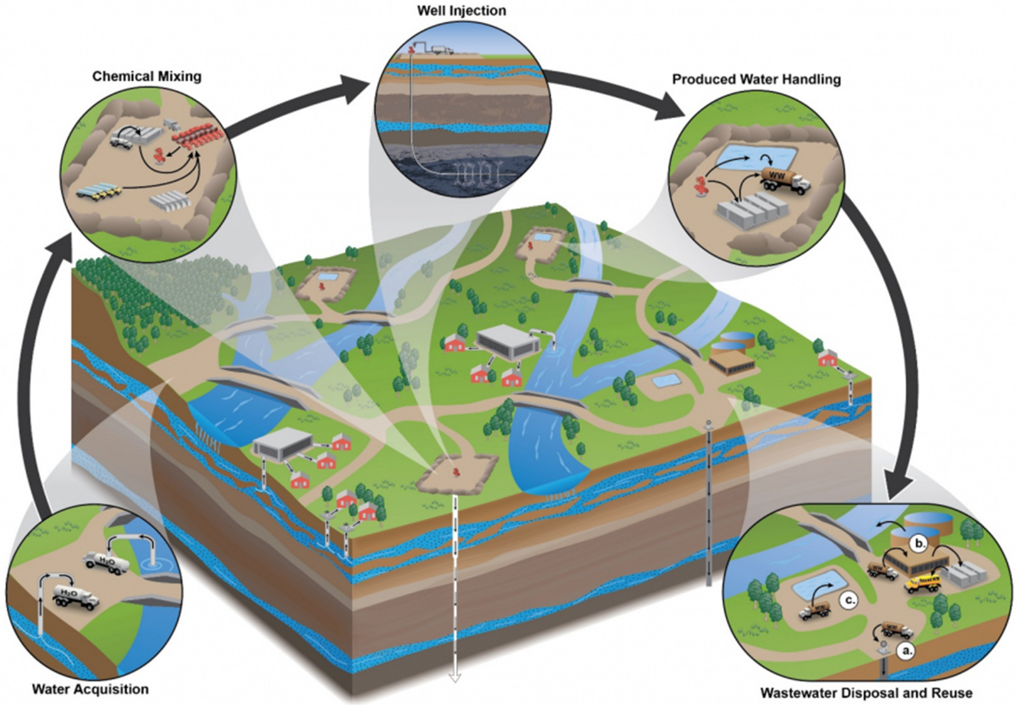


Figure 6. Diagram of a typical hydraulic fracturing process.[15](Figure reproduced from Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States (EPA-600-R-16-236ES, December 2016, www.epa.gov/hfstudy)

1.2.1 The Lifecycle of Water

The success of UD relies heavily on the accessibility to large volumes of water and the management of produced waste. Water acquisition can be from surface or ground water sources; however, the reuse of wastewater from previously stimulated production wells is increasing in popularity, particularly in petroliferous basins dealing with water scarcity.

The development of an unconventioalwell includes three distinct phases: drilling, completion, and production phases; all of which are required to bring a well online for the production of oil and gas. The first step in the process, drilling, requires only a small fraction of the total amount of water that is used throughout the process (Table 1). Water use for drilling and cementing is not reported, but one study has estimated the volume water used for the first stage of well development to be 6x the volume of the borehole which was 905 bbl/well on average or about 8% of the volume of water used for hydraulic fracturing.[7] The primary purpose of drilling fluid, also referred to as drilling mud, is to prevent a collapse of the borehole by using hydrostatic pressure to balance the pressure inside the wellbore.[42,43] It is also used to bring cuttings (rock particles) and other matter from the formation back to the surface, as well as to lubricate the drill bit and keep it cool. At the completion of the drilling process, the drilling mud is typically disposed of either on-site or at a permitted solid waste facility. The amount of water used for drilling will vary with the length of each well. A drilling unit on a horizontal well typically consists of a 1 mi^2 section. The distance of each lateral section can range from 4,500-7,500 ft and is dependent on surface location (pad site); however, horizontal production wells can be drilled across 2 sections or up to 10,000 ft+ as shown in figure 7. In the Bakken formation, the lateral section has increased from 7,200 ft in 2005 to 9,500 ft in 2013.[7]

Table 1. Water use in shale plays.[44] Adapted from Mantell M.

Gas Shale Plays	**Average drilling water use per well (bbl (gal))**	**Average hydraulic fracturing water use per well (bbl (gal))**
Barnett	6,000 (250,000)	90,000 (3,800,000)
Fayetteville	1,600 (65,000)	117,000 (4,900,000)
Haynesville	14,000 (600,000)	119,000 (5,000,000)
Marcellus	2,000 (85,000)	131,000 (5,500,000)

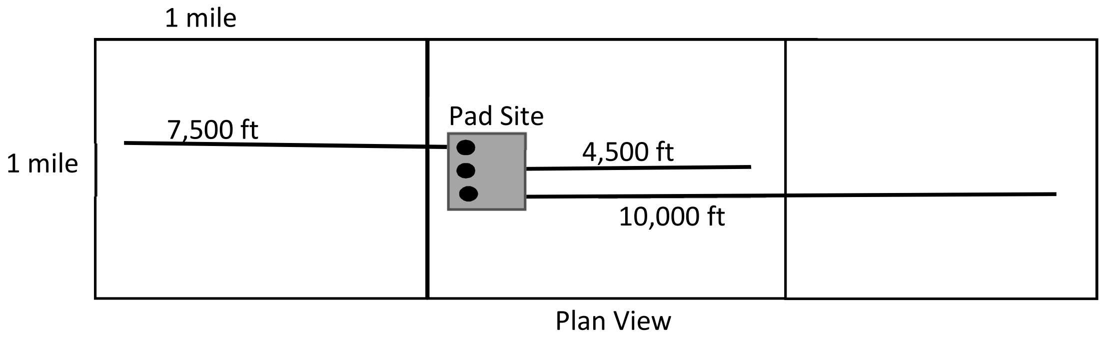
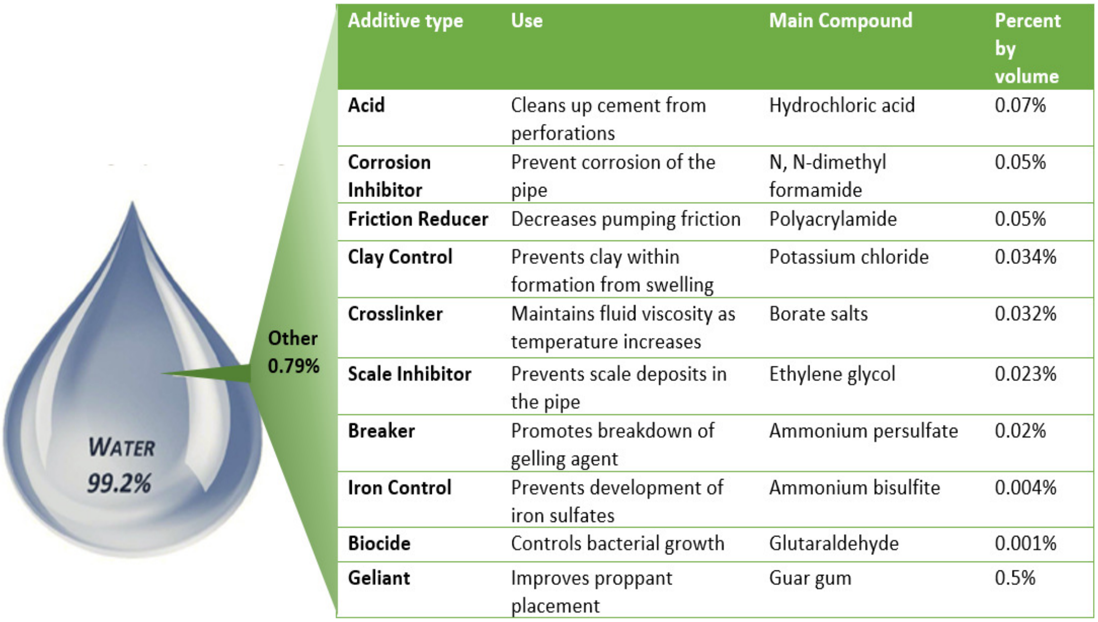


Figure 7. Plan view of a horizontal drilling site. Each section is 1 square mile. The distance listed represents the length of the horizontal well from the pas site location. This is determined in large part by which property the production company has access to too.

Following the drilling of a well (or multiple wells), the pad and well are prepared for completion. The drilling rig and supporting equipment are removed and the site is cleaned up to make way for the pumping and sand equipment used for completion. The second major step during the completion process is when well stimulation is performed. For hydraulic fracturing, fluid is prepared by mixing additives, such as proppants and chemicals into the water. Proppants are hard solid particles such as coated silica sand that are used to prop open the fractures formed during hydraulic fracturing, so the oil and gas can flow to and up through the well hole.[12,20,45] The portion of chemicals is relatively small (<1 – 3%) compared to the volume of water (Figure 8). The additives are used to kill bacteria in the water to prevent the production of H_2S in the well, and increase injection velocities of the water, as well as to help suspend the proppant entrained in the fluid, thereby extending the distance to which the proppant can be placed within the fractured formation. In figure 9 the variation of the amount of water used during hydraulic fracturing across the nation is clearly shown. The discrepancies are dependent upon a number of factors, such as the intrinsic properties of the target formation, the type of well (conventional or unconventional), the depth of the well, and the form of water-stimulation used.[3,16,46] In 2014, 21,800 barrels (bbl) represents the national median amount of water that was used to hydraulically fracture vertical production wells. Comparatively, the national median volumes for horizontal wells were 128,000 bbl and 163,000 bbl per oil and gas well, respectively.[7] These values represent considerable increases from the 5,600 bbl that was required to bring a production well online in 2000, prior to the expansion of the shale energy boom.[46]



Additive type	Use	Main Compound	Percent by volume
Acid	Cleans up cement from perforations	Hydrochloric acid	0.07%
Corrosion Inhibitor	Prevent corrosion of the pipe	N, N-dimethyl formamide	0.05%
Friction Reducer	Decreases pumping friction	Polyacrylamide	0.05%
Clay Control	Prevents clay within formation from swelling	Potassium chloride	0.034%
Crosslinker	Maintains fluid viscosity as temperature increases	Borate salts	0.032%
Scale Inhibitor	Prevents scale deposits in the pipe	Ethylene glycol	0.023%
Breaker	Promotes breakdown of gelling agent	Ammonium persulfate	0.02%
Iron Control	Prevents development of iron sulfates	Ammonium bisulfite	0.004%
Biocide	Controls bacterial growth	Glutaraldehyde	0.001%
Geliant	Improves proppant placement	Guar gum	0.5%

Figure 8. Typical composition of hydraulic fracturing fluid, modified from Information on Shale Resources, Development, and Environmental and Public Health Risks by US Goverment Accountability Office and Chemical Use In Hydraulic Fracturing by FracFocus. [42,47]

Hydraulic fracturing is completed in multiple stages, allowing for a more intensive injection of water and proppant within a desired section of the well. These stages are typically 300 ft or less in length. The steel casing that is cemented in place to hold the wellbore open, and to protect the surrounding groundwater resources, is perforated and then water and proppant are pumped through the perforated holes. Over the course of several days, approximately 10,000 to 20,000 bbls of water are injected into the individual stages at an estimated rate of 70-100 bbl/min.[20,48] To improve the cost efficiency of production, multiple wells can be drilled from one pad site. For example, modern pad sites in the Permian Basin can house as many as 12+ wells/bench/section.[49]

Gas-dominated plays, such as the Barnett shale, often use slick water stimulation and a higher volume of water on average compared to oil-dominated plays. Water sensitive, oil-dominated plays, such as the Bakken Shale, frequently use less water per well and gel stimulation.[7,15] Recent studies have shown that the composition of the target reservoir is the primary factor that influences the volume of water used rather than the type of stimulation that is employed.[7] When comparing the water usage for hydraulically fractured shale-gas wells vs shale-oil wells in the Eagle Ford Basin (where both forms of hydrocarbons reservoirs are developed), the water usage per well was relativity similar. For example, one study revealed shale-oil wells required an average of 116,000 bbls/well, whereas and shale-gas wells required an average of 114,000 bbls/well.[7] However, the variability was high, and ranged from 54,000 to 214,000 bbls/well. The same study compared the volume of water used for hydraulic fracturing of oil wells in the Eagle Ford and Bakken formation. The calculated average volume used in the Bakken formation was 66,000 bbls/well in 2013, but the average lateral lengths were almost 2 times longer in the Bakken than Eagle Ford. It is worth noting that the geological structure in the Bakken region is comprised of tight sandstones, silt, and dolomitic mudstone sandwiched between shale layers, whereas the Eagle Ford play yields oil and gas primarily from shale.

In 2011, 4.9 billion gallons of water was used to stimulate UD production wells in Texas, accounting for less than 1 % of the state's water usage.[20,50] While the overall volume is low compared to other anthropogenic activities (i.e., agriculture and farming) within the state, these volumes tend to be highly localized, especially in arid and semiarid regions, which can lead to notable cones of groundwater depletion. Interestingly, from 2013-2016, the water use per well went up by approximately 434% in the Permian Basin of west Texas.[51] The increase is attributed to drilling activity and completions where the average horizontal length as increased from 5,700 to 6,800 lateral ft.

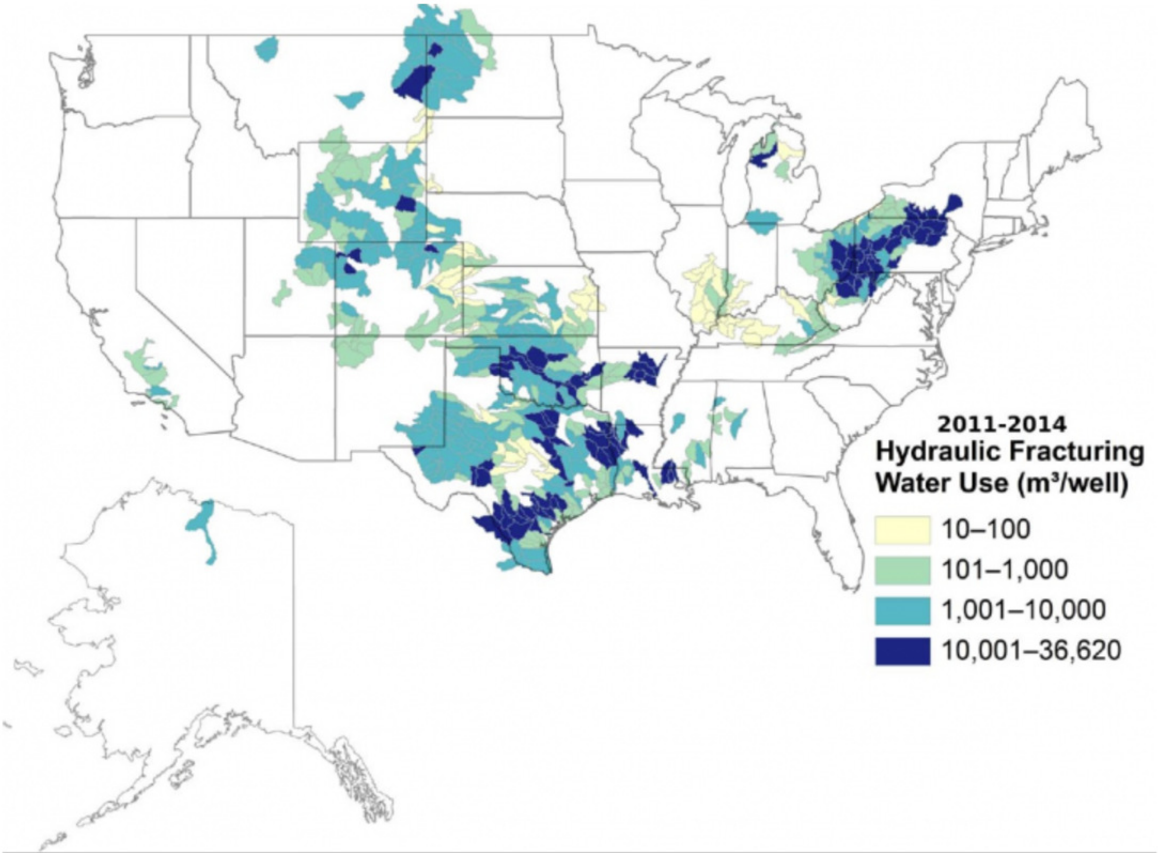


Figure 9. Average water volumes used (injected) per well to hydraulically fracture oil and gas wells (horizontal, directional, and vertical) drilled from January 2011 to August 2014 in watersheds.[46] Adapted from Gallegos T. et al.

By comparison, conventional exploration requires less water to stimulate a well; however, both conventional and unconventional oil and gas development can generate substantial amounts of wastewater in the production phase.[52] After the completion of the stimulation process in a production well, the pressure fluid is released allowing the water to flow back into a storage tank as the well is put in production. Large volumes of wastewater migrate to the wellhead, which are mixed with oil and gas, and some other solids. Initially, a crew can expect a water flowback rate of approximately 3,500 to 4,500 bpd, but this has been recorded as high as 6,000 bpd at some shale production sites.[13,53] Beyond the first week, the rate of waste production can decrease dramatically, to near 1,000 bpd or less which continues to decrease over time.

The wastewater stream is comprised of two distinctive sub-components, flowback water and produced water. The definition of the distinction between the two components has evolved over time. With conventional oil and gas practices, water that is injected during stimulation that returns to the well head is called flowback,[49,52] whereas the natural formation water recovered from the targeted zone(s), along with the hydrocarbons, is referred to as the produced water.[54,55] The distinction between the two has been referred to as the change in chemical composition of water returning to the well head to match the formation from which the produced water came.[16,56] Conversely, when assessing unconventional oil and gas wastewater fractions, the distinction between flowback and produced waters can be more challenging to define. Comparatively speaking, the natural formation water from unconventional oil and gas operations is a minor component of returning water.[52] The longer the flowback remains in the formation, the more the chemical composition of the flow-back will resemble the geology of the formation. At the point where the water retrieved from the well is comingled with the commodity, the waste stream is no longer a depreciable asset and becomes an expense termed produced water.[49] Therefore, the distinction between the two wastewater components in UD is primarily an accounting one. An alternative definition of produced water is water brought to the surface with the oil and gas.[52] As such, the two components will be referred to collectively as produced water for the remainder of this chapter since the majority of the wastewater is brought to the surface comingled with hydrocarbons.

The chemical profile and quantity of produced water varies with each shale play, well location, and depth, as well as the age of the reservoir and type of hydrocarbon produced.[20,57,58]

Constituents of concern in produced water include dissolved and suspended organics (measured as total petroleum hydrocarbon (TPH)), production chemicals, suspended solids, components that can cause corrosion and scaling, bacteria, naturally occurring radioactive isotopes, and total dissolved solids (TDS) (including hardness and heavy metals).

Collecting hydrocarbons is the goal of oil and gas exploration and is a key constituent in produced water. TPH is made up of three forms: free oil, dispersed oil, and dissolved oil. The droplet size of oil is a major factor for their classification and the approach to achieve separation from produced water will vary based on the form.[59] Free oil or nonpolar hydrocarbons are the easiest to separate from produced water typically through the use of gravity separation methods as part of the production process.[58,60] Dispersed and dissolved oil are the most challenging to treat and the most environmentally dangerous oil components in produced water.[59] They are formed from a mixture of hydrocarbons including BTEX (benzene, toluene, ethylbenzene and xylene), PAHs (polyaromatic hydrocarbons) and phenols. Dispersed oil is formed from small droplets of oil suspended in the aqueous phase. These include less-soluble components, such as PAHs and heavy alkyl phenols. Polar organic compounds and small low molecular weight components such as BTEX, small phenols, and carboxylic acid form the dissolved oil in produced water. Lastly, residual production chemicals can persist in produced water. These include proppants, surfactants, biocides, corrosion inhibitors and scaling reducers (Figure 8).[50,58] A recent analysis of produced water from the Cline Shale region revealed residual levels of surfactants such as 2-butoxyethanol and N-alkyl-N,N-dimethylamine.[61] Non-emulsifiers such as diethanolamine salts were also identified. Non-emulsifiers are used to break emulsion before the well is put into production and to speed up the separation of water and oil.

Radioactivity of produced water results primarily from radium that is co-precipitated with barium sulfate (scale) or other forms of scale.[58] The most abundant naturally occurring radioactive materials (NORM) present in oilfield produced water are radium isotopes, ^{226}Ra and ^{228}Ra. Additionally, produced water from UD is generally rich in dissolved inorganic compounds or minerals classified as cations and anions, and heavy metals. Sodium, Na^+, and chloride, Cl^-, are the primary components responsible for salinity. However, sulfate, carbonate, bicarbonate, calcium, barium, magnesium, iron, and strontium are frequently found to varying degrees in produced water, which affect conductivity and scale-forming potential. The salinity of produced water can vary from brackish levels (1,000-15,000 parts per million (ppm) TDS) to varying degrees of saline (15,000 ppm to 40,000 ppm TDS) to brine (> 40,000 ppm).[20,44] For example, produced water from the Barnett Shale has been found to have TDS levels ranging from 500-200,000 ppm, whereas produced water from the Marcellus Shale formation varies from 10,000 to 300,000 ppm.[20]

Produced water requires proper treatment to avoid environmental damage and contamination. However, it is a challenge to treat because of its complex physiochemical composition and the fact that the composition can change over the lifetime of the well.[62] Current conventional treatment technologies are targeted for the removal of heavy metals, oil and grease, and suspended solids, which often lead to the generation of large volumes of secondary waste. For instance, heavy metals are removed as sludge using current treatment technologies.[58] Initial processing is generally effective at removing the bulk of suspended solids, TPH, as well as scaling compounds.[44,63] Ultimately, the extent to which the produced water is further processed or treated is determined by the final destination. The general objectives for treatment operators consist of 7 primary focuses based on the produced water quality in the region.[58,62,64]

1. Removing organics including oil and grease,
2. Disinfection,
3. SS removal: removing of suspended particles and sand,

4. Dissolved gas removal: removing of light hydrocarbon gases, carbon dioxide, and hydrogen sulfide (if needed in the production region),
5. Desalination: removing dissolved salts,
6. Softening: removing excess water hardness and reducing scaling,
7. Removal of naturally occurring radioactive material

Management of the expanding volumes of produced water from oil and gas operations is an issue of increasing importance. Not only is the number of unconventional oil and gas wells increasing, but the issue is compounded by the continuous volumes that are steadily produced over the lifetime of the well. Few worldwide estimates have been published. However, in 2012, it was estimated that 250 million bbl of wastewater was produced daily in both oil and gas fields globally, with more than 40% being discharged into the environment.[58] The total volume of produced water being generated annually by United States from oil and gas development in 2012 (the most recent year for which national volume data have been collected), was estimated to be 21.2 billion bbl (58 million bbl/day). Texas, which produced the highest volumes of water, oil, and gas in 2012, accounted for 35% of the national produced water volume with more than 7.4 billion bbl of produced water being generated.[52]

1.2.2 Wastewater Management and Treatment Challenges

One of the biggest challenges associated with maintaining the favorable economics of UD operations is managing the produced water.[50] How the produced water is handled is dependent on local resouces,[61] local regulations, and economics.[16] Its fate is also highly influenced by three major factors: quantity, duration, and quality.[44,50] Infrastructure and geological conditions play a role in determining viable options as well. Oil reserves commonly have larger volumes of water than gas reservoirs.[65] For example, the Marcellus shale formation (a gas play) typically generates the lowest quantity of produced water when compared to the six other key basins in the United States. In contrast, the Permian Basin (a series of predominantly oil plays) produces the highest amount of produced water. Between June 2015 and May 2016, the Permian Basin yielded approximately 24 times the volume of wastewater than in the Marcellus formation. Two of Texas' liquid plays, the Permian Basin and the Eagle Ford shale, yielded ratios of nearly 6.5 and 0.9 bbls of produced water for every one barrel of produced oil, respectively, represented in figure 10.[51] Options to manage these waste fluids include surface discharge, agricultural use, evaporation ponds, reuse in future hydraulic fracturing, recycling for other industrial uses, or disposal in an injection well.[15,61,65,66]

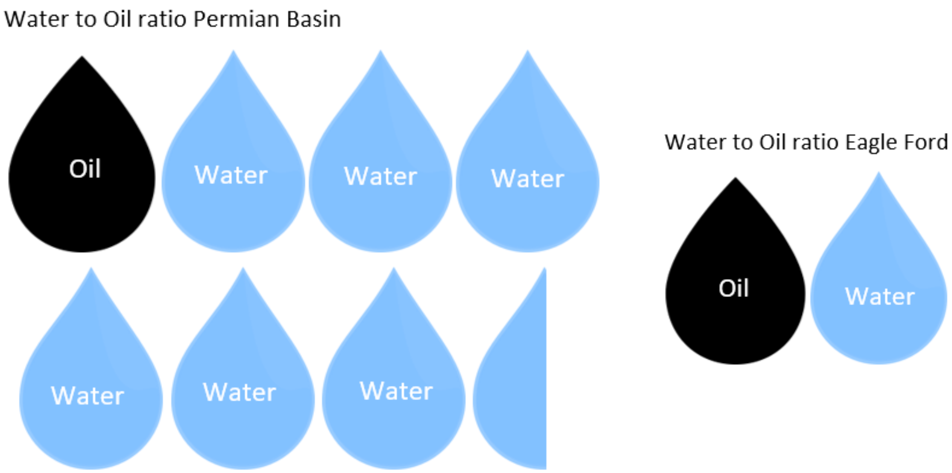


Figure 10. Produced water volumes to oil volumes ratios for the Permian Basin and Eagle Ford.

The least common method of waste disposal currently being employed by the oil and gas industry is surface discharge. One reason for this is attributed to the fact that the required permits from the National Pollution Discharge Elimination System (NPDES) are challenging to obtain. Nonetheless, in Pennsylvania, disposal by surface discharge was the primary method used in 2008 because geological conditions are not favorable for disposal wells.[64] However, this option has declined since 2010, after some contamination incidents prompted the state to modify TDS limits for discharge to a monthly average of 500 mg/L.[50] The majority of the produced water is reused or recycled in the Marcellus shale, but increased salinity in produced water can be problematic.[16] Produced water can be challenging to recycle in part due to high TDS which requires desalination, traditionally an energy intensive and thus costly process.[50,51] Therefore, reuse without desalination has become more common in the region.[44,57]

Alternatively, produced water has been designated for the beneficial use of agriculture and wildlife. For example, produced water with less than 1,000 ppm TDS is considered acceptable for livestock, but up to 7,000 ppm can be used.[60] Furthermore, for agricultural use, not only is the salinity taken into consideration, but a limited amount of sodium and other pertinent ions are important as well. An example of this agricultural use is in Kern County, California, where operators have begun selling produced water to local municipalities that distribute to local farms all across the county. The consequences of consuming produce and seeds that have been watered with produced waste are currently unknown. However, the lack of studies with respect to human ingestion of produced water constituents, the long-term buildup of untreated contaminants in soil, and the potential for *ex situ* uptake all cast doubts and uncertainty over the sustainability of using produced water for agricultural purposes.

Evaporation ponds are another form of waste management. These artificial ponds are constructed by excavating a large pit that is then sealed with either a bentonite clay and/or a protective lining. These structures require a large space of land to efficiently facilitate the evaporation of water and the photovolatilization of volatile organic compounds.[58] They are used predominantly in more arid regions, such as Wyoming and Colorado because of the higher evaporation rates. Ponds are usually covered with netting to prevent potential problems with wildlife encountering the contaminants. The rate of evaporation depends on the size and depth of the pond and the characteristics of the influent.[67] The evaporation rate of a solution will decrease as the relative shares of solids and chemicals rise. Evaporation rates can be enhanced by spraying the water through nozzles. The nozzles create many small droplets and increased surface area for evaporation. However, this practice can lead to salt damage to soil and vegetation. Therefore, misting towers are not currently recommended as a management practice.

For oil and gas operations in regions with significant initial volumes and ample continuous volumes over the lifetime of the well, it is more practical to consider the reuse of produced water in subsequent hydraulic fracturing activities. It is important to ensure that the produced water intended for reuse in subsequent production well stimulations is compatible with the receiving formation to prevent premature fouling of the formation or damage to the equipment. TPH needs to be < 20 ppm, the separation of which can be accomplished via physical processes such as centrifugation, coalescence, floatation, solvent extraction, or adsorption with products like activated carbon and zeolite mixtures.[60] Additionally all bacteria, algae, and fungi must be eliminated, which is generally achieved with ozonation, such as chlorine dioxide or peroxide, and/or UV treatment. This is of paramount importance to avoid biofouling and damage to equipment as many pertinent bacterial species can proliferate quickly under substrate-rich conditions, and can produce corrosive gases like carbon dioxide and dihydrogen sulfide.[60] Solids must be reduced to less than 20 μm, which is often accomplished via filtration. For the effective reuse of produced water, the concentration of iron should be less than 10 ppm to prevent the inhibition of gel cross-linking, corrosion, and the formation of scale.[68] High levels of boron (26-28 ppm), are also characteristic of produced water and need to be removed prior to reuse to ensure that gel cross-linking is not hindered.[69] One of the terminal venues frequently considered for recycled produced water is irrigation, which can introduce high levels of boron to plants, to the point of being toxic. Furthermore, when produced water with elevated concentrations of boron is used for irrigation without treatment, boron complexes can form with heavy metals like Pb, Cu, Co, Ni, and Cd, which increase the toxic potential of those metals. The remaining TDS levels in produced waters are rarely problematic and can be diluted with fresh water if needed.[44] Collectively, the ability of operators to treat and achieve the necessary water quality requirements is not as challenging as managing the rate at which they would have to treat the produced water, which can be acquired at rates up to 80 bpm of wastewater. For example, if 100% recycled water is used, a site would have to process produced water fast enough to yield 115,000 bpd or store the produced water until the required total volume is reached. Storage capacities at treatment facilities can vary significantly, particular when there is mixing of produced water with fresh water. If a 1:1 ratio of fresh water and recycled water is used, then a site would need to process produced water to return to operators at a rate of 45 bpm.

High volumes of produced water create an excellent opportunity to explore recycling options; however, the composition of the influent plays a critical role in determining if recycling is economically feasible. For instance, dissolved solids are traditionally treated with energy intensive techniques such as reverse osmosis membranes, thermal distillation, or freeze-thaw evaporation processes, which also make their implementation in water recycling efforts economically infeasible.[70] Furthermore, each of these desalination approaches has its own set of limitations. For example, Freeze-thaw evaporation is only viable in cold climates; while, reverse osmosis is limited to approximately 40,000 mg/L TDS, or about the concentration of dissolved constituents in seawater. [64,70] The Permian Basin has high salinity produced water, which ranges from 8-12%, or approximately 2 to 3.5 times higher than seawater. As such, membrane desalination, mechanical vapor compression, or forward osmosis are better suited to handle these high TDS matrices.[50] However, a liquid permeate is required to complete a phase change during treatment with membrane desalination and mechanical vapor compression, and this creates significant discharge. Alternatively, forward osmosis is a membrane process that is not restricted to the low TDS limits of reverse osmosis and does not require an energy intensive phase change process. Recently, there has been some promising research evaluating forward osmosis to treat low salinity produced water followed by direct discharge into the sea.[71]

Salt water disposal (SWD) wells, one form of Class II wells, are the most popular option for produced water management in the conventional and unconventional oil and gas industry, because they are frequently the most cost-effective choice. In 2011, 98% of produced water from onshore drilling in the United States was injected into Class II wells.[66,72] These wells are used to inject non-hazardous fluids associated with oil and gas production for disposal, hydrocarbon storage wells, or enhanced recovery.[73] It is estimated that approximately 57 million bbl (2.4 billion gallons) of produced water is injected daily into the 180,000 underground injection wells operated throughout the United States .[73] Approximately 20% of Class II wells are SWD wells, located primarily in Texas, California, Oklahoma, and Kansas. Furthermore, ~58% of the produced water is used for enhanced recovery, which is also referred to as water flooding. This technique is used to increase production and prolong the life of production wells. Through this process, fluid is injected into the producing formation to drive the commodity into the pumping well, as depicted in Figure 11. The remaining 40% of produced water is disposed of through subsurface injection via SWD wells.

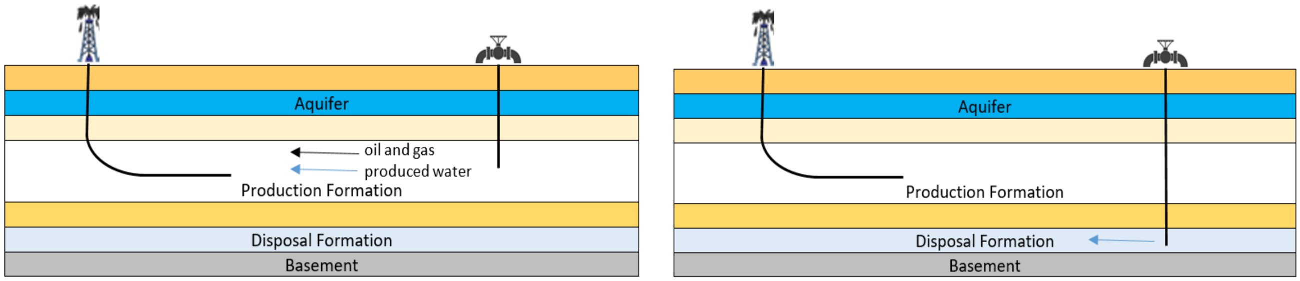


Figure 11. Enhanced recovery using produced water, termed water flooding (left) and traditional salt water disposal (right).

Through the use of SWD wells, fluids are injected into underground formations, often over a mile in depth, into sub-surface zones that already contain naturally occurring saltwater.[74] SWD intervals must be sealed above and below by unbroken, impermeable rock layer.[74] Figure 12 displays the three layers of casing are typically required protect overlying groundwater. The first protective layer is comprised of steel pipe from the ground surface to the base of the deepest usable quality groundwater. This surface casing also acts as a protective sleeve through which deeper drilling occurs. The second protective layer is a pipe inside the surface casing that extends the total depth of the well. It is permanently cemented in place. The third protective layer is the injection tubing string and packer. The tubing/packer assembly is what the produced water flows through to reach the underground formation. It contains individual sensors that are monitored to detect any pressure changes that may indicate a leak or other type of mechanical issue.

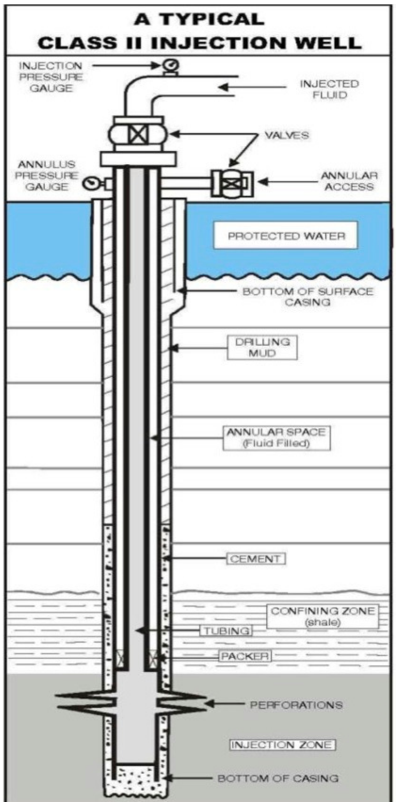


Figure 12. Typical Class II injection well.[75] Reproduced from North Dakota https://www.dmr.nd.gov/oilgas/undergroundfaq.asp.

Concerns over increased seismic activity have grown along with the increasing volume of produced water being disposed of by injection into non-productive subsurface formations.[40] Most injection wells are not associated with the earthquakes that can be felt by the public and many factors are required to induce notable seismic events. However, the total volume and the rate of injection are factors that have been related to the induction of anthropogenic earthquakes in some geographic locations. Additionally, the presence of faults that are large enough to produce notable earthquakes is also a factor, as well as the presence of pathways for the fluid pressure to travel from the injection point to the faults. In 2008, the first confirmed earthquake was measured in the Bend Arch-Fort Worth Basin in northern Texas. Since then earthquakes have been increasing in frequency and magnitude with the largest being M4.0 in 2015.[40] It is thought that seismic events are caused due to increased fluid pressure on already stress faults, triggering preexisting faults to slip.[76] Currently, wastewater is injected into several formations in the Fort Worth Basin: Cisco, Canyon, Strawn, Caddo, Atoken, Marble Falls, and Ellenburger. The Ordovician Ellenburger formation is the most frequently used terminal subsurface location for produced water disposal across the state of Texas. In the Fort Worth Basin in particular, more than 65% of produced water from the Barrett Shale is injected into the Ellenburger formation, which is located between the Mississippian Barnett Shale (above) and a Precambrian granite basement (below).[40]As shown in Figure 13, since 2006, the volume of wastewater injected in the Ellenburger formation in this basin has increased from less than 6 million bbl per month to more than 16 million bbl for most of the months in 2014.

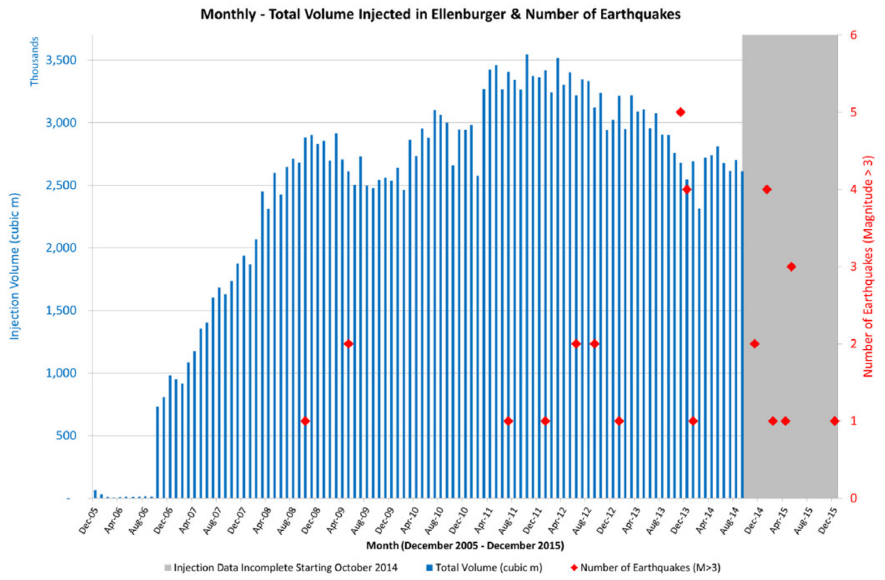


Figure 13. Earthquakes with magnitudes greater than 3 (red diamonds) and monthly injection rates into the Ellenburger in the Fort Worth Basin (blue bars) from December.[40] Reprinted with permission from Hornbach, M. et al. with permission.

If SWD is the terminal point for produced water, then further processing is not required, but it is frequently completed to prolong the life of the disposal well. Upon produced water entering a SWD facility, oil constitutes generally 0.1- 0.5%. Figure 14 is a diagram that shows the progression of produced water through the SWD facility traditionally begins by allowing remaining organics and water to separate via gravity flow by hydrostatic pressure. After separation, the remaining hydrocarbons range from about 20-40 ppm (0.002 - 0.004%). In the Permian Basin and other regions where iron is a concern, iron reducers are added to prevent scaling. Solids are then collected from the base of the separation holding tanks and 200 µm filters that the produced water passes through. Surfactant is added to emulsify any remaining organics followed by well injection. The greatest challenge with SWD is keeping up with the demand in high production regions. A bottleneck can be formed at a disposal site based on how quickly water can be injected into the ground without over pressurizing the well. The rate at which the produced water can be injected into the ground can vary significantly across a given formation. For example, in the Permian Basin, one SWD well may have a maximum limit of ~11,000 bbl/day, while another site might have a limit of approximately 25,000 bbl/day, both of which could be using the Ellenburger formation for disposal.

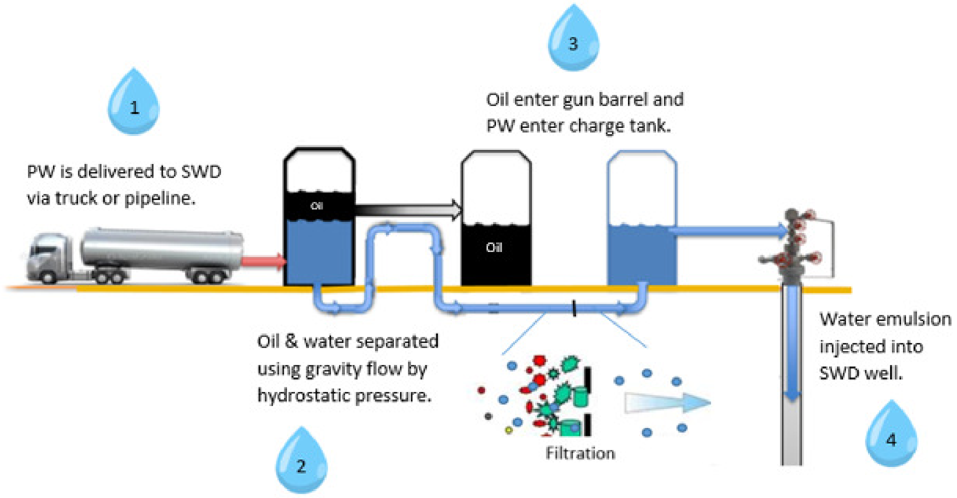


Figure 14. SWD Treatment Process at Water Midstream Partners-Permian Basin.

Cost

Ultimately, cost is the major driving force behind the treatment option that is chosen for UD operations. However, oil and gas operators are increasing their efforts to collaborate with scientists to develop best management practices that consider both cost and environmental stewardship. The US oilfield water market was estimated to be a $12.6 billion industry in 2015,[77] which is best illustrated by the fact that approximately 40-55% of UD operational costs are associated with produced water management and disposal.[51] The proximity of disposal wells or recycling plants to UD production wells, as well as the type of transportation, each play key roles in determining the most cost effective option, especially for high volume long-term production sites. For example, in Pennsylvania there is a limited number of disposal wells, which has increased the cost of in-state SWD, resulting in a large portion of UD waste being disposed of in neighboring Ohio. Conversely, Texas currently has approximately 8,000 active disposal wells, making waste disposal more convenient and cost-effective.[74] Across the nation, the cost ranges from \$1.00/bbl to \$8.00/bbl of water for transportation and SWD injection.[51] Currently, trucks are the primary method to transport water,[13] because of their versatility and low upfront cost. However, pipelines are also being utilized as they carry a lower lifetime cost, but a higher up-front cost. Given the expenses associated with transporting and disposing of produced water, reusing it for subsequent hydraulic fracturing operations could theoretically lower water costs by approximately 45% per well, while also reducing the reliance on fresh water resources.[51] However, the current treatment options tend to be a more expensive alternative to SWD disposal, and can range from \$5.00/bbl to \$14.00/bbl.[60]

1.3 Summary

It is inevitable that the expansion of UD will be required to meet the growing energy demands in the United States. The combination of three factors have made unconventional oil and gas practice economically viable: advances in horizontal drilling, advances in hydraulic fracturing,[20] and most importantly, increased energy consumption and demand. Currently, the most cost-effective choice for oil and gas associated wastewater is disposal in Class II disposal wells. However, in order to maintain responsible practices, the development of cost effective recycling technologies that allow produced water to be reused in an economical fashion is essential. There are several oil and gas plays in the United States with large enough volumes of produced water that make them suitable markets for investigating recycling options. A single technology is not an effective option for treating produced water due to its complex and highly variable biogeochemical composition. Instead, viable treatment options need to be a series of techniques that are inexpensive, modular in design, have a low tendency for fouling,[50] can handle significant throughput, and are able to desalinate effluent if recycling for other industrial applications is the ultimate objective. Concerns about water usage and water contamination can be addressed through continued research into practical and cost-effective reuse and recycling options.

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CHAPTER TWO

ANALYTICAL METHODS FOR THE COMPREHENSIVE CHARATERIZATION OF PRODUCED WATER

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Analytical Methods for the Comprehensive Characterization of Produced Water

Tiffany Liden[1], Inês C. Santos[1,2], Zacariah L. Hildenbrand[2,3*], Kevin A. Schug[1,2]*

AUTHOR INFORMATION:

1. Department of Chemistry and Biochemistry, The University of Texas at Arlington, 700 Planetarium Place, Arlington, TX 76019, USA
2. Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, USA
3. Inform Environmental, LLC, 6060 N. Central Expressway, Suite 500, Dallas, TX 75206

Correspondence should be addressed to: 6060 N. Central Expressway Suite 500, Dallas, TX 75206, USA. Tel.: +1 214 800 2829; e-mail address: zac@informenv.com; and 700 Planetarium Pl.; Box 19065; Arlington, TX 76019-0065, USA. Tel.: +1 817 272 3541; Fax: +1 817 272 3808; e-mail address: kschug@uta.edu

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2.1 Abstract

During the unconventional oil and gas development stimulation process, referred to as hydraulic fracturing, millions of gallons of fresh water can be used, as well as the production of millions of gallons of wastewater with a highly variable, chemically-rich composition. This waste stream can contain a mixture of organic and inorganic additives, transformation products, as well as inorganic and organic substances from the formation. Unfortunately, there is limited knowledge with regard to the composition of chemical additives used during hydraulic fracturing. Additionally, there currently does not exist any methods approved by U.S. regulatory agencies for the evaluation of produced water. Collectively, these two factors have led to significant knowledge gaps with respect to exposure, hazard data, and analytical methods. As a result, there is an inadequate understanding of the environmental and human exposure implications during contamination events. Furthermore, pursing a deeper understanding of the chemicals that could be present in produced water can provide valuable insight when monitoring the efficacies of various treatment technologies for the reuse of produced water. This chapter will discuss the analytical methods that have been used to evaluate five key constituent categories found in produced water: bulk measurements, organics, biological, inorganics, and naturally occurring radioactive material. In addition, the chapter will touch on the outstanding concerns and remaining knowledge gaps.

2.2 Introduction

Currently, the American economy relies heavily upon oil and natural gas resources to support approximately 81% of the nation's growing energy demands (U.S. Department of Energy, 2015). Most recently, this has been accomplished through the expansion of unconventional oil and gas development (UD), which in itself has been one of the most controversial topics in the climate change era. Through this process, water is injected into the production well at a high rate and pressure in order to cause fissures in low porosity rock to allow oil and natural gas a path to migrate back to the surface. Once stimulation is completed, the water and the commodity are pumped back to the surface (Liden et al., 2017). From 2000 – 2007, there was a 39% increase in unconventional natural gas production in the United States. The growth was a result of a combination of advanced methods in horizontal drilling and hydraulic fracturing (U.S. Energy Information Administration, 2017). By 2015, two-thirds of the natural gas output in the US came from hydraulically-fractured production wells (Ground Water Protection Council and All Consulting, 2009; Perrin and Cook, 2016; Wang et al., 2014), with 92% of production growth being derived from unconventional resources in seven key oil and gas basins: Bakken (North Dakota and Montana), Niobrara (Colorado), Marcellus and Utica (Pennsylvania, Ohio, and West Virginia), Haynesville (Louisiana and East Texas), Eagle Ford (South Texas), and the Permian Basin (West Texas and Southeast New Mexico).

The success of UD relies heavily on the accessibility to large volumes of water, frequently in the form of surface and groundwater. The amount of water used during hydraulic fracturing varies across the nation and is dependent upon a number of factors, such as the intrinsic properties of the target formation, the type of well (conventional or unconventional), the depth of the well, and the form of water-stimulation used (Alessi et al., 2017; Gallegos et al., 2015; U.S. Department of Energy, 2015). In 2011, 4.9 billion gallons of water was used to stimulate unconventional well production in Texas (Ground Water Protection Council and All Consulting, 2009; Shaffer et al., 2013). Overall this volume of water used is relatively low compared to other anthropogenic activities (i.e., agriculture and farming), accounting for less than 1% of the state's water usage. However, these volumes tend to be highly localized, which can lead to cones of groundwater depletion, especially in arid and semiarid regions.

An example of where this is occurring is the Permian Basin located in west Texas, which is one of the most prolific production basins in the world (Ewing et al., 2014). In 2012, this region accounted for two-thirds of Texas' and 14% of the nation's crude oil production, respectively ("Permian Basin Information," 2017). Additionally, the expansion of horizontal wells also lead to increased water usage. From 2005 – 2015, horizontal wells represented only a third of the unconventional wells, but they accounted for approximately two-thirds of the hydraulic fracturing water use (Scanlon et al., 2017). The national median water use for a horizontally drilled well is ~5 million gallons, which is approximately 5 times more than vertical wells in the Permian Basin. From 2013 – 2016, the water use per well went up by approximately 434% in the Permian Basin (Barclays and Columbia Water Center, 2017), with a median of 12 million gal/horizontal well stimulation (Backstrom, 2018). This increase is attributed to drilling activity, particularly for horizontal unconventional wells, and completions where the average horizontal length was increased from 5,700 to 6,800 lateral ft (Barclays and Columbia Water Center, 2017).

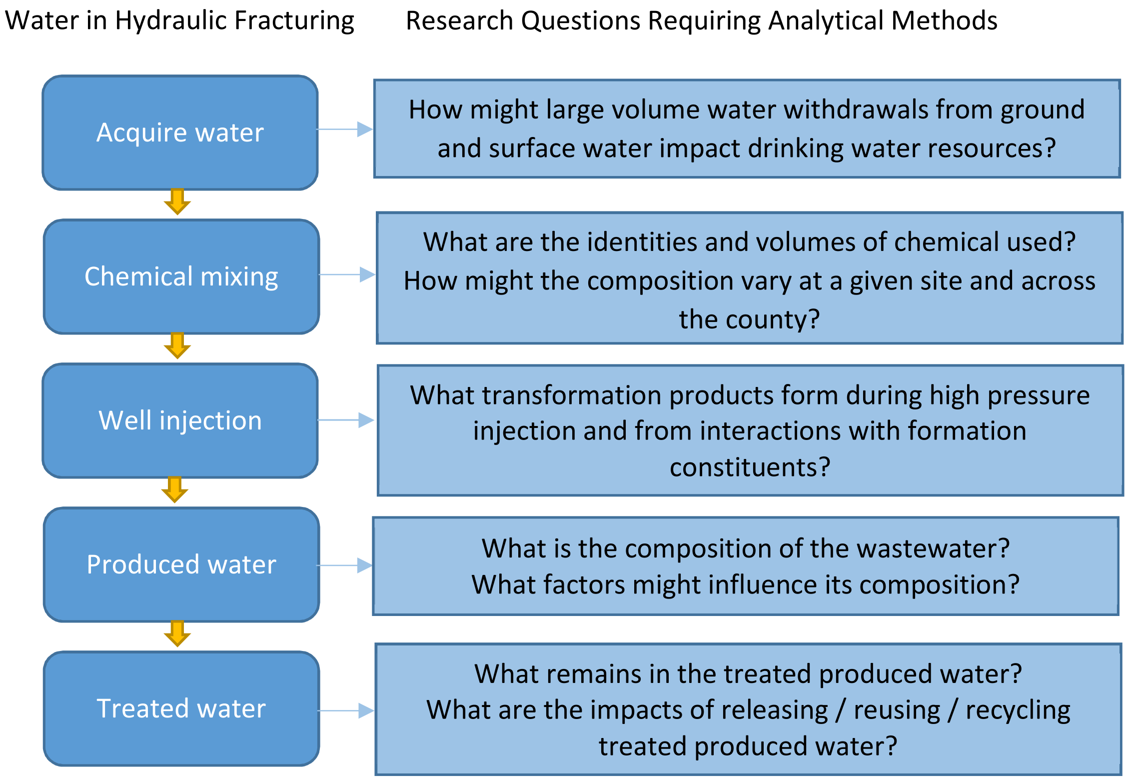
In addition to requiring large amounts of water for hydrocarbon extraction, UD wells also produce large volumes of waste. This waste stream is comprised of two distinctive sub-components, termed flowback water and produced water. Initially, flowback water is extricated during the initial two weeks of production, which is primarily comprised of production chemicals. The longer the solution remains in the formation, the more the chemical composition will resemble the geology of the formation (Liden et al., 2017). At this point, the waste stream is referred to as produced water (Veil, 2015). Since produced water is the major component of the waste stream, the two components are often collectively referred to as produced water.

Produced water is typically disposed of into the subsurface via Class II wells, rather than treating the aqueous waste and releasing it back into the water system. Class II injections wells are the most popular choice for produced water management because of convenience and cost. This is best illustrated by the fact that 98% of the 21.2 billion bbl (58 million bbl/day) of produced water from oilfield activities generated in 2012 was disposed of via Class II Injection wells (Arthur et al., 2008; Clark and Veil, 2009; Igunnu and Chen, 2014). These wells are used to inject "non-hazardous" fluids associated with oil and gas production for disposal, hydrocarbon storage wells, or enhanced recovery (U.S. Environmental Protection Agency, 2016a). Enhanced oil recovery accounted for 58% of overall disposal, which is beneficial to oil and gas production with respect to yield. However, this waste stream is primarily from conventional wells cycled back into conventional wells (Scanlon et al., 2017). The remaining 40% is disposed of through subsurface injection via saltwater disposal wells (SWD) into non-oil producing geological intervals located primarily in Texas, California, Oklahoma, and Kansas (Arthur et al., 2008; Clark and Veil, 2009).

Despite the economic benefits, the increase in UD across the American shale energy landscape has been not without concern and controversy. In addition to the potential for groundwater (Darrah et al., 2014; Fontenot et al., 2013; Hildenbrand et al., 2016b, 2016a, 2015), surface water (Drollette et al., 2015; Lauer et al., 2016), and air quality contamination (Harriss et al., 2015; Hildenbrand et al., 2016b; Payne et al., 2017), there are also trepidations about the induction of seismic activity when managing the waste from UD (Wang et al., 2014). For example, it has been determined that there is a direct correlation between the number of earthquakes and the volume of produced water being injected into disposal wells (Elst et al., 2016; Hornbach et al., 2016, 2015). Factors that influence the occurrence of induced seismic events include variations in geology (e.g., existence of faults, pore pressures, capacity of the geologic formation, and rock type), and the volume of water injected into the SWD well (Gallegos et al., 2015). It is believed that induced seismic events are caused by increased fluid pressures on already stressed faults, triggering preexisting faults to slip (Walsh and Zoback, 2015). In 2008, the first confirmed UD-related earthquake was measured in the Bend Arch-Fort Worth Basin in northern Texas. Since then, earthquakes have been increasing in frequency and magnitude with the largest being M4.0 in 2015 (Hornbach et al., 2016). The same trend was found in Oklahoma, where regulators called for a 40% reduction in the volume of salt water being injected into seismic-active areas (Jula, 2016). The dramatic reduction in disposal volumes was in response to the 900 anthropologically-induced earthquakes in 2015 that were of a magnitude of 3.0 or greater, as compared to the average of 1.2 seismic events annually before 2009. As such, the greatest challenge for SWDs is now keeping up with the disposal demands in high production regions, while monitoring and modulating injections rates. Moving forward, it is expected that the disposal option will be subject to growing constraints due to the concerns regarding earthquakes increasing the need for treatment options that allow for reuse of produced water (Parker et al., 2014).

With respect to environmental stewardship and greater sustainability within the UD shale basins, further innovation is required to reduce localized groundwater usage and waste disposal volumes. In order to accomplish this, efficient and cost-effective treatment modalities are vital to facilitating the reuse of produced water for production well stimulation. (Hildenbrand et al., 2018). However, this is not without significant challenge. A study performed by Khan *et al*. suggested that produced water from oil-bearing shale may be one of the most complex aqueous mixtures identified to date (Khan et al., 2016). These fluids contain a complex mixture of inorganic and organic compounds used as additives (Camarillo et al., 2016; Elsner and Hoelzer, 2016;

Hildenbrand et al., 2015), as well as compounds extracted from the shale itself including salts, metals, oil and gas compounds, and natural organic matter, and naturally occurring radioactive material (NORM) (Abualfaraj et al., 2014; Chapman and Palisch, 2014; Engle and Rowan, 2014). Understanding the complete composition of these complex fluid mixtures is essential to evaluating the efficacy of additives, the effectiveness of different water treatment technologies, as well as the impacts of exposure due to leaks and spills (Luek and Gonsior, 2017) (Figure 1). Unfortunately, due to the limited information that is currently available, there are knowledge gaps related to exposure, hazard data, and analytical methods (Mueller, 2017). The lack of information and standardized methods has left unanswered questions (Ferrer and Thurman, 2015; Luek and Gonsior, 2017; Mueller, 2017; Rogers et al., 2015). For example, what are the most pertinent constituents of concern? How do we comprehensively test for these constituents? What chemical reaction byproducts are formed under subsurface conditions and how can they vary over the lifetime of UD wells? How to identify and evaluate potential exposure.



How might large volume water withdrawals from ground and surface water impact drinking water resources?

What are the identities and volumes of chemical used? How might the composition vary at a given site and across the county?

What transformation products form during high pressure injection and from interactions with formation constituents?

What is the composition of the wastewater? What factors might influence its composition?

What remains in the treated produced water? What are the impacts of releasing / reusing / recycling treated produced water?

Figure 1. Pertinent research questions held about the various stages if water procurement and waste management in UD.

Further to this point, the Energy Policy Acts of 2005 left reporting requirements for chemical additives used during production well stimulation up to the individual states (Konschnik and Dayalu, 2016). As of 2016, only 28 states had required companies to disclose the chemicals being used during UD, but the content of submission and methods of these disclosures still varies from state to state. Currently, Fracfocus.org contains the most comprehensive dataset on chemicals used in hydraulic fracturing; however, relatively little information is known about the additives used by production companies due to protected intellectual property and trade secrets. The protection of proprietary knowledge encourages innovation; however, it creates challenges in terms of determining the exposure safety, the efficacy of treatment modalities, or the transformation products in produced water. In addition to the aspect of proprietary knowledge, concerns can also arise from issues with nomenclature as many compounds generally have multiple names and/or incorrect CAS numbers during reporting (FracFocus, 2017). Currently, there are approximately 2,500 different additives that could be found in wastewater from UD, which does not account for chemicals from the formation or transformation byproducts (Danforth, 2018). Of the known compounds, less than 20% have standard analytical methods or toxicity data.

This chapter will address analytical methods that are required to comprehensively characterize produced water. The discussion will incorporate known contaminants found in produced water. These include chemical additives that are used during the stimulation process, such as alcohols used for surfactants, corrosion inhibitors, scale inhibitors, and biocides, as well as aliphatic and aromatic hydrocarbons (i.e., benzene, toluene, ethylbenzene and xylenes (BTEX), and bacterial species that can reduce the permeability of production strata, residual oil and gas, and produce H_2S. Pertinent metals and minerals also need to be characterized. In addition, the chapter will touch on the outstanding concerns that currently remain unaddressed.

2.3 Analysis of Produced Water

The complex physiochemical nature of produced water makes it challenging to treat. Additionally, the composition can change over the lifetime of the well which amplifies the challenges of treatment. (Fakhru'l-Razi et al., 2009). The chemical profile and quantity of produced water varies for each shale play, well location, and depth, as well as the age of the reservoir and type of hydrocarbon produced (Ground Water Protection Council and All Consulting, 2009; Igunnu and Chen, 2014; Shih et al., 2016). When characterizing produced water, there are five primary categories to evaluate: basic water quality metrics and bulk measurements, organics, biological, inorganics, and naturally occurring radioactive materials (NORM). Currently, there are not approved regulatory metrics for the management of produced water, and standardized analytical procedures specifically for characterizing produced water are not well established. Nonetheless, as interest continues to expand in this important field of research, so too have the applicable techniques.

2.3.1 Bulk Measurements and Basic Water Quality Parameters

Bulk measurements do not allow for determination of chemicals or ions present; however, they are quick measurements that provide significant insight into the general state of the produced water matrix. These basic parameters can be used for process control with more detailed analyses being subsequently performed if any notable fluctuations are observed. Typically, bulk measurements are more cost- and time-effective than advanced analytical techniques. The most informative bulk measurements with respect to the analysis of produced water include alkalinity, the relative abundance of dissolved (TDS) and suspended (TSS) solids, total organic carbon (TOC), and total nitrogen (TN).

Alkalinity is considered the buffering capacity of a solution or the ability to resist pH changes (Davis and Masten, 2014). In natural waters, it encompasses any weak bases such as hydrogen sulfate or hydrogen and dihydrogen phosphate, but the primary components are carbonate and hydrogen carbonate (bicarbonate). Produced waters generally have elevated levels of alkalinity largely due to the contribution of carbonate, which can induce scaling while also potentially affecting fluid stability and pH (Wasylishen and Fulton, 2012). Methods used to monitor alkalinity levels include titrations and colorimetric testing such as Environmental Protection Agency (EPA) methods 310.1 and 310.2, respectively (National Water Quality Monitoring Council, 2017; U.S. Environmental Protection Agency, 2017a). EPA method 310.1 is preferable for the quantification of alkalinity in produced water, which uses titration with an endpoint of pH 4.5 and determination being performed electrometrically thereby eliminating interferences. On the contrary, colorimetric analysis using methyl orange, as called for by EPA method 310.2, can be problematic with produced water. Residual hydrocarbons, turbidity from solids, as well as discoloration from biological contaminants, can leave produced water with a yellow hue that absorbs in the same range as methyl orange.

Solids, which also impacts a solution's clarity and influences water quality, can be broken into groups based on the size of the particle. Large particles, which are typically greater than 1 μM, are classified as total suspended solids (TSS). These particles are representative of formation sands and clays, proppants, corrosion by-products, and precipitate crystals. Fine, solid particles may stabilize an emulsion if they are of correct size and abundance (Nalco Chemical Company, 1988) leading to increased turbidity or cloudiness of the solution. Constituents that contribute to turbidity are generally less than 1 μM in size and can be present in the form of dissolved solids, colloids, and bacteria (Hildenbrand et al., 2018). Dissolved inorganic compounds or minerals are introduced into UD wastewater through contact with the formation or through the addition of clay stabilizers. The total dissolved solids (TDS) is primarily composed of charged particles, referred to as cations and anions. The salinity or concentration of inorganics can vary considerably across a given region. For example, produced water from the Barnett Shale has been found to have TDS levels ranging from 500-200,000 ppm (0.5-20%), whereas produced water from the Marcellus Shale formation varies from 10,000 to 300,000 ppm (1-30%) (Ground Water Protection Council and All Consulting, 2009). For the most accurate measurements of TSS and TDS, glass fiber, binder-free filters with a nominal pore size of 1.5 µm are used to separate particles, and then, the weights of recovered materials are measured gravimetrically. Filter paper needs to be rinsed and dried before analysis, and a post wash of the filter paper is also required after separation is complete. Currently, the methods approved by the EPA Clean Water Act for analysis of solids residue from domestic and industrial wastewater are Standard Method (SM) 2540 (A-F), ASTM International (ASTM) D5907-13 and USGS methods I-3750-85, I-1750-85, I-3765-85, and I-3753-85 (Figure 2) (U.S. Environmental Protection Agency, 2017a). While gravimetric analysis is preferred for solids, concentrations of TDS can be estimated by measuring the salinity or conductivity with probes, but this will not include dissolved constituents that do not have an electrical charge, such as neutral organics. As with TDS, TSS can be estimated from turbidity (Williamson and Crawford, 2011). Turbidity methods determine the amount of cloudiness in solution based on the transmission and scattering of light (The Editors of Encyclopedia Britannica, 2017) As a beam of light is passed through a turbid sample, the intensity is reduced by the scattering of light, which will depend on the concentrations and sizes of the particles in solution. Current analytical methods approved by the EPA's Clean Water Act to measure turbidity are EPA 180.1 Rev. 2.0, SM 2130 B-2011, ASTM D1889-00, and USGS I-3860-85 shown in Figure 2.

Total organic carbon (TOC) and total nitrogen (TN) can also be classified as bulk measurements. TOC is an analytical technique that quantifies the concentration of organic molecules in solution. It provides a direct expression of total organic carbon, in contrast to biological oxygen demand (BOD) or chemical oxygen demand (COD) methods, which are only proxy measurements for organic content, and TOC is a more convenient measurement to perform. (ASTM International, 2017a; Standard Methods Committee, 2011). To measure TOC, first, the carbon is oxidized to form carbon dioxide, which is then measured (U.S. Environmental Protection Agency, 2004). TOC can be classified into dissolved organic carbon (DOC) and suspended organic carbon, as well as purgable and nonpurgable organic carbon. The distinction between DOC and suspended organics is defined by the ability to separate the organic component from solution using a 0.45 μm filter. DOC will remain in solution while the suspended organic carbon will be removed from the solution. Purgeable organic carbon, also referred to as volatile organic carbon, pertains to the fraction of TOC removed from an aqueous solution by gas stripping, whereas nonpurgeable organic carbon is the fraction of TOC, which remains in solution following gas stripping.

TN is a method that converts all nitrogen compounds, including nitrates, nitrites, ammonia, and organic nitrogen to NO, which is reacted with ozone to form excited NO_2 (ASTM International, 2016). As the NO_2 relaxes, it emits radiation that is measured photo-electrically. ASTM D8083 allows for the simultaneous analysis of TN for a sample if TOC is measured using ASTM D7573 (Figure 2). While TOC and TN measurements do not provide the same level of specific information as other methods, they still provide valuable insight about water quality. They can be used to determine if mass balance has been achieved, based on singular or combined results using more specific and advanced analytical techniques.

Basic water quality measurements, such as pH, conductivity, oxidation-reduction potential (ORP), and temperature, are also useful when beginning to characterize oilfield waste streams. For example, pH values can help evaluate the equilibrium state between bicarbonate scaling (elevated pH) compared to the potential of producing corrosive CO_2 (low pH). ORP values not only provide insight into the balance between metals and anions but can also help judge the possible microbial content of the solution (Hildenbrand et al., 2018; Suslow, 2004). A higher reduction potential (more positive) is observed with species in solution that preferentially gain electrons. Conversely, species with a lower (more negative) reduction potential tend to lose electrons. From a microbial perspective, when cell membranes succumb to reduction by other species in solution, the integrity of the cell membrane is destroyed, leading to death. Collectively, these measurements are quick and can be performed *in situ* using a multimeric probe. Lastly, multimeric probes can also be used to collect multiple measurements simultaneously, including those that measure TDS, TSS, and turbidity.

2.3.2 Organic

Organics constituents found in produced water can be categorized into three forms based on solubility: insoluble, dispersed, and dissolved (Kajitvichyanukul et al., 2011). Insoluble organics or nonpolar hydrocarbons are the easiest to separate from produced water (Igunnu and Chen, 2014; National Energy Technology Laboratory, n.d.). These are the primary target for recovery of oil and gas operations. As the polarity of the molecules in solution increases, the organics are more soluble making them challenging to separate using conventional means such as gravity separation (Liden et al., 2017). These compounds represent dispersed and dissolved organics and are the most environmentally dangerous forms (Kajitvichyanukul et al., 2011). Diverse sample preparation and analytical techniques, including gas chromatography (GC) and liquid chromatography (LC), are required to identify and quantify individual organic compounds among the complex mixture of additives, oil and gas compounds, natural organic material, and transformation products (Ferrer and Thurman, 2015; Luek and Gonsior, 2017).

Higher TOC levels are indicative of increased organic content in water samples and will therefore, yield increased total GC and LC peak areas. However, mass balance between TOC and combined LC and GC techniques has been problematic for produced water. Several studied have worked to identify analytical methods, which are appropriate for quantifying organic compounds in produced water originating from diverse geological environments and industrial operations. However, as of yet, there lacks comprehensive knowledge of all organic compounds and constituents within these fluids. For example, produced water from the Permian Basin was evaluated, and only just more than 300 of the 1,400 chemicals separated and detected were identified (Luek and Gonsior, 2017). Understanding these complex fluid mixtures is essential for understanding fluid treatment options and efficiencies for reuse in future UD, as well as exposure threats for the natural environment and humans.

To date, more than 200 oil and gas wastewaters have been analyzed, whereby GC has been the preferred analytical tool (Luek and Gonsior, 2017). According to one survey, 54% of studies reported identifying organics were based solely on the use of GC, while another 34% used LC only. 32% of the studies analyzed samples using both LC and GC for a more comprehensive characterization (Luek and Gonsior, 2017).

Analyses using GC generally target volatile and semi-volatile organic compounds (VOC and SVOC) with the most frequently analyzed being BTEX, acetate, and acetone. VOCs such as methanol and ethanol can be analyzed using headspace gas chromatography (HS-GC), thereby reducing the required sample preparation. Alcohols, which are used as solvents, surfactants, and corrosion inhibitors, are the dominant additives used in stimulation fluid (Elsner and Hoelzer, 2016; Konschnik and Dayalu, 2016; Luek and Gonsior, 2017). Overall, the four most frequently reported compounds used in production wells were methanol, isoparaffin, hydrochloric acid, and ethylene glycol (Konschnik and Dayalu, 2016). Alkylated phenols, commonly used as surfactants, have been analyzed using GCMS, following a DCM or ethyl acetate extraction (Orem et al., 2014;

Thacker et al., 2015). Other routinely used surfactants in hydraulic fracturing, ethoxylated compounds, have been analyzed using LC tandem-MS (MS/MS), following solid phase extraction (SPE) (Cluff et al., 2014; Thurman et al., 2014). A recent analysis of produced water from the Cline Shale region revealed residual levels of surfactants, such as 2-butoxyethanol, which was analyzed in a targeted approach using GC-MS combined with an ethyl acetate extraction (Thacker et al., 2015). In the same study, N-alkyl-N,N-dimethylamine was identified using SPE and LC-MS/MS.

Hydrocarbons are the second most common additive reported by production companies which is frequently used as a solvent (Konschnik and Dayalu, 2016). The determination of total petroleum hydrocarbon (TPH) can also be regarded as a bulk measurement (Carlton Jr. et al., 2017); however, it can provide more information than some of the other aforementioned bulk measurements. For example, TPH analyzed with EPA Method 1664B, as indicated in Figure 2 , can be used to determine the concentration of hydrocarbon species present in produced water; these will have originated either through their intentioned addition to fluid pumped down-hole or from the formation, which the fluid contacted (Elsner and Hoelzer, 2016).

Polyethylene glycols (PEG) and polypropylene glycols (PPG) have been identified in produced water using LC-MS by some researchers (Heyob et al., 2017; Thurman et al., 2017). The nonionic composition of the aforementioned surfactants functions as weatherizers, emulsifiers, corrosion inhibitors, and wetting agents. Benzothiazole and other heterocyclic compounds have also been identified in wastewater from gas production using LC-MS (Orem et al., 2014).

One of the greatest challenges is a lack of standardized methods. With the continued expansion in UD, methods need to be developed for this type of wastewater (Oetjen et al., 2017). While standard methods for evaluating domestic and industrial wastewater have been used to analyze produced water, they have not been verified to perform as expected in produced water matrices, which can be up to four times saltier than seawater. To date, the greatest opportunity for the elucidation of unidentified compounds in produced water is non-targeted analysis using LC (Luek and Gonsior, 2017).

2.3.3 Biological

So far, not much attention has been given to the microbial quality of produced water, particularly after treatment. Even so, recent studies have shown the levels of bacteria in produced water can vary with the shale and overall conditions used during hydraulic fracturing (Mouser et al., 2016). A diverse array of bacteria, including those within the taxa *γ-proteobacteria*, *α-proteobacteria*, *δ-proteobacteria*, *Clostridia*, *Synergistetes*, *Thermotogae*, *Spirochetes*, *Bacteroidetes*, and *Archae* have all been found in untreated flowback water samples (Murali Mohan et al., 2013b). Care must be taken to determine the types and levels of microorganisms present when evaluating the potential risk to human health and the reusability of this wastewater. Depending on the application, different standards and recommendation values for microbial levels are applicable (Table 1).

As shown in Table 1, currently, there are no standards with respect to acceptable levels of bacteria in the water used in hydraulic fracturing. However, it is known that the control of sulfate-reducing bacteria (SRB), iron-oxidizing bacteria (IOB), and acid-producing bacteria (APB) is of paramount importance. These microorganisms have previously been found in produced water (Cluff et al., 2014; Hildenbrand et al., 2018; Murali Mohan et al., 2013a; Struchtemeyer and Elshahed, 2012) and are known to form biofilms and produce acid that will lead to product "souring" and degradation. They can also cause corrosion of well casings, which can potentially lead to casing failure and unwanted connections between operational/waste fluids with the environment. Furthermore, some of the additives used in hydraulic fracturing provide a food source for bacteria that facilitates their proliferation (Daly et al., 2016). Therefore, the removal of microorganisms needs to be ensured since, if not well treated, the reuse of produced water can lead to their re-growth, and ultimately a negative impact on production-well performance, or other intended uses of the fluid.

Table 1. Standards and maximum levels (colony-forming units (cfu)/100 mL) of microorganisms allowed in water according to its intended use (Office of Science and Technology et al., 2012; U.S. Environmental Protection Agency, 2017b, 2017c).

	Desired Water Application				
Bacteria (cfu/100 mL)	Drinking water	Agriculture	Recreation	Industry	Hydraulic fracturing
Total Coliforms	0	-	-	-	-
Fecal Coliforms	0	<10	-	-	-
E. coli	0	-	126	-	-
Enterococci	-	-	35	-	-
Heterotrophic plate count	<500	-	-	-	-
Legionella	0	-	-	-	-

Different methods can be used to detect and quantify bacteria (National Research Council, 1999); however, the most common ones used in industry are plate methods where the sample is plated in different agar media and colonies are allowed to grow overnight. Identification is based on a colorimetric scheme and quantification of the number of colonies per sample volume used. Additionally, the colonies can be further isolated and characterized by microscopy, Gram staining, and biochemical tests. These methods are good for the identification of coliforms and heterotrophic bacteria. As it is known, only 1% of the microorganisms that occur in nature are able to grow under artificial conditions (Palková, 2004). Due to this reason, molecular methods have been developed to aid bacterial identification. The identification of unculturable and slow-growing microorganisms is possible, as their cultivation is not necessary and identification can be achieved in a more timely manner.

Molecular methods include immunological and nucleic acid-based techniques. Immunological methods rely on the use of antibodies, which specifically bind to bacterial antigens. An example is the enzyme-linked immunosorbent assay (ELISA), which uses a chromogenic reaction to detect the presence of a certain microorganism. In spite of its high-throughput capacity, this method does not provide good specificity since it requires the presence of large amounts of antigen and is unable to indicate the viability of the organisms (Peruski and Peruski, 2003).

Nucleic acid-based techniques, such as polymerase chain reaction (PCR), DNA/RNA sequencing, and others, can provide for high-throughput identification with a high degree of specificity. These methods use genetic sequences that are unique to each microorganism, usually conserved genes (housekeeping genes), for their identification. PCR amplifies the DNA or RNA and therefore allows for the detection of small amounts of genetic material. Nevertheless, this technique only works for microorganisms whose sequence is already known and is not ideal for the identification of unknown species. On the other hand, DNA/RNA sequencing provides for the identification of unknown microorganisms (Emerson et al., 2008). While viable and useful, these methods are expensive, and they do not provide any information on the metabolic state of the microorganism.

Recently, matrix-assisted laser desorption/ionization – time-of-flight – mass spectrometry (MALDI-TOF-MS) has been applied for the identification and differentiation of microorganisms based on their protein profile (Havlicek et al., 2013; Jo Jr., 2001). This technique not only provides identification, but it also delivers insight into the metabolic states of the detected cells. Beyond the initial capital cost, which is not trivial, subsequent analyses are cheaper and faster than nucleic acid techniques. Due to its detection limit and to ensure purity, the culturing of bacteria before analysis is required, and therefore, the appropriate culture media needs to be chosen. Preferably, broad-spectrum media should be used for the isolation of major bacterial groups. Of course, only culturable microorganisms can be analyzed by this technique, and this is certainly a drawback. However, the need for culturing is a common step for other conventional identification methods, as described before, and this step also ensures that only viable (i.e., live) organisms in the sample are identified.

Subsequent innovations should be emphasized for the sake of using MALDI-TOF-MS for the identification of unculturable bacteria and bacteria from environmental settings. Commercial databases used to support MALDI-TOF-MS identification of bacteria are clinically biased, given the desire to identify organisms associated with human infections. Despite this shortcoming, the applicability of this technique has also been demonstrated in the environmental field (Santos et al., 2016). Previous works show that MALDI-TOF-MS is a good option for bacterial identification and can be used as a tool to study environmental microbiomes (Martin et al., 2017; Santos et al., 2018). Identifications made by MALDI-TOF-MS were confirmed by 16S RNA biochemical sequencing methods. More recently, this method was used to characterize the microbiome of produced water and determine the efficiency of a wastewater treatment facility (Hildenbrand et al., 2018a). A number of unique organophilic bacteria, such as *Pseudomonas*, *Paracoccus*, *Aeromonas*, and *Bacillus*, were identified. Importantly these bacteria exhibited resilience to traditional disinfection modalities.

2.3.4 Inorganic

The primary purpose of monitoring inorganic constituents in produced water is to preserve the life of equipment in the field and to maintain stable stimulation fluids. Conductivity provides a relative idea of the concentrations of dissolved solids in solution, but TDS measured using gravimetric analysis provides more accurate values of dissolved inorganic constituents. Sodium and chloride are the predominant ions in produced water, but, other cations and anions are of greater interest. For examples, barium, calcium, magnesium, and strontium are generally the largest contributors to problematic scale formation (Hu et al., 2016), which in itself can have devastating financial implications for any production well operator. Elevated levels of boron, iron, titanium, and zirconium can lead to over crosslinking, reduced gel viscosity, altered temperature stability, and inefficient proppant dispersion (Hildenbrand et al., 2018; Wasylishen and Fulton, 2012) . Anions such as sulfate and carbonate can also be found in produced water, which readily interacts with multivalent cations to form scale (Zielinski and Otton, 1999). Of these inorganic constituents, iron, magnesium, and calcium are the most pertinent given their affinity to interact with carbonate and sulfate minerals (Zielinski and Otton, 1999). Calcium is also a major contributor to hypersaline produced waters, in addition to boron, magnesium, iron, lithium, potassium, and manganese. Metals that have been detected in produced waters from the Permian Basin region include barium, beryllium, boron, calcium, cadmium, copper, iron, potassium, lithium, magnesium, manganese, and selenium (Khan et al., 2016).

Metals or cations can be measured individually or as a group. Methods that focus on individual elements, such as EPA 130.1 and ASTM D1126, which is used to evaluate the hardness of water, traditionally prescribe the use titrations or spectrophotometric methods (ASTM International, 2017b; U.S. Environmental Protection Agency, 1971). Hardness, the potential to form scale, can be caused by any number of polyvalent cations; however, those other than calcium and magnesium are seldom present in more than trace amounts in produced water. Individual metal ions can also be evaluated using flame atomic absorption (FAA) or graphite furnace atomic absorption (GFAA) (Thermo-Fisher Scientific, 2017) using methods such as ASTM D1971 (ASTM International, 2017a). The Clean Water Act (CWA) approves various EPA methods for the analysis of metals (Figure 2), such as Method 265.2 or 267.2, in domestic and industrial wastewater; in spite of that, there are only a handful of the metals approved using GFAA and FAA which do not include calcium, iron, or magnesium.

Inductively coupled plasma – optical emission spectroscopy (ICP-OES), also referred to as inductively coupled plasma – atomic emission spectroscopy (ICP-AES), allows scientists to confirm multiple elements at one time. These are prescribed for use in standard methods SM 3120B, EPA 200.7, and ASTM D1976. ICP – mass spectrometry (ICP-MS) is also a technique that enables the simultaneous determination of multiple elements in a single analysis from a sample. ICP-MS is generally more sensitive than ICP-OES, and it can provide detection down to parts-per-trillion (ppt) concentration levels in a sample. Methods, such as EPA 200.8, SM 3125, ASTM 5673, and USGS I-4020-05 prescribe the use of ICP-MS (U.S. Environmental Protection Agency, 2017a). Minimal sample preparation is required for these ICP-based elemental determination techniques, apart from filtration and/or dilution of the sample, and the addition of acids, prior to analysis (Ferrer and Thurman, 2015). The high temperature of an ICP torch alleviates many interferences, which can hamper other techniques like GFAA and FAA.

For the analysis of pertinent anions in produced water (i.e., chloride, bromide, fluoride, nitrate, sulfate, and sulfide), ion chromatography is the preferred analytical technique (Ferrer and Thurman, 2015). Several standard methods for the analysis of anions have been established for domestic and industrial waste, including SM 4110, EPA 300.0 and 300.1, as well as ASTM D4327 (ASTM International, 2017c; Standard Methods Committee, 2000; U.S. Environmental Protection Agency, 2017a). Samples can potentially require drastic dilution due to the high concentrations of anions, particularly chloride; otherwise, there is an increased risk for inaccurate results. In one study, the PW samples from the Niobrara shale formation were diluted 30 times to bring the chloride concentration below 500 mg/L in order to accurately determine the anion concentrations (Coday et al., 2015). Therefore, when using IC to analyze PW with TDS levels up to 300,000 ppm and chloride accounting for 50% of the ions samples should be diluted 300 times.

2.3.5 Naturally-Occurring Radioactive Material (NORM)

Oilfield waters that are particularly rich in chloride enhance the solubility of other elements, including naturally-occurring radioactive material (NORM) (Zielinski and Otton, 1999). The health concerns associated with radioactive material being brought up to the surface with produced water were first realized in the 1980s when unacceptable radiation levels were detected by scrap metal dealers (Zielinski and Otton, 1999). The most abundant NORM constituents in produced water are radium isotopes, ^{226}Ra and ^{228}Ra. However, shale and sandstone formations can also contain uranium, thallium, and thorium (Guerra et al., 2011; U.S. Environmental Protection Agency, 2016b; Zielinski and Otton, 1999). Radium accumulates on oilfield equipment through co-precipitation with scale deposits, which coat equipment (Akob et al., 2015; Guerra et al., 2011; Igunnu and Chen, 2014). The mineral barite ($BaSO_4$) is the most likely host of radium in the subsurface formation (Zielinski and Otton, 1999). Environments which host sulfate-reducing bacteria, such as produced water, increase the solubility of barium sulfate, which can potentially liberate the radium, which was previously encapsulated (Akob et al., 2015). The half-lives of the two principal radioactive isotopes in the produced water, ^{226}Ra and ^{228}Ra, are 1,600 and 5.75 years, respectively. Approximately 10 half-lives are needed for the radioactivity to decay to reach negligible quantities (Rowan et al., 2011). When radium is brought to the surface, prolonged exposure becomes the primary concern due to the long half-lives of these species.

Rapid and robust methods to evaluate levels of NORM and thus the associated safety of personally handling that produced water are critical (Zhang et al., 2015). ^{226}Ra primarily emits alpha particles, which can be measured directly (Zhang et al., 2015). Conversely, ^{228}Ra levels are determined indirectly by measuring the beta-decay process of ^{228}Ac which is a product of ^{228}Ra (Johnson, 1971; U.S Environmental Protection Agency, 2014). However, long counting times (24–48 h) are required for traditional methods, thereby limiting sample throughput (Rowan et al., 2011). As indicated in Figure 2, there are currently three standard methods for evaluating radioactive material in domestic and industrial wastewater (EPA Method 900.0, 903.0, and 903.1) (U.S. Environmental Protection Agency, 2017a). Using the techniques described in these methods, alpha- and beta-particles can be identified using alpha spectrometry or liquid scintillation counting (LSC), respectively, to quantify emission rates. Gamma spectrometry is used to quantify the emission rates of γ rays; however, the EPA only approves method 901.1 for the analysis of drinking water, and not other water-based samples (U.S. Environmental Protection Agency, 1980). One study successful used ICP-MS for the rapid detection of ^{226}Ra. The result of which were compared to those obtained using gamma spectroscopy (Zhang et al., 2015). The study indicated that rapid ^{226}Ra analysis using ICP-MS is not only feasible but is also incredibly robust with recoveries near 100% from produced water samples.

2.4 Conclusion

Understanding the biogeochemical composition of produced water can provide valuable insight into environmental and human exposure concerns, especially in the event of spills, leaks, and other contamination events. This information can also help verify the efficacy of treatment technologies applied to clean produced water, a relatively new operational paradigm shift that will lead to a reduction in groundwater usage and disposal volumes. Currently, there are no approved methods for the analysis of produced water, so scientists have primarily used methods approved for the analysis of domestic and industrial wastewater, or they have developed their own. As such, verifying the accuracy of these methods for produced water, especially where high salinity levels can potentially lead to analytical interferences, is of paramount importance. Moreover, the development of new, standardized, and robust methods with proper validation is necessary. Additionally, future research should encompass multiple analytical techniques, including GC, LC, and ICP, to provide a compressive characterization of produced water.

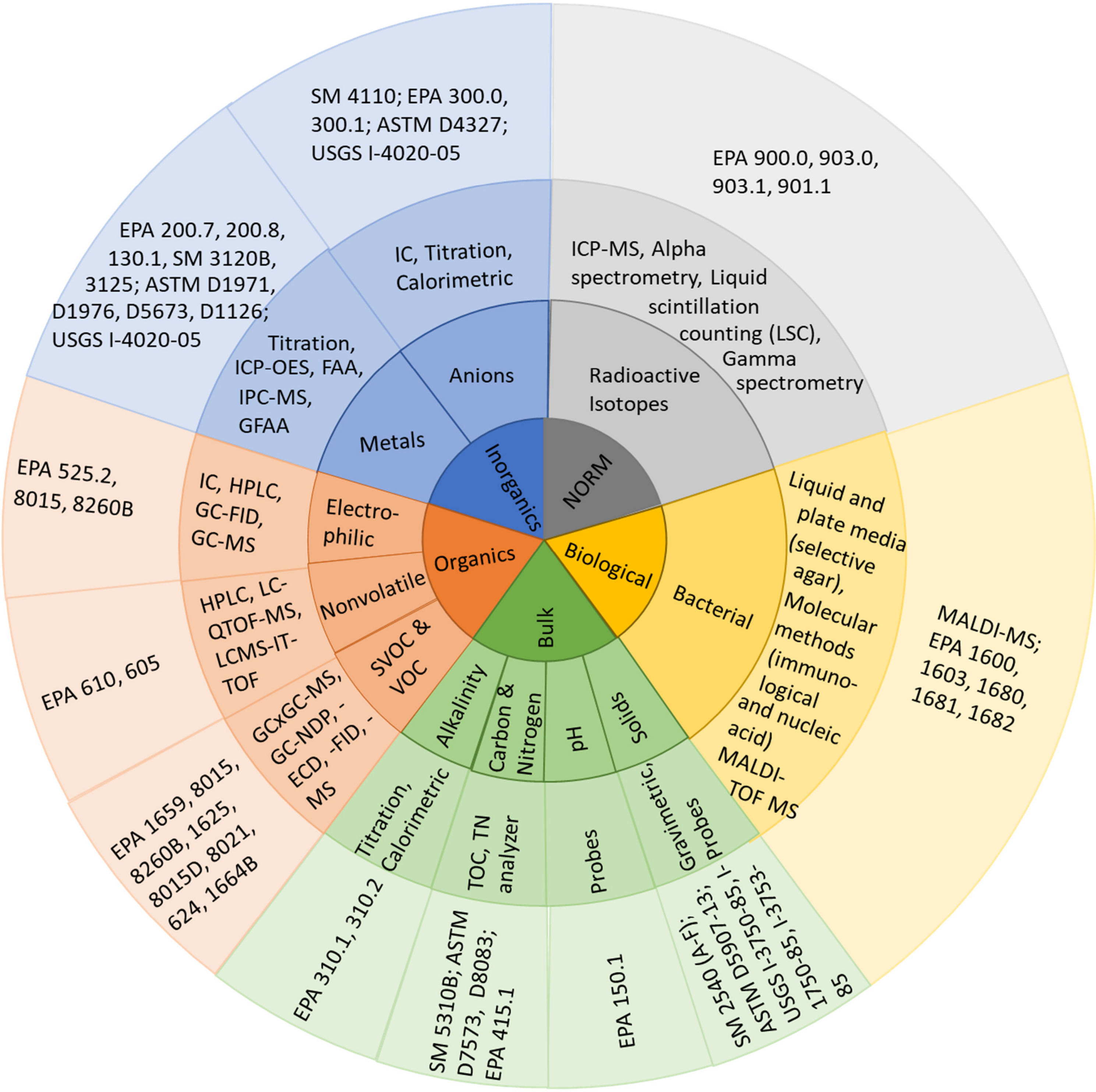


Figure 2. Schematic of various analytical methods and tools that can be utilized to comprehensively characterize produced water (Ferrer and Thurman, 2015; Hildenbrand et al., 2018; Jo Jr., 2001; Luek and Gonsior, 2017; Oetjen et al., 2017; U.S. Environmental Protection Agency, 2017a).

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CHAPTER THREE

CHARACTERIZING VARIOUS PRODUCED WATER FROM SHALE ENERGY EXTRACTION WITHIN THE PARAMETERS OF RESUE

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Characterizing Various Produced Waters from Shale Energy Extraction within the Context of Reuse

Tiffany Liden[1], Zacariah L. Hildenbrand[2,3*], Kevin A. Schug[1,2*]

AUTHOR INFORMATION:

1. Department of Chemistry and Biochemistry, The University of Texas at Arlington, 700 Planetarium Place, Arlington, TX 76019, USA
2. Affiliate of Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, USA
3. Inform Environmental, LLC, 6060 N. Central Expressway, Suite 500, Dallas, TX 75206

Correspondence should be addressed to: 6060 N. Central Expressway Suite 500, Dallas, TX 75206, USA. Tel.: +1 214 800 2829; e-mail address: zac@informenv.com; and 700 Planetarium Pl.; Box 19065; Arlington, TX 76019-0065, USA. Tel.: +1 817 272 3541; Fax: +1 817 272 3808; e-mail address: kschug@uta.edu

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3.1 Abstract

Oil and gas operations have become an increasingly controversial topic since the turn of the century when unconventional oil and gas development rapidly expanded. Environmental concerns are frequently centered on elevated water usage and, more recently, the induction of seismic events during waste disposal. Reuse of produced water for subsequent production well stimulation can effectively address these concerns, but the variability among such samples must be well understood. As such, 24 samples of wastewater from unconventional oil and gas development were collected from south and west Texas to characterize their variability and to assess the feasibility for direct reuse without treatment. Bulk metrics were collected, including total organic carbon, total nitrogen, as well as total dissolved and suspended solids. Profiles of pertinent inorganic constituents were also evaluated for each of the samples. Variations were not only seen in the between region but among samples collected from the same region. For example, the average total organic carbon for Eagle Ford samples collected was 700 ± 500 mg/L while samples collected from the Permian Basin 600 ± 900 mg/L. The high standard deviation for the Permian Basin total organic carbon was indicative of the variability of samples with values of 1,032 mg/L, 889 mg/L, 38 mg/L, 46 mg/L, 51 mg/L, 147 mg/L, 73 mg/L, and 2,600 mg/L. The total dissolved solids levels had the same variability between regions with an average value for Eagle Ford was 20,000 ± 10,000 mg/L, and the Permian Basin value was 150,000 ± 40,000 mg/L. However, samples were more reproducible within a given region. Collectively, the data indicate that the direct reuse of raw produced water for subsequent production well development without treatment is not feasible based on reported reuse thresholds. Unconventional development wastewater samples from the Permian Basin were also compared to produced water values from conventional oil and gas wells in the same region, as reported by the USGS. Ion concentrations for

samples collected in the Permian Basin consistently fell toward the lower end of the spectrum when compared to conventional produced water data.

3.2 Introduction

Unconventional oil and gas development (UD) provides the fossil fuel necessary to meet a majority of the ever-growing energy needs in the United States (Kim et al., 2016; Mobilia and Comstock, 2017; U.S. Energy Information Administration, 2017). This highly articulated process requires large amounts of water to extract oil and natural gas from formations previously considered to be uneconomical (Liden et al., 2017). Upon stimulation by hydraulic fracturing (HF), the primary byproduct of UD is a waste stream comprised of flowback (FB) and produced water (PW). The FB is predominantly stimulation fluid returning to the surface that contains some dissolved minerals, as well as additives used to optimize the HF process. FB is a minor component of the wastewater, and its return to the surface lasts for 1-2 weeks once production begins. In contrast, the production of PW, the major component of the waste stream, continues over the lifetime of the well. It is brought to the surface comingled with the commodity and contains increased levels of dissolved minerals, as well as formation water, when applicable.

In 2011, 4.9 billion gallons of water was used to stimulate unconventional wells in Texas, which accounted for less than 1% of the state's water usage (Ground Water Protection Council and All Consulting, 2009; Shaffer et al., 2013). Overall, the volume of water used is low compared to other anthropogenic activities (i.e., agriculture and farming), but UD frequently occurs in arid and semiarid regions (Nicot et al., 2014). Moreover, high water usage can negatively impact a local region through the development of water depletion cones. Actual water usage data can be challenging to obtain since companies are not required to report their water usage in some regions. However, during HF, it is estimated that 5 million gallons of water are used on average for a horizontal well completion (Mantell, 2011). The largest expansion in water usage for HF has taken place in the Permian Basin (PB). Located in Texas and New Mexico, the PB is currently considered to be the most prolific energy basin in the world (Ewing et al., 2014; Liden et al., 2017). From 2005-2015, horizontal wells represented only a third of the unconventional wells in the region, but they accounted for approximately two-thirds of the HF water used (Scanlon et al., 2017). Backstrom et al. discovered that the PB exceed the national average with a median of 12 million gal per well for stimulation (Backstrom, 2018). Interestingly, from 2013-2016, the water use per well went up by approximately 434% in the PB of west Texas (Barclays and Columbia Water Center, 2017). The increase is attributed to expanded drilling activity and completions, where the average horizontal length had increased from 5,700 to 6,800 lateral ft, with lateral stretches reaching up to and even greater than 10,000 ft (Liden et al., 2017).

Another concern associated with UD, particularly with respect to the production and disposal of PW, is the link to increased seismicity. Currently, 98% of PW is disposed of through the use of enhanced oil recovery wells and salt water disposal (SWD) wells (Arthur et al., 2008; Clark and Veil, 2009; Liden et al., 2017). Enhanced oil recovery is typically used for conventional development, whereas SWD is the preferred disposal option for UD because of economics and convenience (Railroad Commission of Texas, 2017). However, the volume of PW injected into SWD wells has been shown to have a direct correlation to the number and magnitude of seismic events (Elst et al., 2016; Gallegos et al., 2015; Hornbach et al., 2016, 2015; Magnani et al., 2017; Wang et al., 2014). A recent example can be seen in Oklahoma, where the number of earthquakes increased after 2009 from an average of 1.2 events/year to 25 annually (Jula, 2016). It is expected that this disposal option will continue to be subject to growing constraints and scrutiny due to these induced events (Parker et al., 2014).

To mitigate the concerns associated with high water usage and induced seismic events, there is a growing need to reuse or recycle PW. The ability to reuse PW is largely dependent on the concentration of inorganic constituents (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018; Thacker et al., 2015). In this study, 24 PW samples were collected from the south and west Texas regions to compare inorganic matrices and total organic content, to ultimately characterize the different PW samples and determine the feasibility of their direct reuse for production well stimulation. To date, there has been limited data regarding the composition of PW from UD, in part, due to the challenges to access it. Therefore, PB samples were also compared to USGS PW data from the PB region from conventional oil and gas development, to determine if past samples could potentially be a predictor of the relative composition of the PW from UD.

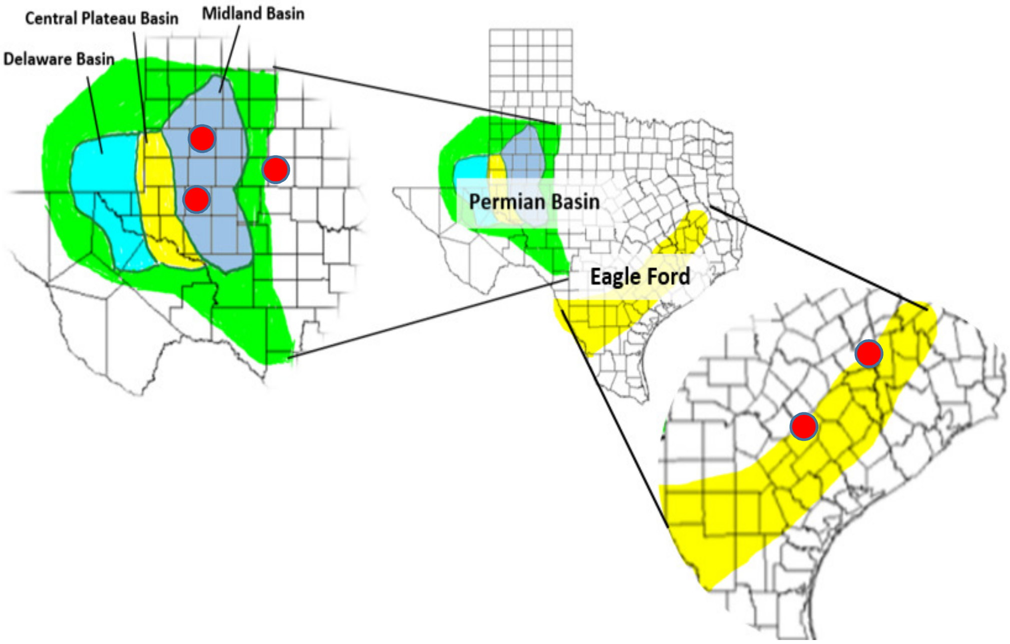


Figure 1. Sampling locations for the produced water samples in this study. Nine were collected from the Permian Basin: One considered FB from Nolan County TX, one from a SWD well in Dawson County TX, and seven from a SWD in Midland County TX. 15 samples were collected from the Eagle Ford Shale: 13 from a PW treatment center in Bebe TX and two from EF Production wells in Brazos County TX.

3.3 Methods and Materials

3.3.1 Samples

Nine of the samples used were collected from the PB in west Texas (Figure 1). One sample (PB FB), classified as FB because of its age and chemical composition,(Thacker et al., 2015) were collected from an unconventional oil exploration on-site waste pit approximately one week after well completion. Eight samples collectively referred to as PB SWD, were collected from saltwater disposal site (SWD) located in the PB: seven from a site in Midland County and one from a site in Dawson County. The PW from Midland County was a composite mixture, delivered to this specific SWD site by six pipelines, as well as trucks purported to be from production sites up to 50 miles away. The PW collected in Dawson County was also from a community SWD well similar to the Midland site, except that all of the PW was delivered to the site by truck. It is important to note that the PB samples could potentially be a mixture from multiple conventional and unconventional oil and gas wells. However, the SWD operator declared that the wastewater was from UD. The remaining sample set, EF Treatment, included 13 samples of PW from a treatment facility located in Eagle Ford Shale in Bebe TX (Hildenbrand et al., 2018). Two samples, EF Wells, were from production wells located in Brazos County and were collected before separating the PW from the oil.

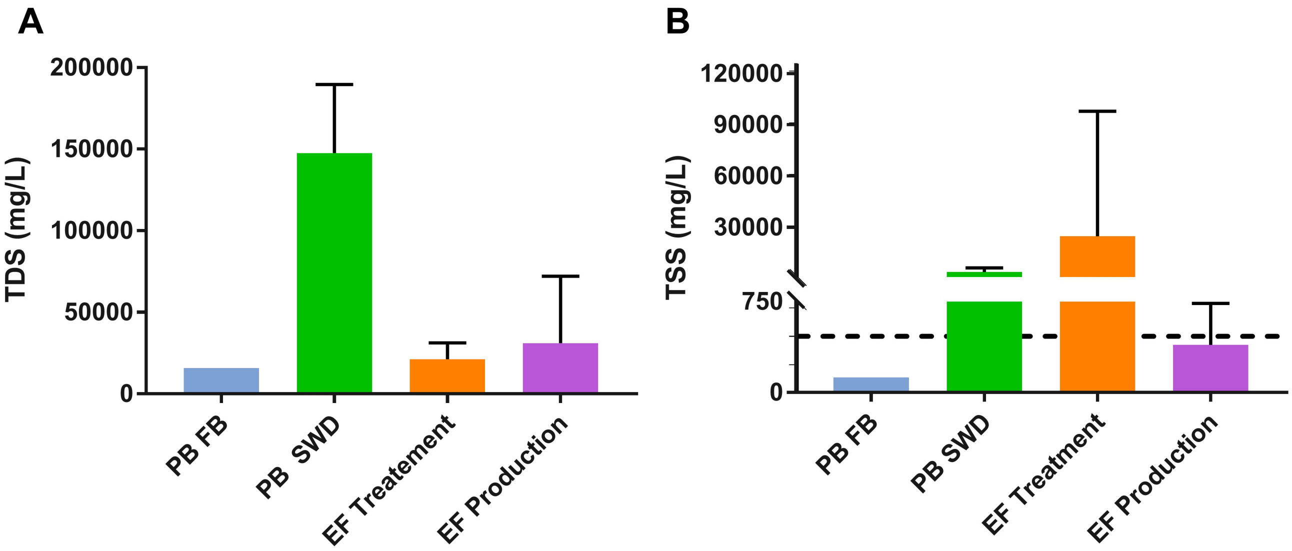
3.3.2 Compositional Analyses

Total suspended and dissolved solids were quantified using gravimetric analysis. PW samples were filtered using Ahlstrom 1 µm Glass Microfiber Paper (Leominster MA) that were dried overnight at 90 °C. Metal analysis was completed using Shimadzu’s ICPE-9000 (Columbia MD) based on Environmental Protection Agency (EPA) method 200.7 to determine the concentration. Standard solutions for the metals were from High-Purity Standards (North Charleston SC). Ion chromatography (IC) and titration were used to quantify pertinent anions, as per EPA methods 300 and 310.1. Total organic carbon (TOC) concentrations were determined using Shimadzu's TOC-L, as described previously (Hildenbrand et al., 2016, 2015; Thacker et al., 2015).

3.4 Results and Discussion

3.4.1 Bulk Measurements and Basic Parameters

The measurement of total dissolved solids (TDS) corresponds to the number of dissolved particles in solution; typically, these are metals and anions. Values can range from freshwater levels (<1,000 mg/L) through saline (15,000 – 30,000 mg/L) to brine (>300,000 mg/L); (Otton and Mercier, n.d.) however, values are relatively inconsequential with respect to reuse for production well stimulation. Notably, samples collected from the PB SWD ranged from 10-12% salinity, 2.0-3.5 times higher than seawater, with an average TDS value of 150,000 ± 40,000 mg/L. The samples collected from the EF region ranged from 2-5% salinity, which is roughly equivalent to seawater (SI Table 1). Similarly, total suspended solids (TSS) is a simple bulk measurement that can provide significant insight into the nature of the particulates in solution. Typically, components such as oil droplets, formation sands, and proppants that are greater than 1 μm in size, contribute to the measurement of TSS. Ideally, TSS should be less than 500 mg/L for reuse (King, 2011; Liden et al., 2018). Figure 2B indicates that TSS levels exceeded the reuse limit for both the PB SWD set and the EF treatment samples. For the EF treatment samples, the average was skewed due to one sample reaching 220,000 mg/L (SI Table1). The remaining 12 samples were near or below accepted reuse levels ranging from 50 mg/L to 780 mg/L. On the other hand, the TSS levels for the PB SWD samples were typically higher than the EF treatment samples; values ranged from 300 to 6,100 mg/L.



lines represent recommended water quality guidelines for the reuse of PW for production well stimulation, as made by Hildenbrand, King, Oetjen, and Liden et al. (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018; Oetjen et al., 2018).

A viable alkalinity threshold (carbonate + bicarbonate) to determine whether or not PW is suitable for reuse is considered to be 300 mg/L (Hildenbrand et al., 2018; Liden et al., 2018; Oetjen et al., 2018). Alkalinity not only influences the pH due to its buffering capacity, but it also contributes to scaling, which is a primary concern with respect to PW reuse (Wasylishen and Fulton, 2012). Scale formation is problematic because it can have devastating financial implications throughout the lifecycle of production (Liden et al., 2018). Figure 3A shows alkalinity was only 26 mg/L for the PB FB but ranged from 74 to 840 mg/L for the PB SWD samples. The samples from the EF Treatment facility had a similar range from 170 to 910 mg/L for 11 of the 13 samples with the remaining 2 reaching as high as 2,200 and 4,000 mg/L, respectively.

The pH was within an acceptable range for reuse (6-8) for all of the collected samples (Figure 2B). Defined maximum reuse levels for TOC have not been published as far as the authors are aware. However, anecdotal feedback from the PB SWD operator indicated that TOC values above 20 mg/L were unfavorable when considering potential reuse for production well stimulation. All average values of each of the PW sample sets exceeded this threshold. The average TOC value was highest for samples from the EF production wells (Figure 2C). However, given the significant variability with one sample having a TOC value of 20,000 mg/L and the other 380 mg/L (Table SI 1), the average value does not provide the most representative insight. Samples collected from the EF treatment center ranged from 240 to 1,500 mg/L (SI Table 1). The eight PB SWD samples ranged from 38-2,600 mg/L (SI Table 1).

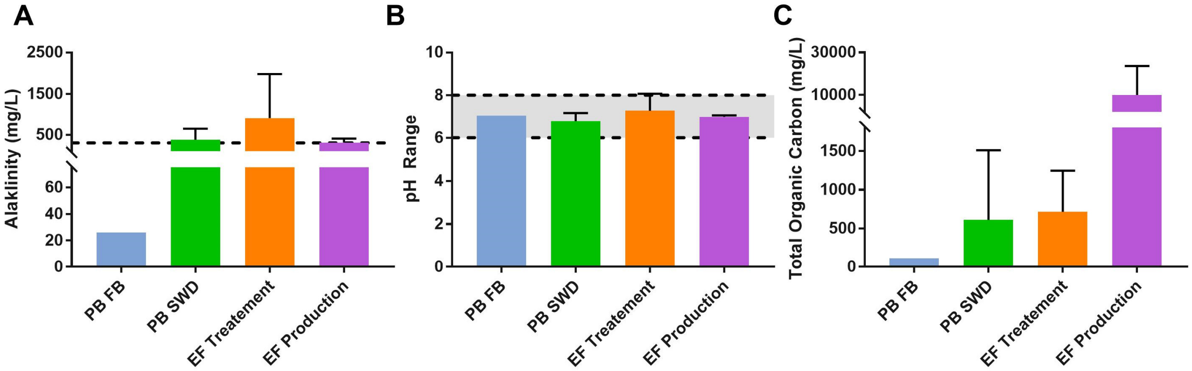


Figure 3. The analysis of (A) alkalinity, (B) pH, and (C) TOC in the various PW samples. Data is presented as mean values with the error bars representing one standard deviation. The dashed lines represent recommended levels for the reuse of PW for production well stimulation made by Hildenbrand, King, Oetjen, and Liden et al. (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018; Oetjen et al., 2018).

3.4.2 Metals

The salinity of PW is a result of dissolved ions, primarily sodium and chloride (Fakhru'l-Razi et al., 2009). To a lesser extent, other cations, and anions influence the salinity, such as calcium, magnesium, sulfate, and those that influence the alkalinity of the solution. Ions that contribute to scaling are the most pertinent metals to determine with respect to PW reuse for production well stimulation, followed by those that affect crosslinker efficiency, and lastly, ions, which are of lesser consequence, that only influence the TDS levels.

Scaling concerns are dominated by multivalent cations (Liden et al., 2018) where barium, calcium, magnesium, and strontium are at the forefront of this issue. Barium from the formation can result in the precipitation of barium sulfate scale (Hu et al., 2016). As the pressure and temperature decreases when the PW is brought to the surface, the solu.bility of barium sulfate decreases as well, leading to the scale formation (Moghadasi et al., 2006) As such, an acceptable level for reuse is 20 mg/L of barium (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018), shown in figure 4A. Sample sets from the EF region exceeded the threshold with averages of 35 mg/L and 48 mg/L for the EF treatment and EF production well samples, respectively. In contrast, the PB SWD sample set had a mean value of 16 mg/L. Barium is not a simulation additive as far as the authors are aware. Therefore, it not surprising that was not detected in the PB FB samples, which is expected to be predominately composed of stimulation fluid. Calcium and magnesium both have a suggested limit of 2,000 mg/L (Hildenbrand et al., 2018; Liden et al., 2018; Oetjen et al., 2018). All but one of the samples collected from the PB SWD exceeded the recommended reuse level for calcium, represented in Figure 4B, ranging from 1,600 mg/L to 3,000 mg/L with an average value of 2,600 mg/L; however, all of the other samples fell below the threshold. All of the average values for each sample set fell below the prerequisite limit for magnesium (Figure 4C). Strontium behaves similarly to barium in the presence of sulfate and under similar conditions; however, strontium sulfate is slightly more soluble (Moghadasi et al., 2006). Samples from the EF treatment facility and EF production wells exhibited similar strontium concentrations, as expected, with averages of 140 mg/L and 150 mg/L, respectively (Figure 4D). Conversely, the samples from the PB SWD site, with an average value of 440 mg/L, contained three times the concentration of strontium compared to the EF samples. Silica monitored as silicon, can also lead to scaling concerns when detected. While there is not a limit set for silicon, highly saline environments, such as PW, can enhance scale formation by silica (Lunevich, 2015). In regions such as west Texas, where silica can cause up to 80% of scale formation (Moghadasi et al., 2006), silica is a major concern. Interestingly, silicon levels for the EF sample sets had higher average values than the PB SWD samples (16 mg/L), with average values of 48 and 35 mg/L, respectively (Figure 4F).

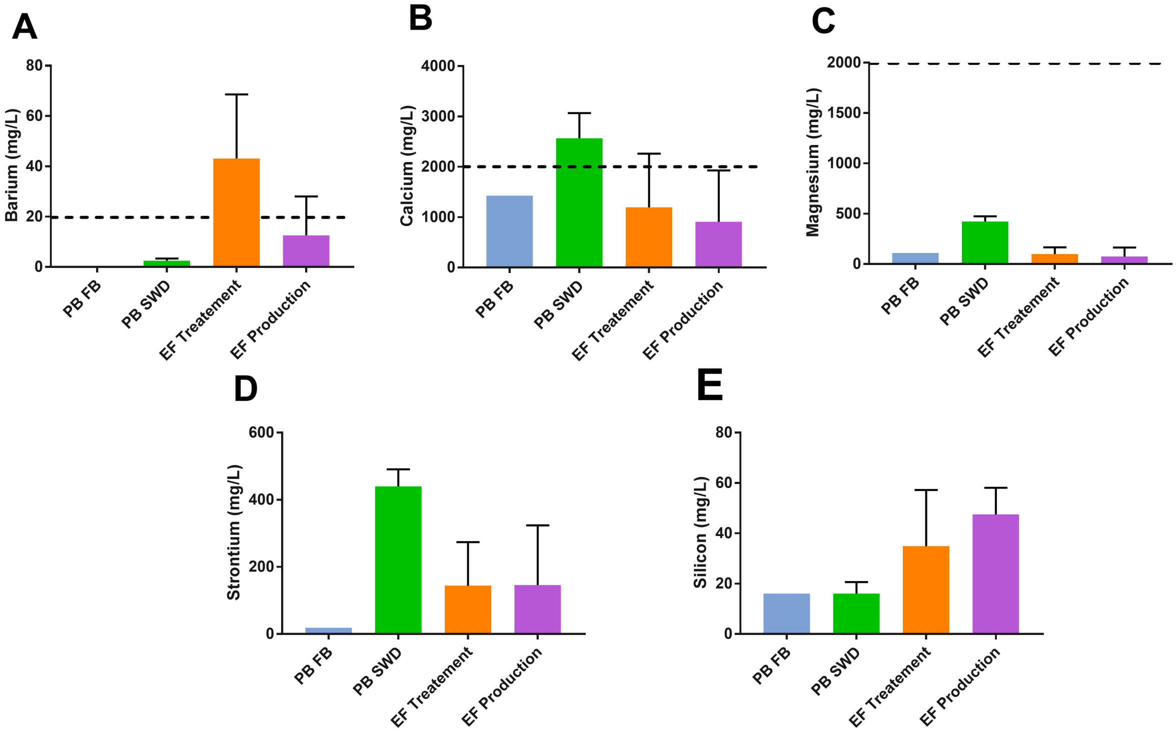


Figure 4. Scaling contributors for each PW sample sets, including Permian Basin flowback, Permian Basin SWD, EF treatment facility, and EF production wells are represented in the graphs. Data is presented as mean values for (A) barium, (B) calcium, (C) magnesium, (D) strontium, and (E) silicon with the error bars representing one standard deviation. Dotted lines mark the recommended maximum reuse limit suggested by Hildenbrand, King, Oetjen, and Liden et al. (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018; Oetjen et al., 2018).

Crosslinkers or viscosifiers are used to increase the molecular weight by crosslinking a polymer backbone, thereby extending the distance to which the proppant can be placed within the fractured formation (Montgomery, 2013). Typically, these compounds are formed from metals such as boron, titanium, or zirconium that have been conjoined with ligands (Esmaeilirad et al., 2016; Montgomery, 2013). Zirconium and titanium were not detected in any of the samples. Nonetheless, each of the three PW averages exceeded the 10 mg/L limit for boron (Figure 5A). Additionally, iron levels exceeding 10 mg/L can cause over-crosslinking and adversely affect the temperature stability of fracturing fluid (Liden et al., 2018; Oetjen et al., 2018). The average iron concentration for the EF samples from the treatment facility, represented in Figure 5B, surpassed the limit with an average value of 22 mg/L. However, these samples exhibited significant variability with values ranging from 0.5 to 68 mg/L, with 6 of the 13 samples surpassing the reuse limits (Table SI 2). Samples from the PB SWD had an average value of 3.0 mg/L; however, the collection of these samples was made after the addition of an undisclosed iron reducer.

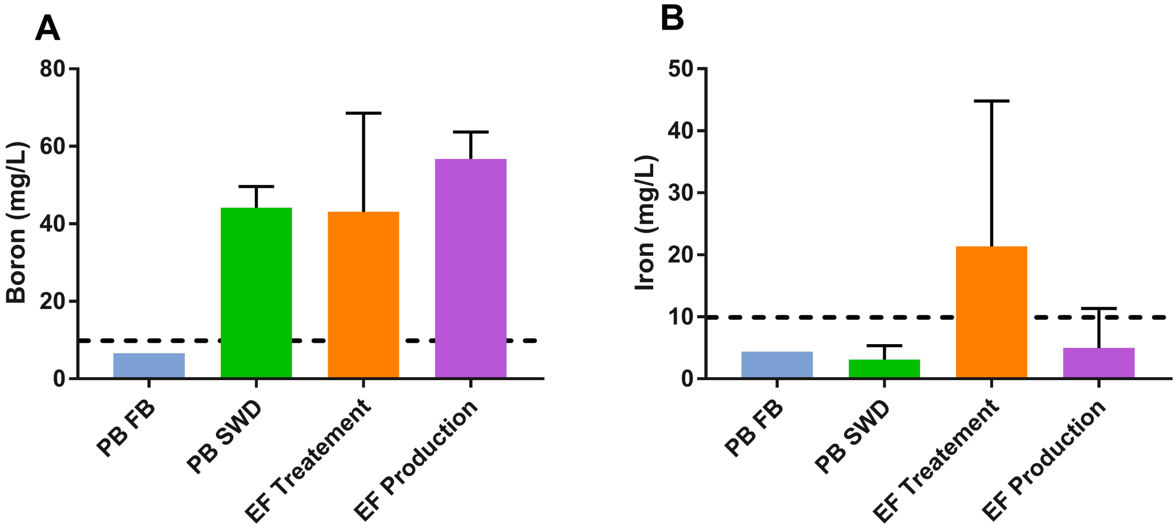


Figure 5 Boron (A) and iron (B) concentrations for the PW sample set. Data is presented as mean values with the error bars representing one standard deviation. The reuse limits recommended by Hildenbrand, King, Oetjen, and Liden et al. are represented with black dotted lines (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018; Oetjen et al., 2018).

Sodium, potassium, lithium, and manganese were also detected in all samples procured for this study. These ions affect the TDS level but have limited influence on the solution chemistry. The average concentrations of sodium (39,000 mg/L), potassium (430 mg/L), and lithium (17 mg/L) were highest for the PB SWD, which is expected due to the elevated TDS levels (Figure 6 A-C). The PB FB had elevated levels of sodium and potassium with values of 26,000 mg/L and 74 mg/L, respectively. As FB's composition is reflective of the original stimulation fluid prepared, it is suspected that sodium and potassium chloride were used as clay stabilization additives, a common practice that began the 1960s (Fink, 2015; Gulbis and Hodge, 2000; King and Durham, 2017; Liden et al., 2018; Montgomery, 2013; U.S. Environmental Protection Agency, 2004). Samples collected at the EF treatment facility had the largest standard deviation of 6.6 mg/L for lithium with a mean of 9.5 mg/L. Relatively low levels of manganese were detected in all of the sample sets with the highest concentrations being found in the PB FB sample, with a concentration near 3.0 mg/L (Figure 6D). Manganese, like iron, can potentially be an issue when PW is brought to the surface, leading to the formation of manganese oxides, which can precipitate out of solution forming scale. An added benefit of oxidized manganese, in the form of permanganate, is that it can react with hydrogen sulfide (H_2S) (Jennings and Muroski, 1964), thereby eliminating this harmful toxin. Hydrogen sulfide is a biodegradation product formed by sulfur reducing bacteria (SRB) and is the primary cause of costly product quality degradation, referred to as souring, and the biocorrosion of metal infrastructure, which can potentially lead to casing failure and environmental contamination.

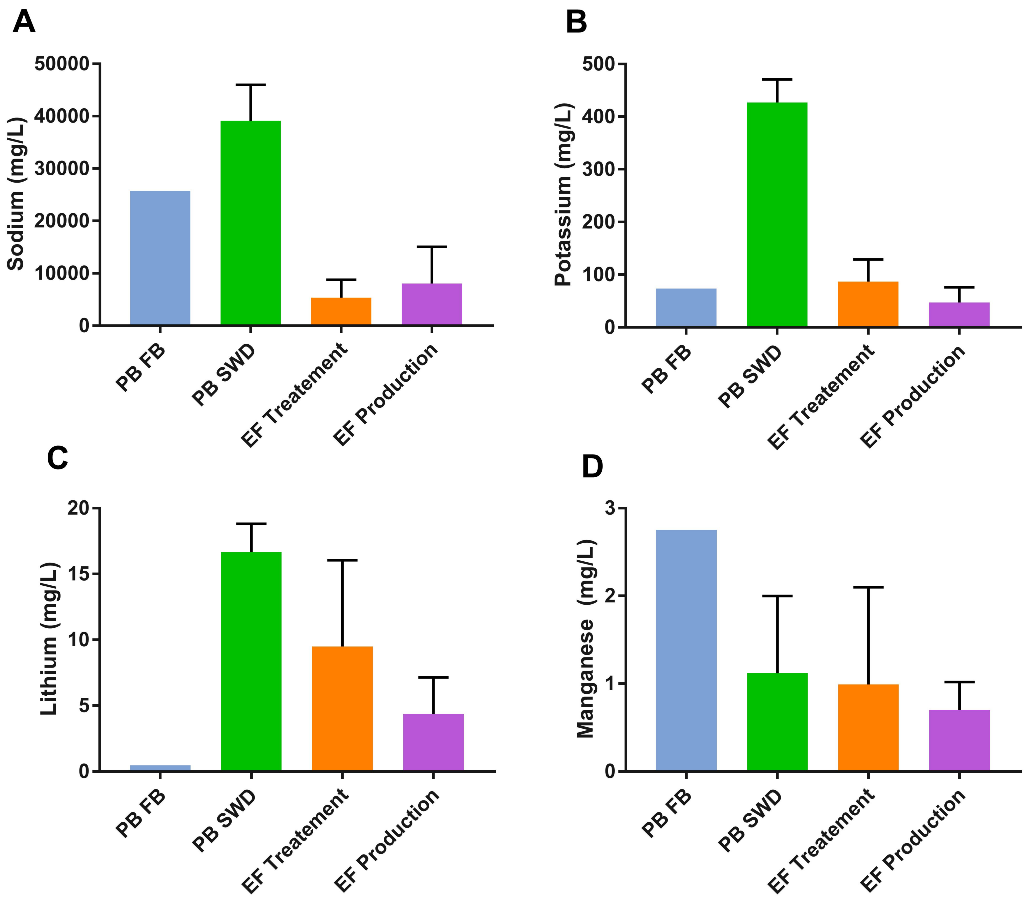
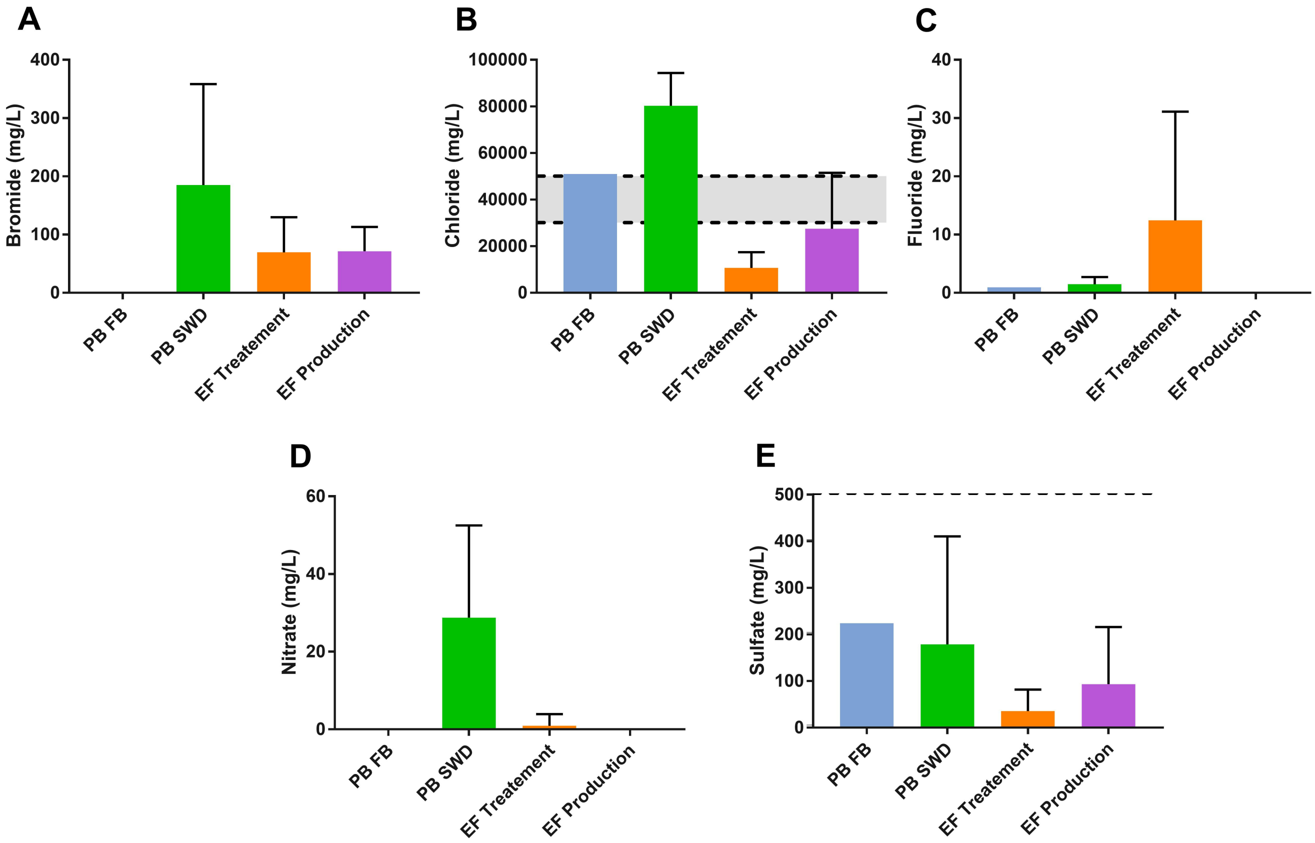


Figure 6. Metals in produced waters that primarily contribute to TDS levels. The average concentrations for (A) sodium, (B) potassium, (C) lithium, and (D) manganese are presented, along with error bars, which represent one standard deviation.

The anions bromide, chloride, fluoride, sulfate, and nitrate were also monitored with the average values illustrated in Figure 7. Chlorine and chlorine dioxide, commonly used disinfectants, are known to produce toxic disinfection by-products (DBPs) (Chang et al., 2000; Hua et al., 2006; Vashishtha et al., 2017). However, when bromide is present in solution, at concentrations as low as 0.1 mg/L, it has been shown to oxidize quickly and react with organic materials, which can lead to the formation of brominated and chlorinated DBPs. Elevated levels of bromide preferentially generate brominated DBPs (Symons et al., 1993). While bromide was not detected in the PB FB, concentration in the remaining samples exceeded the minimum levels for the formation of DBP.

Average values of 190 mg/L, 70 mg/L, and 72 mg/L were measured for PB SWD, EF treatment, and EF production sample sets, respectively (Figure 7A). Elevated levels of bromide are potentially problematic since toxicological studies suggest that brominated DBP are more carcinogenic compared to their chlorinated counterparts. The ideal range for chloride is 30,000-50,000 mg/L for slickwater fracturing fluids (King, 2011), which both PB sample sets surpassed; however, the PB FB only slightly exceeded this range by 1,000 mg/L (51,000 mg/L) (SI Table 3). This fact, plus the increased levels of sodium and potassium, alludes to the possibility that sodium and potassium chloride are commonly used clay stabilizers (Fink, 2015; Gulbis and Hodge, 2000; King and Durham, 2017; Liden et al., 2018; Montgomery, 2013; U.S. Environmental Protection Agency, 2004), which were added to the fracturing fluid. Fluoride concentrations, which are an important metric regarding the formation of exotic scales like CaF_2, were the highest for samples from the EF treatment facility and ranged from <0.034 to 28.9 mg/L. All other sample sets exhibited average values below 12 mg/L (Figure 7C). Nitrate levels were the highest in the PB SWD samples, with an average value of 46 mg/L. As for the solution chemistry, nitrate is not problematic for reuse; however, it is a nutrient for bacteria, the widespread proliferation of which can result in the formation of problematic biofilms, among other problems. All of the average values were below the reuse limit of 500 mg/L for sulfate (Liden et al., 2018; Oetjen et al., 2018). A value of 220 mg/l was measured for the PB FB sample, followed by the PB SWD, EF Production, and EF treatment sample sets with values recorded at 180 mg/L, 93 mg/L, and 36 mg/L, respectively. Elevated levels of sulfate can inhibit the effectiveness of crosslinkers, which maintain viscosity in fracturing fluids (Esmaeilirad et al., 2016). Additionally, elevated sulfate levels can induce reactions with barium, strontium, and iron in the formation water of a production well, which can result in the precipitation of $BaSO_4$ and $SrSO_4$ scales (Hu et al., 2016). Lastly, sulfate can provide a substrate for SRBs that produce H_2S, and this can ultimately lead to the deterioration of hydrocarbon products and production infrastructure (Murali Mohan et al., 2013).



chloride, (C) fluoride, (D) nitrate, and (E) sulfate. The reuse limits recommended by Hildenbrand, King, Oetjen, and Liden et al. are represented by black dotted lines. The error bars represent one standard deviation (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018; Oetjen et al., 2018).

3.4.3 Permian Basin Salt Water Disposal Samples Compared to National Values

As previously mentioned, relativity few PW samples from UD have been analyzed compared to those from conventional development, in part due to difficulties in obtaining samples and to protect proprietary information. Therefore, an analysis was performed to compare PB SWD samples from UD to PW data from conventional oil and gas development reported by the USGS

(Blondes et al., 2017). The principle behind the comparison was to determine if past samples could potentially be a predictor of the relative concentration of the PW of UD.

A relatively linear trend was seen when comparing sodium and chloride ions found in sub-terrain water sources (Figure 8). Both sodium and chloride from PB SWD samples fell in line with

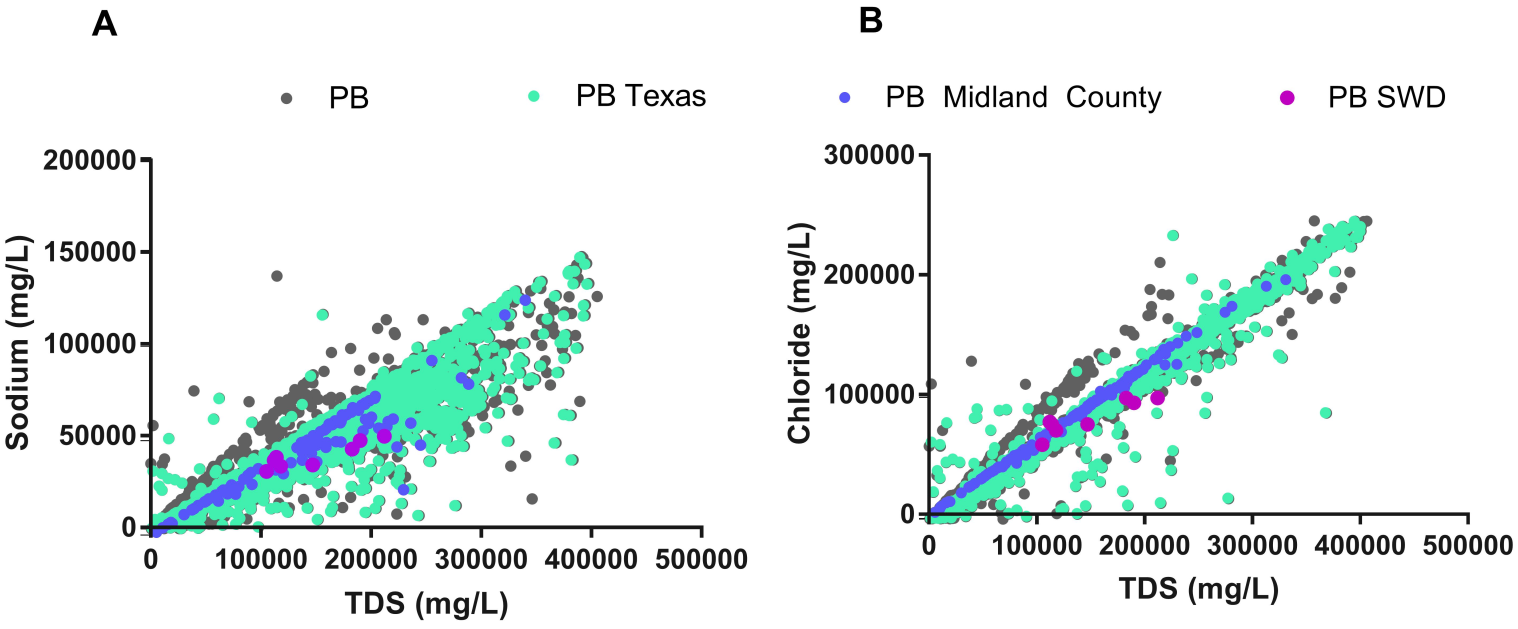


Figure 8. Correlation of (A) sodium and (B) chloride concentrations with TDS levels, plotted from conventional well PW data reported by the USGS for the PB (grey), Texas-based PB wells (cyan), production wells located in Midland county (purple), as well as the values measured for PW from UD labeled PB SWD (magenta). The USGS's data set for the Permian Basin data included 16,000 samples from conventional oil and gas operations (Blondes et al., 2017).

The TDS levels detected in the PW samples collected from PB SWD were: 183,000; 212,000; 190,000; 147,000; 118,000; 112,000; 105,000; and 114,000 mg/L. This sample set was in the same range as other PB PW data gathered from the same county, which had an average concentration of 140,000 ± 60,000mg/L (Figure 9).

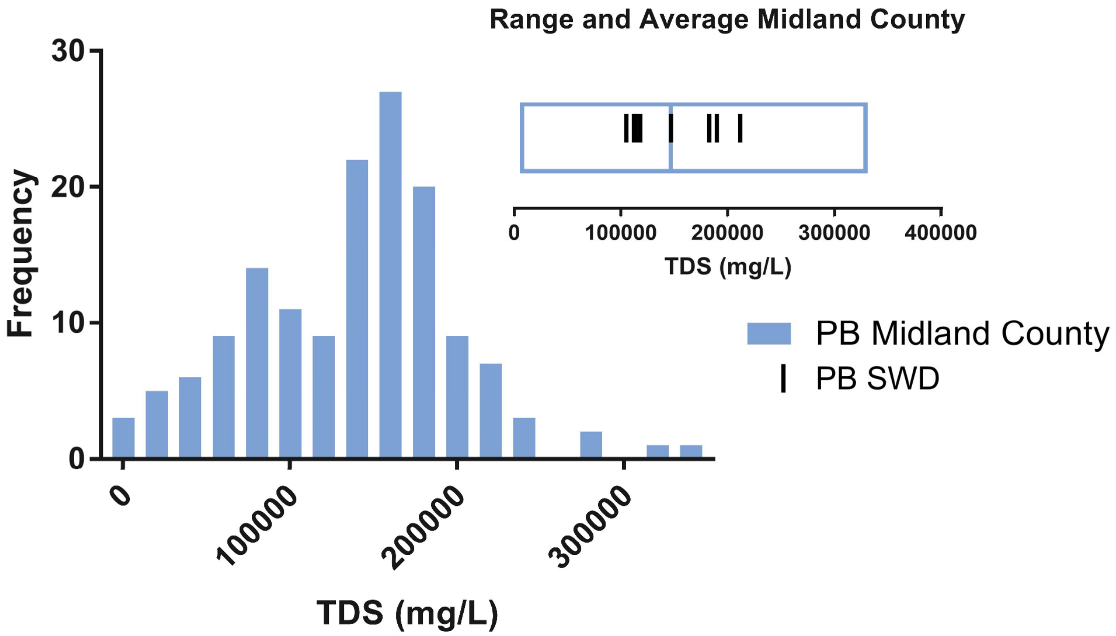


Figure 9. Histogram of TDS concentrations from PB data reported by the USGS for wells located in Midland County (Blondes et al., 2017). The data illustrate the concentrations stated for conventional wells. The graph inset in the top right corner represents the conventional waste range and the average of 149 Midland County PW data points. The black lines denote individual TDS values from the PB SWD sample set.

The most pertinent inorganic constituents, calcium, and magnesium, are problematic, due to their propensities to interact with carbonate and sulfate minerals (Zielinski and Otton, 1999). Such interactions can be influenced by changes in temperature, pressure, pH, and salinity as the water is brought to the surface and processed. The PB SWD magnesium levels were relatively low, even though calcium levels exceeded reuse limits. Despite what appeared to be elevated calcium concentrations, the values observed in the PB SWD samples fell below the mean of the reported Midland County values from conventional development (Blondes et al., 2017). This is represented in Figure SI 10.

Alkalinity and sulfate values observed in the PB SWD samples fell on the lower end of the PB spectrum reported by the USGS. The USGS PB dataset exhibited average values of 320 mg/L and 810 mg/L for alkalinity and sulfate, respectively. Alkalinity values for the PB SWD sample set were measured to be 162, 426, 204, 73.7, 841, 208, 622, and 515 mg/L ($p=0.0048$). Sulfate in the samples were 49.4, 33.1, 83.2, 77.1, 2.22, 416, 113, and 656 mg/L ($p=0.0658$) (Table SI 3 and Figure SI 2).

3.5 Conclusions

It is inevitable that unconventional oil and gas practices will continue to grow to meet the growing energy demands of this nation (U.S. Department of Energy, 2015). There is an increasing need to facilitate the reuse and recycling of PW, to mitigate the concerns related to induced seismic events and water usage. In this study, PB PW samples from UD were found to be comparable to the conventional PW samples. However, in general, PB PW samples from UD had ion concentrations measured to be on the lower end of the spectrum for conventional PW samples. PW samples from two highly prolific shale basins in Texas regularly surpassed at least one of the reuse thresholds, indicating direct reuse of raw PW is not appropriate without some degree of treatment. More specifically, elevated levels of boron, calcium, and TSS could preclude raw PW from the PB region from being reused directly; whereas elevated levels of alkalinity, barium, boron, iron, and TSS would restrict the potential reuse of raw PW in the EF region. As has been observed in previous studies (Hildenbrand et al., 2018), the use of a single treatment modality is not sufficient when attempting to repurpose produced water, which is an inherently complex matrix of undesirable constituents. Viable treatment options need to be a series of techniques that are inexpensive, modular in design, have a low tendency for fouling (Shaffer et al., 2013), produce significant throughput, and be able to desalinate effluent or eliminate pertinent ions of concern.

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3.7 Supplemental Information

TableSI 1 Basic Produced Water Parameters

Location	Sample	Basic Parameters				
		Total Alkalinity $CaCO_3$ (mg/L)	TDS (mg/L)	TSS (mg/L)	TOC (mg/L)	pH
PB	FB	26	15,700	126	115	7.05
PB SWD	PW 2 Raw	162	183,000	4,900	1032	6.45
	PW 3 Raw	426	212,000	5,600	889	7.12
	PW 4 Raw	204	190,000	6,100	38	7.22
	PW 5 Raw	73.7	147,000	5,400	46	6.72
	PW 6 Raw	841	118,000	4,952	51	6.49
	PW 8 PS	208	112,000	300	147	7.06
	PW 9 Raw	622	105,000	1,600	73	6.27
	PW 10 Raw	515	114,000	998	2,600	7.12
EF Treatment	PW1 Raw	225	4,732	-	239	8.55
	PW2 Raw	2,174.9	9,461.5	-	1,499	8.50
	PW2B Raw	799	23,134.5	-	1,042	7.56
	PW3 Raw	913	25,210.5	260	1,096	7.52
	PW4 Raw	4,000	7,515.5	110	1,434	8.47
	PW4B Raw	817	28,912.5	-	1,180	7.00
	PW5 Raw	170	23,762	782	-	7.22
	PW6 Raw	259	22,389.5	700	-	7.06
	PW7 Raw	632	16,160	50	258	6.39
	PW8 Raw	710	18,532.5	60	321	6.57
	PW9 Raw	421	40,144	100	254	6.97
	PW10 Raw	218	32,884	220,000	217	6.39
	PW11 Raw	559	23,189	50	313	6.51
EF Production	Tucker Raw	380.59	2,000	151	372.8	6.95
	R&B Raw	247	60,000	636	19,628	7.05

Table SI 2 Produced Water Metals

Location	**Sample**	**Metals (mg/L)**										
		B (249.773)	Ba (249.773)	Ca (315.887)	Fe (259.940)	K (766.490)	Li (670.784)	Mg (285.213)	Mn (259.373)	Na (589.592)	Si (251.611)	Sr (216.596)
PB	FB	6.65	0.1	1424.5	4.4	73.5	0.45	109.05	2.75	25740	16	18
PB SWD	PW 2 Raw	46.8	2.65	2946	4.4	450	17.9	490.35	0.05	42742	14.5	518.5
	PW 3 Raw	36.8	2	1571.5	7.35	374.5	13.2	333.2	0.25	49800	18.5	394
	PW 4 Raw	50.15	2.8	2365.5	1.3	444	16.55	429.55	0.2	47380	12.5	456
	PW 5 Raw	47.4	2.1	3047.5	5	457	18.465	464.45	2.4	34080	10.5	505
	PW 6 Raw	44.8	2.7	2352	0.95	414.5	15	390.45	1	33380	25.5	415
	PW 8 PS	49.05	2.4	3018	1.65	459.5	16.8	432	1.9	36500	15	425
	PW 9 Raw	35.4	4.25	2410	1.55	348	20	374.3	1.65	30600	17.5	372
	PW 10 Raw	43.1	1.3	2835	2.55	466	15.4	459.35	1.5	38220	14	433
EF Treatment	PW1 Raw	4.8	4.8	182.4	2.4	5.0	0.0	9.2	0.0	270	8	4.5
	PW2 Raw	21.4	21.4	302.8	0.5	80.0	3.1	27.1	0.1	2100	16	39.3
	PW2B Raw	60	60	1107.6	8.6	65.0	12.6	85.4	0.4	6500	39	143.1
	PW3 Raw	77	77	1884.7	8.2	95.0	16.9	140.6	0.6	5200	44	239.2
	PW4 Raw	17.8	17.8	261.2	0.5	50.0	2.5	18.8	0.1	1700	14	29.0
	PW4B Raw	68	68	2081.8	68.1	90.0	14.9	133.5	1.5	5200	45	223.8
	PW5 Raw	56.0	56.0	1068.8	53.8	102.5	14.6	82.9	1.0	6500	78	134.0
	PW6 Raw	44.0	44.0	833.6	56.0	67.5	8.1	83.1	0.9	4200	63	94.2
	PW7 Raw	23.6	23.6	1010.0	24.7	80.0	4.9	99.6	1.4	4400	24	80.5
	PW8 Raw	24	24	495.7	22.7	75.0	4.9	65.0	0.7	4100	24	62.2
	PW9 Raw	87	87	1893.6	4.5	116.5	14.2	176.3	0.7	13600	63	245.7
	PW10 Raw	50	50	4009.0	4.4	186.3	21.1	252.9	4.3	8900	17	486.3
	PW11 Raw	27	27	401.0	23.3	117.5	5.6	105.9	1.2	7000	19	88.2
EF Production	Tucker Raw	61.65	1.575	188.75	0.45	27	2.4	10.675	0.475	3090	55	20
	R&B Raw	51.875	23.5	1630.75	9.475	67.5	6.325	138.5	0.925	13000	40	271.5

TableSI 3 Produced Water Anions

Location	**Sample**	**Anions (mg/L)**				
		Bromide	Chloride	Fluoride	Nitrate	Sulfate
PB	FB	<0.0260	51,000	0.939	<0.0300	224
PB SWD	PW 2 Raw	60.9	97,000	2.48	45.6	49.4
	PW 3 Raw	67	97,000	2.37	45.6	33.1
	PW 4 Raw	58.8	93,000	2.63	45.7	83.2
	PW 5 Raw	58.7	75,000	2.24	46.6	77.1
	PW 6 Raw	58.1	70,000	2.15	46.4	2.22
	PW 8 PS	429	77,000	<0.034	<0.06	416
	PW 9 Raw	347	58,000	<0.034	<0.06	113
	PW 10 Raw	402	75,000	<0.034	<0.06	656
EF Treatment	PW1 Raw	0.052	774	0.222	0.06	12.6
	PW2 Raw	20.7	3470	17.9	0.06	8.87
	PW2B Raw	62.3	11400	24.9	0.06	17
	PW3 Raw	64	13900	62.9	0.3	17
	PW4 Raw	18.9	2110	20	11	8.76
	PW4B Raw	78.2	13100	29.4	0.06	9.19
	PW5 Raw	74	10700	0.034	0.06	82.5
	PW6 Raw	62.1	10600	1.24	0.06	105
	PW7 Raw	42	7540	0.034	0.06	10.2
	PW8 Raw	50.7	8230	0.034	0.06	2.81
	PW9 Raw	123	22000	5.31	0.06	8.06
	PW10 Raw	242	23400	0.034	0.06	147
	PW11 Raw	66.6	12100	0.034	0.06	36.3
EF Production	Tucker Raw	42.1	10600	<0.034	<0.0600	180
	R&B Raw	101	44500	<0.034	<0.0600	6.95

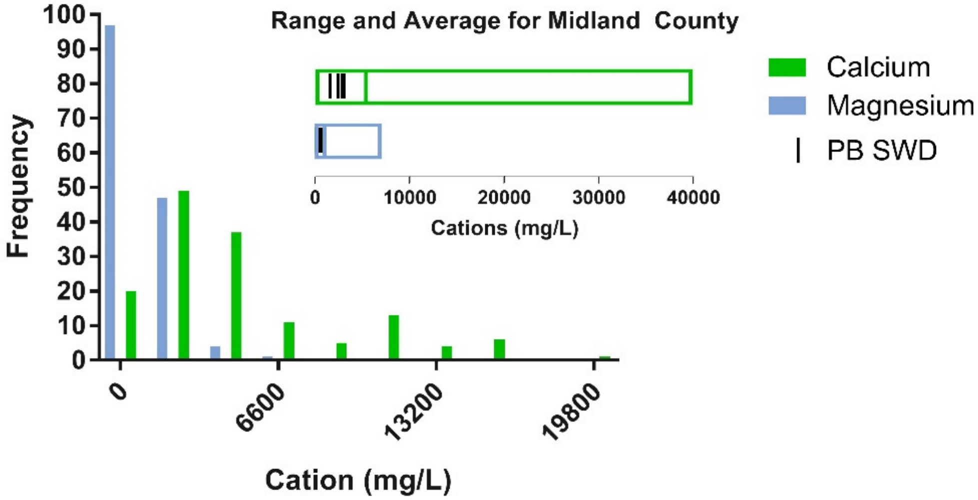
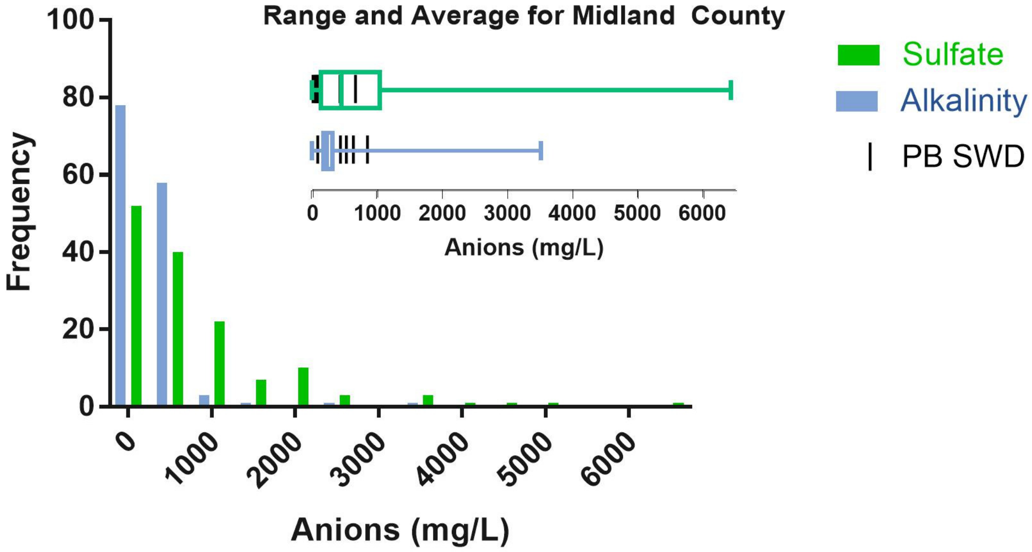


Figure SI 1. Histogram of the occurrence of concentrations ranges for calcium and magnesium from 149 PW samples collected from conventional production wells in Midland County.[49] The range and average of the USGS's Midland dataset from conventional development is compared to the PB SWD samples in the top right-hand corner. The green and blue boxes and lines illustrate the conventional waste ranges and average values for calcium and magnesium, respectively. The black lines denote individual values from the PB SWD sample set.



FigureSI 2 Conventional hydrocarbon PW data from 149 Midland county PW data points for anions, which cause scaling, were compared to the samples collected from unconventional hydrocarbon practices in the PB, PB SWD.[49] The frequency represents the occurrence of concentration ranges for sulfate (green) and alkalinity (blue) with the averages represented on the histogram in pink and grey for alkalinity and sulfate, respectively. The range and average of the USGS's Midland dataset from conventional development is compared to the PB SWD samples in the top right-hand corner. The green and blue boxes indicate the ranges and averages from conventional waste for sulfate and alkalinity, respectively. The black lines denote individual values from the PB SWD sample set.

CHAPTER FOUR

TREAMENT MODALITIES FOR REUSE OF PRODUCED WATER FROM OIL AND GAS DEVELOPMENT[1]

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Treatment Modalities for the Reuse of Produced Waste from Oil and Gas Development

Tiffany Liden[1], Inês C. Santos[1,2], Zacariah L. Hildenbrand[2,3*], Kevin A. Schug[1,2*]

AUTHOR INFORMATION:

1. Department of Chemistry and Biochemistry, The University of Texas at Arlington, 700 Planetarium Place, Arlington, TX 76019, USA
2. Affiliate of Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, USA
3. Inform Environmental, LLC, 6060 N. Central Expressway, Suite 500, Dallas, TX 75206

Correspondence should be addressed to: 6060 N. Central Expressway Suite 500, Dallas, TX 75206, USA. Tel.: +1 214 800 2829; e-mail address: zac@informenv.com; and 700 Planetarium Pl.; Box 19065; Arlington, TX 76019-0065, USA. Tel.: +1 817 272 3541; Fax: +1 817 272 3808; e-mail address: kschug@uta.edu

4.1 Abstract

Unconventional oil and gas development is achieved through a series of sub-processes, which utilize large amounts of water, proppant, and chemical additives to retrieve sequestered hydrocarbons from low permeability petroliferous strata. As a result, a large amount of wastewater is produced, which is traditionally disposed of via subsurface injection into non-productive stratum throughout the country. However, this method of waste management has been linked to the induction of seismic events in a number of regions across North America, calling into question the environmental stewardship and sustainability of subsurface waste disposal. Advancements in water treatment technologies have improved the efficacy and financial viability of produced water recycling for beneficial reuse in the oil and gas sector. This review will cover the various treatment options that are currently being utilized in shale energy basins to remove organic, inorganic, and biological constituents, as well as some emerging technologies that are designed to remove pertinent contaminants that would otherwise preclude the reuse of produced water for production well stimulation.

KEYWORDS: unconventional oil and gas development; produced water; water treatment; hydraulic fracturing; shale

4.2 Introduction

The American economy relies upon oil and natural gas acquired through conventional and unconventional exploration of petroliferous strata to meet the growing domestic energy needs (Kim et al., 2016; Mobilia and Comstock, 2017; U.S. Department of Energy, 2015; U.S. Energy Information Administration, 2017a). Until the turn of the century, pockets of hydrocarbons, referred to as conventional resources, were the principal source of oil and natural gas. This commodity was sequestered in subsurface strata comprised primarily of sand and limestone formations that were porous enough to allow the oil, gas, and natural formation water to migrate to the wellhead with minimal aid (Sinclair, 2012; U.S. Department of Energy, 2015). In contrast, unconventional oil and gas resources, which are on the rise today, are found in low porosity tight-sands and shale formations, which require more advanced technologies and processes to achieve hydrocarbon extraction. These include horizontal drilling and hydraulic fracturing (HF) stimulation, (U.S. Energy Information Administration, 2017b), which have contributed to a 39% increase in unconventional natural gas production between 2000 and 2007 in the United States. Moreover, by 2015, two-thirds of the natural gas output came from hydraulically-fractured production wells, (Ground Water Protection Council and All Consulting, 2009; Perrin and Cook, 2016; Wang et al., 2014) with 92% of production growth being derived from unconventional resources in seven key oil and gas basins: Bakken (North Dakota and Montana), Niobrara (Colorado), Marcellus and Utica (Pennsylvania, Ohio and West Virginia), Haynesville (Louisiana and East Texas), Eagle Ford (South Texas), and the Permian Basin (West Texas and Southeast New Mexico).

In this review, our discussion begins with an overview of the water cycle for unconventional oil and gas development (UD). We also address the common chemicals used and the roles that they play during the HF process, followed by an analysis of the composition of the wastewater, which includes organics, inorganics, as well as microbial contaminants. Current disposal practices are also discussed as well as contemporary treatment modalities and challenges associated with reuse of produced water for future oil and gas operations or use in other anthropological activities.

4.2.1 Water Use in the Unconventional Oil and Gas Production Process

Unconventional oil and gas development (UD) is comprised of three primary phases: drilling, completion, and production. Water plays a pivotal role in each step during the process, as shown in Figure 1. Therefore, the success of UD relies heavily on accessibility to large volumes of water, which can be acquired from a variety of sources such as surface- or groundwater.

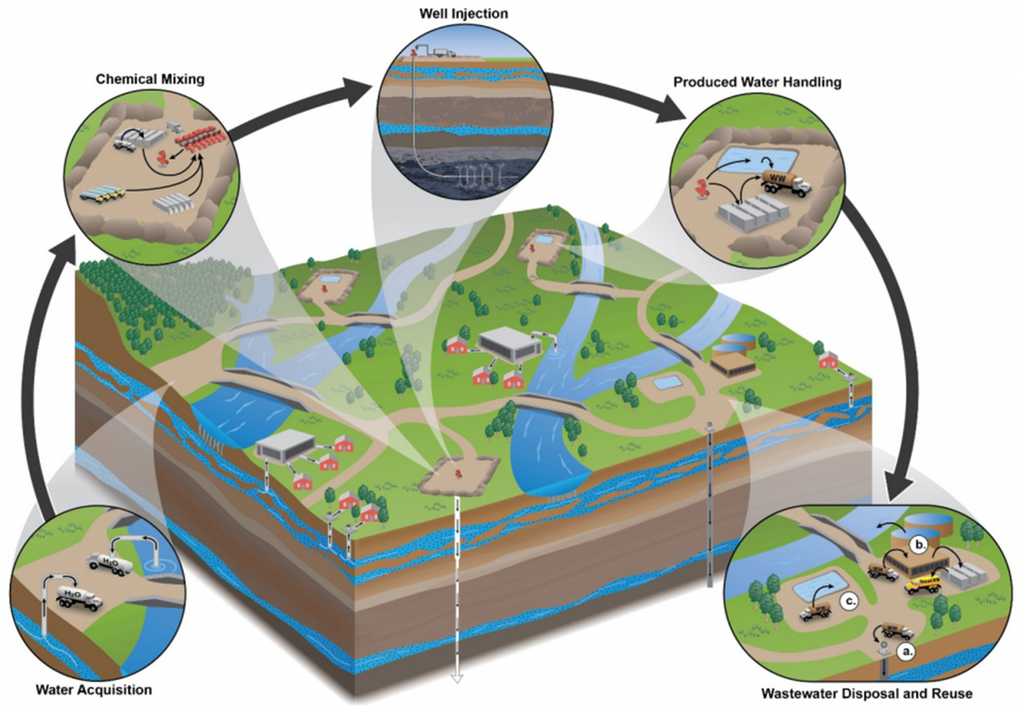

Figure 1: Diagram of a typical hydraulic fracturing process (U.S. Environmental Protection Agency, 2016a). (Figure reproduced from Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States (EPA-600-R-16-236ES, December 2016, www.epa.gov/hfstudy).

The first step in the well development process, drilling, only consumes approximately 1-12% of the overall water used throughout UD (Mantell, 2011). During this phase, drilling fluid, also known as drilling mud, is required to prevent a collapse of the borehole, bringing cuttings (rock particles), and other matter from the formation, back to the surface as well as to lubricate the drill bit and to keep it cool (King and Durham, 2017; The Editors of Encyclopedia Britannica, 2014; US Government Accountability Office, 2012). Drilling mud is typically a salt solution from sodium or potassium chloride that matches the formation fluid's salinity to minimize clay reactions when the drilling fluid is introduced to the formation. Common additives in drilling mud include bentonite clay to increase viscosity, weighting agents such as barite, and polymers from xanthan gum or cellulose derivatives to stabilize the formation (King and Durham, 2017). At the completion of the drilling process, the drilling mud is typically disposed of either on-site or at a solid waste facility.

The completion process, referred to as HF or 'fracking', uses the majority of the water required throughout UD. This process is used to enhance productivity by increasing permeability of the formation near the wellbore (Tayal et al., 1997). It is during the completion process that well stimulation is performed using HF fluid, which is typically a viscous water-based slurry, referred to as slick water, gelled fracturing fluids, or hybrid mixtures of the two (King and Durham, 2017). The primary considerations when preparing the stimulation fluid are fracture conductivity (flow capacity) (Chapman and Palisch, 2014), proppant transport, and preventing damage to the formation during the fracturing operation that would limit permeability (Kim et al., 2016). Proppants are hard solid particles, such as resin-coated silica sand, which are used to prop open the fractures formed during HF, so that the oil and gas can flow up the wellbore to the surface (Fu et al., 2016; Ground Water Protection Council and All Consulting, 2009; Wang et al., 2014). The well performance is largely dependent on how efficiently the proppant is transported down the wellbore and how long the proppant remains suspended in the fracturing fluid.

The stimulation fluid is prepared by mixing additives to help the stimulation process, which can vary in complexity from 1-2 or up to 30 chemicals. Additives for slickwater fracturing fluids include friction reducers, biocides, scale inhibitors, surfactants, clay control agents, and acids (fracline, 2012). Gelled fracturing fluids will also incorporate gellants, crosslinkers, and gel breakers. Friction reducers help reduce friction generated as the fluid is pumped down the wellbore. Four primary friction reducers used are polyacrylic acid (PAAc), polyacrylamide (PAAm), partially hydrolyzed polyacrylamide (PHPA), which is the most common friction reducer used, and acrylamido methyl propane sulfonate (AMPS) (Montgomery, 2013). Biocides are used to kill bacteria in the water to prevent the production of corrosive hydrogen sulfide gas (H_2S), and to limit biofouling, which can hinder production (Liden et al., 2017). Scale inhibitors prevent inorganic precipitate formation from polyvalent cations, such as calcium sulfate, calcium carbonate, and barium sulfate (King and Durham, 2017). Surfactants have a multifaceted purpose and are typically a mixture. Soap-like surfactants help to prevent emulsions, free oil from the formation, as well as assist in friction reduction through surface tension reduction. Clay stabilizers prevent the water from inducing clay swelling, which can decrease the efficiency of the well (Montgomery, 2013). Inorganics salts such as potassium chloride are effective for clay stabilization as well as organic clay stabilizers, typically used in the form of quaternary amine-based compounds. Acids can be beneficial in the well development process as they dissolve materials such as carbonate or clean cement from perforations. However, corrosion control can be problematic (King and Durham, 2017). Gellants increase viscosity, which increases the fracture width so it can accept a higher concentration of proppant, as well as suspend the proppants and provide lubrication. Additionally, this solution helps to transmit up to 20,000 psi of pressure applied at the surface to the formation, so that fractures can be created (King and Durham, 2017; Liden et al., 2017; Tayal et al., 1997). Frequently, gellants are plant-based polymers, the most popular of which is guar. Nonetheless, cellulose is commonly used as well (Montgomery, 2013). ViscoElastic surfactants are a polymer-free aqueous-based fracturing fluid. The performance of the gellants is based on the viscosity, which is a function of its molecular weight and is proportional to the increasing length of the polymer. Crosslinkers or viscosifiers are used to further increase the molecular weight by crosslinking the polymer backbone thereby extending the distance to which the proppant can be placed within the fractured formation. Typically they are formed from metals such as boron, titanium, or zirconium that have been conjoined with ligands (Esmaeilirad et al., 2016; Montgomery, 2013).

The last step in the HF process is to degrade the highly viscous fluid so that it can be removed from the wellbore to bring the well online to begin production (Tayal et al., 1997). Gel breakers are used to facilitate the process of degrading the aqueous based gel back to a low viscosity solution (SPE International, 2015a). Ideally, these materials would be totally inactive during the treatment process and then instantly “spring into action” when pumping stops, thus rapidly decreasing viscosity by breaking down gellants to allow fluid to be returned to the surface (Montgomery, 2013). However, this can be challenging to achieve as the breaker activity is very dependent on temperature, which varies with time. Three classes of breakers are typically utilized: oxidizers, acid, and enzymes. Oxidizers include ammonium and sodium persulfate, as well as calcium and magnesium peroxides. They work by cleaving the linkages among the polymer backbone. Acid attaches to the polymer backbone and breaks bonds, thus reversing the crosslink system. Enzymes are an organic catalyst that can also play an important role in the final steps of bringing a well online (Tayal et al., 1997). They offer an efficient and environmentally responsible method for the degradation of gellants. They digest the polymer or break them into individual units. As they are catalysts, they are not consumed during the degradation process (Montgomery, 2013). Typically, components of this type are formed from a mixture of several proteins such as hemicellulose, cellulose, amylase, and pectinase (Montgomery, 2013; Tayal et al., 1997).

The amount of water used during HF varies across the nation and is dependent upon a number of factors, such as the intrinsic properties of the target formation, the type of well (conventional or unconventional), the depth of the well, and the form of water-stimulation used (Alessi et al., 2017; Gallegos et al., 2015; U.S. Department of Energy, 2015). In 2011, the overall volume of water withdrawn for HF accounted for less than 1% of the state's water usage (Ground Water Protection Council and All Consulting, 2009; Shaffer et al., 2013). While these volumes are low compared to other anthropogenic activities (i.e., agriculture and farming), the water demands for HF tend to be highly localized, which can lead to groundwater depletion, especially in arid and semiarid regions. For example, in 2011 approximately, 5 million gallons of water was used per well across the nation (Mantell, 2011); however, Backstrom's study found that the Permian Basin, located in west Texas, used on average 12 million gallons of water per horizontal well stimulation (Backstrom, 2018).

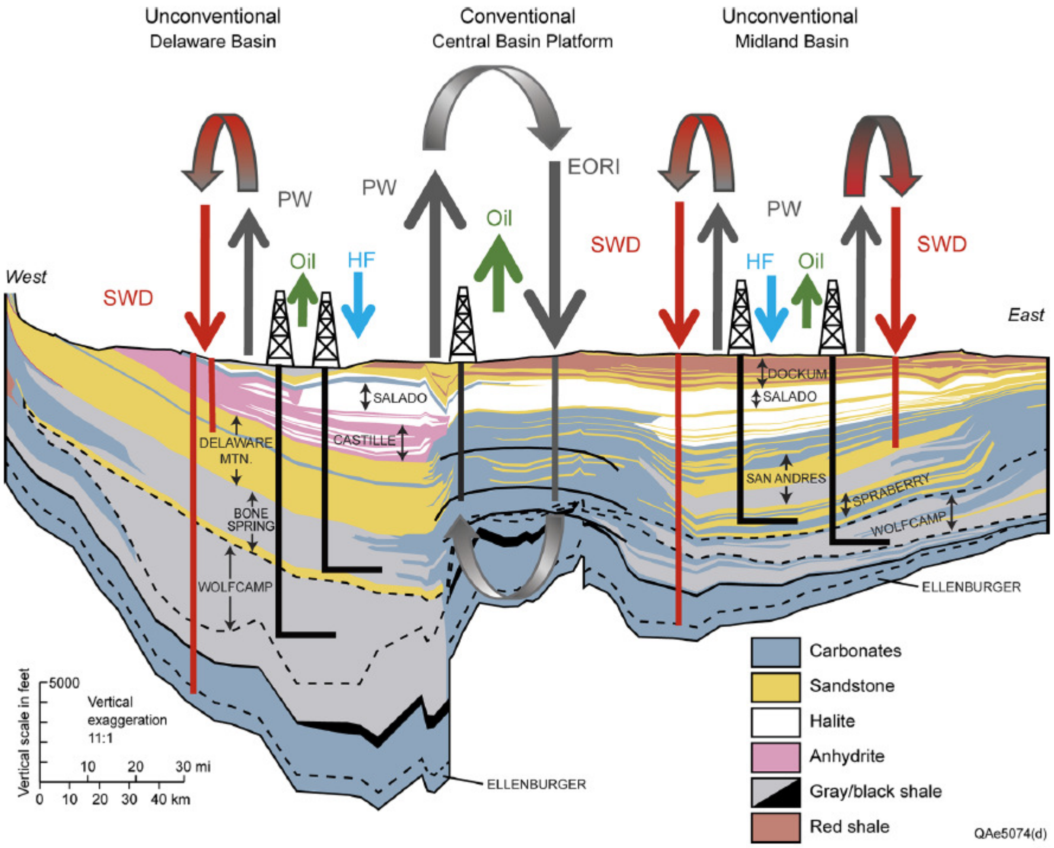

Figure 2: East–west cross section along the southern margin of the Permian Basin. The dominant unconventional reservoirs include Wolfcamp and Bone Spring in the Delaware Basin and Wolfcamp and Spraberry in the Midland Basin. These reservoirs are much thicker in the Delaware Basin than in the Midland Basin. The Central Basin Platform includes predominantly conventional reservoirs. The arrows are used to schematize the inputs and production data. Arrow sizes are used to approximate relative volumes. For example, conventional wells generate ∼13 times more PW than oil; however, most of this water is recycled by injecting into EORI wells for water flooding. PW from conventional wells accounts for ∼90% of total PW volume. Water injection for hydraulic fracturing (HF) is shown in blue arrows. HF water volumes for unconventional horizontal wells are ∼2 times higher than oil production PW from unconventional wells is ∼3 times oil production and is injected into saltwater disposal (SWD) wells in shallow horizons (e.g., San Andres in Midland Basin or Delaware Mtn. Grp. in Delaware Basin) or in deeper units (e.g., Ellenburger unit near the basement). The Dockum Aquifer is shown near the surface. (Scanlon et al., 2017). Reproduced with permission from Scanlon et al (2017), 2018, American Chemical Society. https://pubs.acs.org/doi/abs/10.1021/acs.est.7b02185 Further permissions related to the material excerpted should be directed to the ACS.

After the completion of the stimulation process, the well is put into production. One of the greatest challenges associated with maintaining the favorable economics of unconventional operations is managing the waste stream (Shaffer et al., 2013). The wastewater, commonly referred to as produced water, is comprise of flowback water (initial fracturing fluid returning to the surface), which then transitions into produced water (PW) (a combination for formation water and fracturing fluid that is comingled with the commodity) after a week or two and continues to be produced over the lifetime of the well (Liden et al., 2017). The waste products have always been a byproduct of oil and gas production, but have become a growing concern with the expansion of UD. The waste steam from conventional production wells, primarily consisting of natural formation water, is frequently reinjected into the formation to aide in oil recovery, creating a semi-closed loop system, as represented in Figure 2 (Scanlon et al., 2017). Conversely, the waste stream of unconventional production wells is generally disposed of through subsurface injection via salt water disposal wells (SWD) into non-oil producing geological intervals (Arthur et al., 2008; Clark and Veil, 2009).

4.3 Composition of Produced Water

PW is a challenging matrix to treat because of its complex physiochemical composition and the fact that the composition can change over the lifetime of the well (Fakhru'l-Razi et al., 2009). The chemical profile and quantity of PW varies for each shale play based on the well location and depth, as well as the age of the reservoir and type of hydrocarbon produced (Ground Water Protection Council and All Consulting, 2009; Igunnu and Chen, 2014; Shih et al., 2016). Constituents of concern in PW can be broken into four broad constituent categories: organic, inorganic, naturally occurring radioactive material (NORM), and biological.

4.3.1 Organic

Organic constituents in the waste stream come from a combination of residual hydrocarbons and production chemicals. One study that evaluated PW from the Permian Basin was able to identify more than 300 of the 1,400 structures that were separated using advanced analytical techniques (Khan et al., 2016). The study performed by Khan et al., suggested that PW from oil-bearing shale may be one of the most complex aqueous mixtures identified to date. Bulk analytical measurements for organics are useful metrics of analysis, including TOC (total organic carbon) and TPH (total petroleum hydrocarbon). TOC takes into account any combustible carbon compound while TPH is used to determine hydrocarbon concentrations. At times, organics are reported as COD (carbon oxygen demand), which can be used as a rapid test to determine the nutrient level rather than evaluating the BOD (biological oxygen demand) concentration.

Free oil or nonpolar hydrocarbons are the easiest to separate from PW, and these are the primary target for recovery of oil and gas operations (Igunnu and Chen, 2014; Kajitvichyanukul et al., 2011; National Energy Technology Laboratory, n.d.). Dispersed and dissolved oil are more soluble in water due to their increased polarity, making them challenging to separate. These compounds represent the most environmentally dangerous forms of oil (Kajitvichyanukul et al., 2011). Studies have identified dispersed oil mixtures which include polyaromatic hydrocarbons (PAHs), such as alkylated naphthalenes, phenanthrenes, and anthracenes. Other PAHs included fluorene, indene, pyrene and derivatives as well as BTEX compounds (Fakhru'l-Razi et al., 2009; Orem et al., 2014). BTEX compounds are a class of hydrocarbon constituents that is comprised of benzene, toluene, ethyl benzene, and the *m*-, *p*-, and *o*-xylene isomers. Additionally, production chemicals may reside in PW, which can include water soluble compounds such as corrosion inhibitors, antifreeze, biocides, and surfactants (Igunnu and Chen, 2014; Shaffer et al., 2013).

Alkylated phenols, such as nonylphenols ethoxylates, classified as endocrine disruptors by EPA, are commonly used as surfactants in HF (Orem et al., 2014). A recent analysis of PW from the Cline Shale region revealed residual levels of surfactants such as 2-butoxyethanol and N-alkyl-N,N-dimethylamine (Thacker et al., 2015). Polyethylene glycol carbonates (PEG), polypropylene glycols (PPG), and ethoxylated surfactants have been identified in PW, as well (Heyob et al., 2017; Thurman et al., 2017). The nonionic composition of the aforementioned surfactants function as weatherizers, emulsifiers, corrosion inhibitors, and wetting agents. Non-emulsifiers were identified, such as diethanolamine salts, which are used to break emulsions before the well is put into production and to speed up the separation of water and oil. Benzothiazole and other heterocyclic compounds have also been identified in wastewater from gas production (Orem et al., 2014). While treatment and elimination of organics in PW can be a significant challenge, the addition of other components such as inorganic salts and metals, increases the complexity of the solution.

4.3.2 Inorganic

The wastewater from UD is generally enriched with dissolved inorganic compounds or minerals, which are introduced into the waste stream through contact with the formation. Concentrations of total dissolved solids (TDS) are a reflection of inorganic constituents and can be estimated by measuring the salinity. The salinity or concentration of inorganics can vary each region from brackish levels (1,000 - 15,000 parts per million (ppm) TDS) to varying degrees of saline (15,000 ppm to 40,000 ppm TDS) to brine (> 40,000 ppm) (Ground Water Protection Council and All Consulting, 2009; Mantell, 2011). For example, PW from the Barnett Shale has been found to have TDS levels ranging from 500-200,000 ppm, whereas PW from the Marcellus Shale formation varies from 10,000 to 300,000 ppm (Ground Water Protection Council and All Consulting, 2009).

Studies analyzing PW from the Marcellus Shale formation indicate that sodium contributes ~19-26% of the total TDS levels, whereas chloride constitutes ~57-61% (Akob et al., 2015). While many oilfield waste streams are rich in chloride, other anions such as sulfate and carbonate can also be found in PW (Zielinski and Otton, 1999). Calcium is also a major contributor to hypersaline PW, in addition to barium, beryllium, boron, cadmium, copper, iron, lithium, potassium, magnesium, manganese, and selenium (Khan et al., 2016). Of these inorganic constituents, calcium, iron, and magnesium are the most pertinent given their affinity to interact with carbonate and sulfate minerals (Zielinski and Otton, 1999). Such interactions can be influenced by changes in temperature, pressure, pH, and salinity as the water is brought to the surface and processed. This can lead to problematic scale formation, which in itself can have devastating financial implications for any production well operator.

4.3.3 Naturally-Occurring Radioactive Material (NORM)

Oilfield waters that are particularly rich in chloride enhance the solubility of other elements, including naturally occurring radioactive material (NORM) (Zielinski and Otton, 1999). The most abundant NORM constituents that are found in oilfield PW are the radium isotopes, ^{226}Ra and ^{228}Ra. However, shale and sandstone formations also commonly contain uranium, thallium, and thorium as well (Guerra et al., 2011; U.S. Environmental Protection Agency, 2016a; Zielinski and Otton, 1999). Radium accumulation on oilfield equipment, and the corresponding health concerns, were first realized in the 1980s when unacceptable levels were detected at a production site. This radioactive material is brought up to the surface with PW. The mineral barite ($BaSO_4$) is the most likely host of radium in the subsurface formation (Zielinski and Otton, 1999). Barium sulfate's solubility is increased in organic rich solids, which host SRB that can potentially liberate radium that was previously encapsulated (Akob et al., 2015). Precipitation formation is influenced by pressure, temperature, pH, and compositional changes (Stewart and Arnold, 2011).

Therefore, the environmental changes that occur as PW was brought to the surface can lead to the co-precipitation of radium with scale, which coat equipment (Akob et al., 2015; Guerra et al., 2011; Igunnu and Chen, 2014).

4.3.4 Biological

Bacteria are ubiquitous in the environment. Therefore, their presence in PW is expected as UD activities are not performed in a sterile environment. Bacteria in a waste stream may originate from the geological formation, infrastructure and equipment for water handling, fracturing fluid amendments, or source water used to create the fracturing fluid (Murali Mohan et al., 2013b). Due to its anaerobic environment and high nutrient content, the main bacteria found in PW are usually sulfate-reducing bacteria (SRB), iron-oxidizing bacteria (IOB), and acid-producers (APB), all of which can be problematic.

Different studies have been performed to evaluate the bacterial communities of PW (Akob et al., 2015; Cluff et al., 2014; Murali Mohan et al., 2013a; Strong et al., 2013; Struchtemeyer and Elshahed, 2012). As an example, Mohan et al. compared the microbial communities in prefracturing and PW samples at different times, which were significantly different from each other (Murali Mohan et al., 2013a). Bacterial communities in the prefracturing fluids were diverse and dominated by the orders *Pseudomonadales* and *Rhodobacterales*, affiliated with the classes *Gammaproteobacteria* and *Alphaproteobacteria*, respectively. The dominant bacterial classes in PW samples included *Gammaproteobacteria*, *Alphaproteobabcteria*, *Betaproteobacteria*, *Epsilonproteobacteria*, *Clostridia*, *Bacilli*, *Fusobacteria*, *Bacteroidia*, and *Flavobacteria.* These have been identified previously in numerous wastewater brines from oil and gas extraction operations. This suggests that specific lineages found in low abundance in the prefracturing fluids increased in relative abundance upon exposure to subsurface conditions. Organisms in the fracturing fluid are rapidly transitioned from oxic and moderate brine waters to higher concentration brines at higher pressure and temperature where there exists a relatively reducing environment. This exposure selects organisms that are able to tolerate and adapt to the broad range of environmental conditions that occur between fracturing fluid and PW. The increase in the relative abundance of orders containing potentially spore-forming species, such as *Lactobacillales*, *Bacillales*, *Clostridiales*, and *Thermoanaerobacterales* in PW, could also indicate a response to the addition of biocides or rapidly changing environmental conditions, such as an increase in temperature or a shortage of essential nutrients. The response to changing oxygen concentrations in the subsurface, and the increase in NaCl concentrations, correlate well with the increase in the relative abundance of facultative anaerobic and halotolerant species within the orders *Vibrionales*, *Alteromonadales*, *Campylobacterales*, *Halanaerobiales*, *Fusobacteriales*, and *Bacteroidales* in PW samples as compared to the prefracturing fluid. Salinity is known to be a major driver for microbial community structure. Additionally, the taxonomic analysis of PW revealed multiple sulfidogenic taxa, *Halanerobium*, *Vibrio*, *Shewanella*, and *Thermoanaerobacter*, which may produce sulfide from nonsulfate oxidants (Murali Mohan et al., 2013a).

Overall, the published research describing bacterial communities in fracturing fluids and PW indicate an emergence of halophilic anaerobes that are associated with the emergence of anaerobic geochemistry (e.g. Fe^{2+} and HS^-) in the water and capable of producing H_2S, which may cause biocorrosion of metal infrastructure and souring of natural gas. With time, a decreased diversity was observed as a result of the loss of virtually all species present in the initial flowback, except the *Halanaerobiales,* which eventually represented >99% of the community (Cluff et al., 2014). In PW, all of the bacteria identified were closely associated and established anaerobic, fermentative, and sulfur-reducing bacteria in the *Halanaerobiales*, as that community is well-adapted to anoxic and saline conditions (Struchtemeyer and Elshahed, 2012).

4.4 Current Waste Management Practices

PW is considered to be one of the most complex water matrices (Chermak and Schreiber, 2014), which renders a challenging prospect to reuse. This is best illustrated by the fact that 98% of all PW from oilfield activities in 2011 was disposed of via Class II Injection wells (Arthur et al., 2008; Clark and Veil, 2009). These wells are used to inject "non-hazardous" fluids associated with oil and gas production for disposal, hydrocarbon storage wells, or enhanced recovery (U.S. Environmental Protection Agency, 2016b). Ultimately, how the PW is handled is dependent on local resources (Thacker et al., 2015), local regulations, and economics (Alessi et al., 2017). Infrastructure and geological conditions play a role in determining viable options, as well. Direct discharge and treatment through local municipality wastewater treatment centers have been tested in Pennsylvania, but have been discontinued due to contamination of surface waters (Harkness et al., 2015). Currently, salt water disposal (SWD) wells, one form of Class II wells, are the most popular and cost-effective choice for PW management in the unconventional oil and gas industry.

In 2011, 40% of PW across the nation was disposed of through subsurface injection via SWD wells into non-oil producing geological intervals located primarily in Texas, California, Oklahoma, and Kansas (Arthur et al., 2008; Clark and Veil, 2009). Through the use of SWD wells, fluids are injected into underground formations, often over a mile in depth, which must be sealed above and below by unbroken, impermeable rock layer (Railroad Commission of Texas, 2017). Another 58% of this waste was used for enhanced oil recovery with the remaining 2% of PW being reused in the oil and gas industry, recycled for other industries, or discharged. In the Permian Basin, from 2005-2015, ~70% of total injection volume was used for enhanced oil recovery; while the remaining ~30% accounted for the volume disposed in SWD wells (Scanlon et al., 2017).

For SWD, per regulations, PW does not require further processing once the waste stream is received from the oil and gas producer; however, frequently some form of treatment is performed to prolong the life of the disposal well. The degree to which the effluent is treated will vary at the discretion of the disposal operator. At a site in the Permian Basin, one commercial operation begins by allowing remaining organics and water to separate. Upon PW entering a SWD facility, the oil content is reduced from 0.1- 0.5% to 20-40 ppm (0.002 - 0.004%) via gravity flow by hydrostatic pressure, as depicted in Figure 3. In the Permian Basin and other regions where iron is a concern, iron reducers are added to prevent scaling. Solids are then collected from the base of the separation holding tanks and 200 µm filters through which the PW has been passed. Surfactant is added to emulsify any remaining organics, followed by well injection.

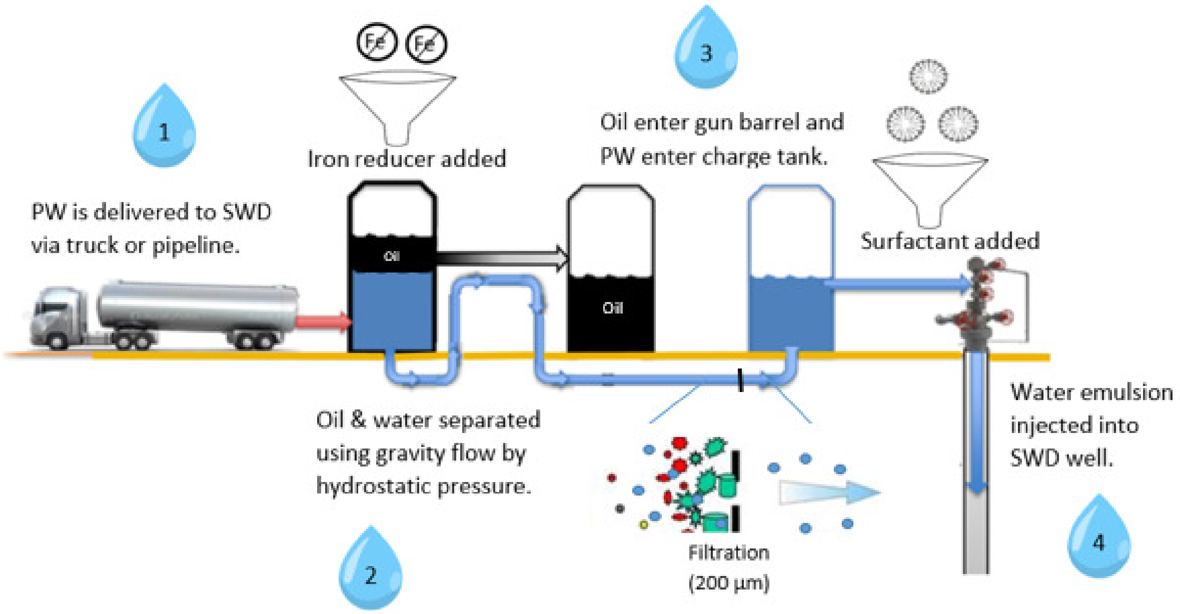

Figure 3 SWD Treatment Process at Water Midstream Partners-Permian Basin. Modified from (Liden et al., 2017).

The greatest challenge with SWD is keeping up with the disposal demand in high production regions. A bottleneck can form at a disposal site based on how quickly water can be injected into the ground without over pressurizing the well. As the volume of PW being disposed of by injection into non-productive subsurface formations increases, evidence indicates that the disposal of the wastewater into SWD wells has triggered seismicity in some areas (Gallegos et al., 2015; Hornbach et al., 2016). For example, until 2000, there were ~21 seismic events per year in the Colorado (Raton Basin) that measured greater than M3.0 (magnitude) on the Richter scale. In 2011, 134 events occurred; the USGS concluded that the increase in the earthquakes is of anthropogenic origin and likely attributable to unconventional development (Wang et al., 2014). As such, it is expected that this form of subsurface disposal will be subject to growing constraints due to the concerns regarding earthquakes, thus increasing the need for effective treatment options that allow for reuse and recycling of PW (Parker et al., 2014).

4.5 Challenges associated with Recycling Produced Water

Recycling PW for beneficial purposes, such as agriculture, or reusing it for future HF is an ideal concept. It would address public concerns about heavy water usage in arid and semiarid regions, while also reducing the occurrence of induced earthquakes that can result from subsurface disposal (Nicot et al., 2014). However, the presence of residual production chemicals, dissolved formation constituents, and bacteria, can limit the reuse of PW, particularly when there is the potential to negatively impact downhole stimulation chemistry. While there are no guidelines available for total organic carbon or total nitrogen within the context of reuse, elevated levels of organic carbon and nitrogen can provide an optimal environment for the proliferation of undesirable bacterial communities (Liden et al., 2018; Santos et al., 2018)). Furthermore, operators will use a recipe that is tailored for each formation; unknown concentrations of chemical contaminants can trigger undesirable interactions during the reuse of stimulation fluid. For example, if gel breakers remain in PW, then the predetermined concentration of gellant and crosslinker will not be effective to achieve the necessary viscosity.

The elevated concentrations levels of multivalent cations, such as calcium, iron, and magnesium competes with the added crosslinkers, destabilizing the interactions and decreasing viscosity (Esmaeilirad et al., 2016; Oetjen et al., 2018). For example, iron greater than 10 mg/L can cause overcrosslinking and adversely affect the temperature stability (Wasylishen and Fulton, 2012). Calcium and Magnesium have an upper limit of 2,000 mg/L due negative effects on crosslinking and shear stability as well as scaling. Formation water with a high level of pyrite, FeS_2, can oxidize forming acidic conditions, which can be corrosive to equipment (Chermak and Schreiber, 2014). PW with alkalinity (CO_3^{-2}) levels that exceed 300 mg/L can not only increase scaling potential, but also make it challenging for producers to control the pH (Oetjen et al., 2018).

The reuse of PW generally introduces enough oxygen for aerobic bacteria, such as heterotrophic biofilm-forming bacteria (HBB), to grow, but not enough to kill the anaerobic bacteria present. SRB, APB, and HBB can form biofilms and therefore cause biofouling of hydrocarbon reservoir rock and reduce the flow capacity in pipes.

SRBs are heterotrophic organisms and absolute anaerobes that can obtain energy by oxidizing organic compounds as a source of carbon and energy while reducing sulfate (SO_4^{2-}), as well as other oxygenated sulfur compounds to hydrogen sulfide (H_2S). Due to the production of H_2S, SRBs are the main cause of costly product quality degradation, referred to as souring, and the biocorrosion of metal infrastructure which potentially can lead to casing failure and environmental contamination.

IOB (iron oxidizing bacteria) are aerobic bacteria that oxidize iron to produce ferric hydroxide [$Fe(OH)_3$] precipitate. These iron hydroxide precipitates promote regions on the surface with different oxygen levels. Additionally, the enhanced deoxygenation promotes the growth of SRB, which can lead to corrosion. Lastly, IOB are also known to cover SRB colonies and protect them from the action of biocides (Emerson et al., 2010).

APB are capable of producing short-chain organic acids such as acetic, formic, lactic, propionic and butyric acids as products of the fermentative metabolism of organic materials which can significantly lower the pH to significantly acidic conditions. These conditions can lead to an acid-driven form of corrosion (Moura et al., 2013), as well as decreased fracture conductivity due to the hydrolyzation of gellant polymers (Montgomery, 2013).

The limitations imposed to reuse PW become increasingly more stringent when considering recycling for other anthropological actives such as agricultural, irrigation and/or surface discharge. Levels drop from parts-per-thousand being acceptable to requiring parts-per-million and lower. Table 1 provides a comparison with respect to drinking water standards for irrigation, livestock and HF reuse.

Table 1 Comparison of maximum contaminant limits for drinking water, irrigation water, livestock water, and production well stimulation (Ayers and Westcot, 1985; Hildenbrand et al., 2018; U.S. Environmental Protection Agency, 2017, 2012; Wasylishen and Fulton, 2012).

	Drinking Water (mg/L) (EPA SDWA)	Agricultural Irrigation (mg/L) (EPA)	Livestock (mg/L) (FAO)	Production Well Stimulation (mg/L) (Hildenbrand et al. 2018; Wasylishen, R., Fulton, S. 2012)
TDS	500	450		
PH	6.5-8.5	6.5-8.4		6.0-8.0
TSS				500
Total Nitrogen	44.3			
Fluoride	4	1	2	
Chloride	250	92		30,000 - 50,000
Bromide				
Nitrate	44.3	5	90	
Nitrite			10	
Nitrate + Nitrite			100	
Sulfate	250		1000	500
Bicarbonate		91.5		300
Silica				35
Silver (Ag)	0.1			
Aluminum (Al)	0.05 - 0.2	5	5	
Arsenic (As)	0.01	0.1	0.2	
Boron (B)		0.7	5	10
Barium (Ba)	2			20
Beryllium (Be)	0.004	0.1	0.1	
Calcium (Ca)				2,000
Cadmium (Cd)	0.005	0.01	0.05	
Cobalt (Co)		0.05	1	
Chromium (Cr)	0.1	0.1	1	
Copper (Cu)	1.3	0.2	0.5	
Iron (Fe)	0.3	5		10
Mercury (Hg)	0.002		0.01	
Lithium (Li)		2.5		
Magnesium (Mg)				2,000
Manganese (Mn)	0.05	0.2	0.05	
Molybdenum (Mo)	0.04	0.01	0.3	
Sodium (Na)	20	69	1000	
Nickel (Ni)	0.1	0.2		
Lead (Pb)		5	1	
Antimony (Sb)	0.006			
Selenium (Se)	0.05	0.02	0.05	
Strontium (Sr)	4			
Thallium (Tl)	0.002			
Uranium (U)	0.03			
Valadium (V)		0.1	0.1	
Zinc (Zn)	5	2	24	
Benzene	0.005			
Dichloromethane	0.005			
Ethylbenzene	0.7			
Toluene	1			
Total Xylenes	10			

4.6 Produced Water Recycling Technologies

Effective treatment options for PW should encompass a compilation of methodologies to effectively remove all constituents that can negativity impact its reuse for oil and gas development and/or other anthropogenic activities. Treatment options should center around seven primary foci based on the PW quality in the region (Fakhru'l-Razi et al., 2009; Gaudlip et al., 2008; Igunnu and Chen, 2014; Wasylishen and Fulton, 2012).

7. Removal of organics, including oil and grease,
8. Solids removal: Suspended particles and sand,
9. Disinfection,
10. Dissolved gas removal: Removal of light hydrocarbon gases, carbon dioxide, and hydrogen sulfide (if needed in the production region),
11. Softening: Removal of excess water hardness and reduction in scaling,
12. Removal of naturally occurring radioactive material,
13. Desalination: Removal of dissolved salts

4.6.1 De-oiling

PW flows up through the wellbore to the processing equipment at a rapid rate, which causes oil to be dispersed into small droplets. Low energy processes are required to allow small droplets to collide and coalesce (join together), so that it can be easily removed (Stewart and Arnold, 2011). PW is typically de-oiled using gravity separation techniques with devices such as holding tanks, hydrocylones, and floatation tanks, or a combination of these separation techniques. Gravity separation is most commonly used, at least as an initial step in the treatment process (Stewart and Arnold, 2011). This method relies on density and immiscibility to separate oil droplets from the waste stream. Limiting the input energy by capturing the PW in a holding tank allows the oil droplets to coalesce (Stewart and Arnold, 2011). The process offers the additional economic benefit of harvesting the separated oil. Also, if the influent stream entering the treatment site is continuous, the progression of the PW optimally will be a cost-effective and low energy system that is driven by hydrostatic pressure.

Hydrocyclones offer a cost option to preform liquid-liquid de-oiling of PW with the use of centrifugal force. They also have limited maintenance due to their lack of moving parts; however, there is a tendency for flow to be blocked due to solids. Flotation tanks encourage coalescence of small oil droplets; therefore, they can be used to for further separation. These units operate via gravity separation, but also use pressurized water, supersaturated with air, to produce bubbles of 30 to 120 µm upon release of pressure in the separation vessel (Nalco Chemcial Comapny, 1988). Floatation is more energy intensive than the other gravity separation methods due to the aeration pumping requirements (Stewart and Arnold, 2011); however, incorporating gravity separation into a treatment system has the added benefit of allowing large solids to settle to the bottom of the tank system, which can then be pumped out.

Organic compounds in PW can also be removed by adsorption to porous media. Activated carbon can be used to remove dissolved oils, and organoclays are effective at removing dispersed organics, which contribute to elevated TPH levels (Fakhru'l-Razi et al., 2009). The activated carbon has the added benefit of being able to be regenerated through the use of the wet air oxidation process (Tungler et al., 2017).

Bioremediation can be used to treat residual organics. The process can be carried out *in situ* at the polluted site without changing the existing land management plans (Vidali, 2001), or *ex situ* where the contaminated material is removed and treated elsewhere. When performing *in situ* bioremediation, two approaches can be performed: 1) the indigenous bacterial population can be stimulated by feeding them nutrients and oxygen to increase their metabolic activity; or 2) certain microorganisms can be introduced to the contaminated site. Usually, *in situ* bioremediation methods are not always easy to monitor, whereas *ex situ* bioremediation methods are more expensive, due to the transportation costs and storage (Vidali, 2001; Wolicka and Borkowski, 2012). Nevertheless, the most common method used to treat wastewater is activated sludge. The microorganisms present in the reactor degrade the contaminants to form additional biomass (sludge). Due to the complex matrix of PW, the choice of bacteria is critical to ensure an efficient removal of contaminants.

Santos et al. demonstrated the ability of two microorganisms isolated from contaminated groundwater located near UD activities to degrade organic compounds such as toluene and chloroform. *Pseudomonas stutzeri* and *Acinetobacter haemolyticus* were identified using MALDI-TOF MS and both were able to degrade toluene and chloroform with higher degradation rates for toluene (Santos et al., 2017). These results indicated that the identified bacteria have the potential to be used for water and/or wastewater bioremediation. Subsequent studies can also be performed to determine the ability of the isolated bacteria to degrade other contaminants such as benzene and aliphatic hydrocarbons. As with every method, bioremediation also has its drawbacks. Not all compounds are susceptible to relatively fast and complete degradation. In some cases, products of degradation of oil-derived products have toxic effects on microorganisms. It is important to note that the use of organophilic bacteria to treat PW would likely go hand-in-hand with bacteriophage therapy. In a cost-effective two-step process, organic constituents could be metabolized by bacteria, which could then be selectively targeted for cell lysis by bacteriophage.

4.6.2 Solids

Solids can be categorized as either total suspended solids (TSS) or total dissolved solids (TDS). TSS, which are formed from formation sands and clays, proppants, corrosion by-products, and precipitate crystals, can filtered out of solution using a 1-2 µm pore size filter or membrane. Fine, solid particles may stabilize an emulsion if they are of correct size and abundance (Nalco Chemcial Comapny, 1988). Stabilization occurs due to the physical characteristics and electronic charge of the solids; they can attract the dispersed oil droplets to form oil-wetted solids. The dispersed droplets cannot coalesce because of the interference or blocking effect caused by the solids. Also, the combined specific gravity of the oil-wetted solid can be similar the aqueous layer making gravity separation difficult, if not impossible (Nalco Chemcial Comapny, 1988; Stewart and Arnold, 2011). The interaction of oil-wetted solids can be broken via chemical, electrolytic, or physical methods by neutralizing the stabilizing factors (Nalco Chemcial Comapny, 1988). Chemical emulsion breakers allow small particles to be combined thus increasing their sizes by inducing coagulation and flocculation. Coagulation is the process of destabilizing particles through charge neutralization, while flocculation is the process of aggregating the destabilized particles to form a floc (Stewart and Arnold, 2011). The addition of chlorine may assist in coagulation by oxidizing organic constituents; inorganic coagulants include alum, ferric chloride, ferric sulfate, or polyaluminum chloride. Polyelectrolytes are a water-soluble class of organic coagulants, which can be anionic, cationic, or naturally charged and typically have a long tail yielding a high molecular weight polymer. The process is performed in a clarifying tank that has a mixer to provide a continuous low energy turbulence to create contact between the solids and chemicals. Additionally, flotation can be used to enhance the uses of polyelectrolytes.

Solids can then be removed by gravity separation or by filtration. Filtration provides a physical trap for the solids, but still allows the water to flow. Filters are available in three categories: non-fixed-pore structure, fixed-pore structure, and screen filters (Stewart and Arnold, 2011). The pore size of non-fixed-pore structures increases with increased pressure and include sock filters, sand, and other granular media filters, as well as diatomaceous earth filters. Fixed filters are engineered so that the structural portions of the medium cannot distort. They have rigidity to the mesh and can include continuous polypropylene, resin bounded fiberglass, or resin-impregnated cellulose cartridges (Stewart and Arnold, 2011). Collectively, filtration is an effective method for removing solids, which can affect formation permeability if the recycled PW is reinjected to the subsurface for HF. However, the aforementioned filtration modalities are generally not effective in removing TDS, which can have negative implications with respect to equipment corrosion and scaling. Nonetheless, there are treatment modalities that can be effectively utilized to manage TDS and these will be discussed in subsequent sections: *Softening & NORM*, as well as *Desalination*.

4.6.3 Disinfection

When reusing PW for subsequent HF, attention needs to be given so that external microbial populations are not introduced to prevent accelerating sour-gas production, biocorrosion, and biofouling. The removal of bacteria can be accomplished by using a number of different modalities such as aeration, biocides (quaternary ammonium compounds, aldehydes), chlorination (hypochlorite, chlorine dioxide), filtration, ozone and UV treatment, and other emerging technologies.

Aeration of PW introduces oxygen into a microaerobic or anaerobic environment and helps in the removal of iron, manganese, hydrogen sulfide, and organics. By doing so, the food source for anaerobic bacteria, especially SRBs and APBs, is eliminated, which inhibits their growth.

Biocides are bioactive organic chemicals and are usually divided in two categories: Non-oxidizing and oxidizing compounds. Non-oxidizing biocides are the most common biocides used in HF to prevent the growth of bacteria. These include quaternary ammonium compounds, aldehydes, bronopol, and others. These can be split in two groups according to their mode of action: Electrophilic and lytic (Kahrilas et al., 2015). In spite of the presence of biocides in the fracturing fluids, some bacteria have become resistant to their presence and are in fact able to biodegrade these compounds (Oh et al., 2013; Strong et al., 2013; Struchtemeyer and Elshahed, 2012). In the work by Vikram et al., the authors demonstrated that PW exposure results in an enhanced tolerance against the typically used biocide glutaraldehyde and increased susceptibility to the oxidative biocide hypochlorite in a native and a model bacterium (Vikram et al., 2014). This altered resistance was attributed to the salinity of the PW. In addition, the genetic response of the model organism *Pseudomonas fluorescens* to PW exposure was assessed, and this demonstrated the induction of genes involved in osmotic stress, energy production and conversion, membrane integrity, and protein transport following PW exposure, which facilitates bacterial survival and alters biocide tolerance.

The use of oxidizing biocides for water disinfection poses the risk of equipment corrosion, can have unwanted reactions with other HF chemicals, and can form byproducts (disinfection byproducts, DBPs). The principal behind these biocides such as bromine and chlorine-based species rely on the action of released free radical species that attack cellular components. Chlorination is frequently a disinfection method of choice because it is cheap and effective. Chloride dioxide (ClO_2) as well as calcium ($Ca(ClO)_2$) and sodium hypochlorite ($NaOCl$) are powerful germicides, which can be used to control a wide range of microorganisms. Initially, $Ca(ClO)_2$ was used to treat the PW against bacteria to be able to reuse it. However, the additional calcium in the water showed detrimental effects by inhibiting the friction reducer (Tischler et al., 2010). For this reason, $NaOCl$ is used instead of $Ca(ClO)_2$. Nevertheless, in a recent study, bacteria was isolated from water that had been heavily chlorinated (Martin et al., 2017), indicating chlorination is not a completely fail-safe disinfection modality.

Ozone has also been widely used for drinking water and food disinfection. It oxidizes membrane lipids, which weakens the cell wall and leads to cellular rupture (Kim et al., 1999; Sugita et al., 1992). Nevertheless, this type of disinfection is also known to generate precursors such as bromate, which can then form DBPs. There are other alternatives to circumvent the need for chemical addition altogether, such as the use of UV light. These technologies have proven to be extremely effective for microbial control, but currently widespread use is limited due to their high energy demands and lack of residual disinfection capacity. (Kahrilas et al., 2015).

Bacteria can also be removed by filtration using membranes with small pore sizes (0.001 - 0.4 µm) that can trap these microorganisms. However, issues can be observed if membrane integrity fails or if bacteria clog the membrane (i.e., biofouling). Therefore, robust membrane materials are necessary. Usually, filtration is not used by itself and is coupled with other treatment technologies, such as UV or chlorine disinfection. This improves the removal of bacteria and avoids membrane biofouling without damaging the membrane (Pearce, 2007).

Due to the drawbacks of the existing technologies, new strategies are being developed to improve the removal of bacteria from PW. Bacteriophages are one example of an emerging technology that is starting to gain a lot of attention in clinical, food, and agricultural fields, but also in the oil industry. Bacteriophages are viruses that exclusively kill bacteria. They are obligate intracellular pathogens since they have no intrinsic metabolism and require the metabolic machinery of the host cell to support their reproduction (Withey et al., 2005). Bacteriophages can enter either a lytic or lysogenic cycle. In the first one, the phages inject their genetic material into the host. This causes the cell machinery to synthesize new phage capsule material and the new phages are released by cell lysis. In the later cycle, the phage nucleic acid recombines with the host cell genome forming a dormant prophage. Nevertheless, stress conditions such as UV light or chemical mutagens can induce a switch to the lytic cycle. For water remediation, it is necessary that the bacteriophage operates within the lytic cycle in order to eliminate the microorganisms of interest. Some recent works show the applicability of this technique in the removal of bacteria from water (Jun et al., 2016; Richards, 2014). In the case of removing bacteria from UD activities, these viruses need to be able to survive extreme environments, more specifically the presence of high temperatures, acidic pH, and high salt content. Bacteriophages are able to survive temperatures up to 90 ºC and are in fact more resistant to thermal treatment than bacteria (Jończyk et al., 2011). Regarding pH, these viruses are stable at a neutral pH (6-8); however, Wick et al showed that MS2 bacteriophages could survive for 66 h in a 0.1 M HNO_3 solution without any decrease in the number of phage particles(Wick et al., 2006). Additionally, osmotic shock has been shown to inactivate bacteriophages, but similar to acidic pH, studies have shown that these viruses can survive in the presence of high salt. In fact, several bacteriophages were isolated from marine water of different salinities (Jończyk et al., 2011). Due to bacteriophages' resistance to extreme physical and chemical conditions, such as low and high temperatures, pH, and salinity, this approach is a feasible option for the removal of bacteria, which can have a negative impact in UD activities.

4.6.4 Gas Removal

Hydrogen sulfide (H_2S) is highly corrosive to equipment, toxic to personnel at low levels, and can have a negative impact on product quality, as well as having a myriad of other negative impacts on the environment. Therefore, its removal and proper treatment are required (Baker Hughes, 2011). H_2S scavengers are frequently used to resolve issues and are considered to be economical and reliable. The chemical scavengers including caustic, peroxides, formaldehyde, nitrites, and various amines, readily react with H_2S to convert it to other sulfur compounds. For example, oxidizers react to generate elemental sulfur or sulfur oxides.

Flaring and venting are used for the disposal of gases (SPE International, 2015b). Flares convert flammable or toxic vapors into less harmful vapors through combustion prior to the release of the gas. Vent systems are used to dispose of gases not burned and disperse these gases into the atmosphere. The primary function of both systems is to prevent pressure build up within the tanks and pipes, as well as to ensure gases released into the atmosphere are at concentration below combustible or toxic levels.

4.6.5 NORM & Softening

Polyvalent cations that create hard water can be reduced through the use of zeolite and bentonite clays (Fakhru'l-Razi et al., 2009). Conventional methods, which involve precipitating heavy metals typically in the form of hydrated metal oxides, or as hydroxides and sulfides, are not favorable when dealing with large volumes of water that contains low concentrations of heavy metals (Dąbrowski et al., 2004). Zeolites are often used as ion-exchange resins (Misaelides, 2011a). A variety of zeolites have been discovered all over the world. They have the general backbone structure of a hydrated aluminosilicate mineral, are porous, and exhibit valuable physicochemical properties, such as cation exchange and molecular sieving (Wang and Peng, 2010). Zeolites have been shown in studies to remove heavy metals and cations, which promote scaling, as well as radioactive material. Surfactant-modified zeolites can enhance cation sorption and the ability to sorb anionic species as well as organic compounds (Misaelides, 2011b; Wang and Peng, 2010). The drawback is that if suspended particles have not been effectively removed from the raw PW, they will occlude the porosity of media and reduce efficiency. Clays, such as bentonite, are found naturally on the Earth's surface and are composed mainly of silica, alumina, water, and weathered rock (Uddin, 2017). Clays can be used as an adsorbent for a variety metals, such as cadmium, iron, lead, magnesium, and more.

Chemical inhibitors are also used in order to prevent the formation of scale by TDS components, which interact and form insoluble precipitates. Common scale inhibitors include phosphate-based compounds and polymers, which primarily work by encapsulating the newly formed precipitate, thereby retarding its further growth (Stewart and Arnold, 2011).

Hydrochloric acid can be used to dissolve calcium carbonate and iron sulfide; however, iron sulfide reacts with the acid to form H_2S gas. Calcium sulfate requires a slow two-step process to treat; it must first be converted to an acid-soluble form then dissolved. Barium and strontium sulfate are the most problematic forms of scale. They must be removed by mechanical means, which intrinsically creates a disposal issue when NORM is imbedded in the solids.

4.6.6 Desalination

The removal of inorganic constituents in solution with high salinity levels is one of the most challenging treatment steps to preform, especially while trying to maintain the economic feasibility of the process. To be able to reuse PW in subsequent well stimulations, reducing the salinity is not necessary, as long as ions that can have adverse impacts on the fracturing process have been removed. However, for use in irrigation or agricultural activities, high salinity is a barrier that must be overcome. Common desalination methods include distillation, membrane processes, freezing desalination, methane hydrate crystallization, high grade water recycling, seawater greenhouses, and others; each has its own set of advantages and disadvantages. Conventional distillation processes, which include multistage flash (MSF) distillation, vapor compression distillation (VCD), and multi-effect distillation (MED), were the technologies of choice before the development of membrane technology (Igunnu and Chen, 2014). These thermal treatment technologies of water are frequently used in regions where the cost of energy is relatively cheap. For MSF, the feed water is pre-heated and then flowed into a chamber with reduced pressure. A relative small portion, approximately 20%, of the feed stream is converted to steam. Typically, further treatment is required to complete the desalination process. For desalination plants, which use distillation processes, thermal and electrical energy usage accounts for the biggest share of operating costs, ranging from 30-50% of the total cost (Ziolkowska, 2015).

Membrane separation processes have become one of the emerging impactful technologies for water treatment in the last few decades (Onsekizoglu, 2012). Membrane processes can be easily scaled up for increased production and can accommodate modular system designs. These desalination techniques include electrodialysis reversal (EDR), reverse osmosis (RO), nanofiltration (NF), membrane distillation (MD), and forward osmosis (FO). RO is a common desalination technique used in industry and community water supply systems, but is limited to TDS levels of 40,000 mg/L, approximately the concentration found in seawater (Gaudlip et al., 2008; Gregory et al., 2011). Notably, PW in the Permian Basin is highly saline ranging from 8-12%, or around 2 to 3.5 times higher than seawater. MD or FO are better equipped to handle high TDS matrices (Shaffer et al., 2013). MD is a thermally-driven separation, in which the liquid permeate is required to undergo a phase change during treatment (Onsekizoglu, 2012). MD offers a relatively lower energy costs as compared to distillation, RO, and evaporation, as well as a high rejection of dissolved, non-volatile species. Also there is a much lower tendency for membrane fouling for conventional evaporation compared with NF and RO.

FO treatment offers the benefit of lower energy cost than RO or MD. The primary difference between RO and FO is the driving force. For RO, hydraulic pressure is applied to overcome the osmotic pressure induced on the feed source by the treated water. In contrast, FO takes advantage of the osmotic pressure. The natural driving force is used to move pure water across the composite membrane formed from a hydrophilic active layer cast onto a micro-porous support (Martin, 2014).

Geothermal and solar desalination provide additional alternatives that can potentially reduce thermal energy cost by using "green" approaches. One potential synergy would be to combine geothermal energy with membrane distillation, allowing a heat exchange to occur between PW and the feed solution (Turchi and Cath, 2015). Solar distillation works on a similar principal, but it requires a large area to accumulate sufficient energy to heat the feed solution. That said, it can be effective for treatment of high salinity solutions, up to ~15% (150,000 mg/L) TDS.

4.7 Conclusions

It is inevitable that the expansion of UD will be required to meet the growing energy demands in the United States. The pivotal factors that have made unconventional oil and gas practice economically viable are the increased energy consumption along with advances in horizontal drilling and HF (Ground Water Protection Council and All Consulting, 2009). However, currently, the world is facing a water crisis due to the lack of clean water. Therefore, in order to maintain responsible practices, the development of cost-effective treatment technologies, which allow PW to be reused in an economical fashion, is essential. A single technology is not an effective option for treating PW due to its complex and highly variable biogeochemical composition. Instead, viable treatment options need to be a series of techniques that are inexpensive, modular in design, have a low tendency for fouling (Shaffer et al., 2013), and can handle significant throughput, as well as efficiently desalinate effluent if recycling for other industrial applications is the ultimate objective. Ultimately, concerns about water usage, water contamination, and induced seismicity can all be addressed through continued research into practical and cost-effective reuse and recycling options.

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CHAPTER FIVE

FORWARD OSMOSIS REMEDIATION OF HIGH SALINITY PERMIAN BASIN PRODUCED WATER FROM UNCONVENTIONAL OIL AND GAS DEVELOPMENT

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Forward Osmosis Remediation of High Salinity Permian Basin Produced Water from Unconventional Oil and Gas Development

Tiffany Liden[1], Doug D. Carlton Jr.[1,2], Shinji Miyazaki[3], Takehiko Otoyo[3], Kevin A. Schug[1,2*]

AUTHOR INFORMATION:

1. Department of Chemistry and Biochemistry, The University of Texas at Arlington, 700 Planetarium Place, Arlington, TX 76019, USA;
2. Affiliate of Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, USA;
3. Asahi Kasei Corporation, 2-1 Samejima, Fuji, Shizuoka 416-8501 Japan

*Correspondence should be addressed to: (email) kschug@uta.edu; Tel.: +1-817-272-3541; Fax: +1-817-272-3808

KEYWORDS: Water treatment; Hydraulic Fracturing; Total Dissolved Solids; Forward Osmosis

5.1 Abstract

Unconventional oil and gas operations are on the rise and an integral component to meeting the nation's energy needs. Produced water is the primary by-product of oil and gas operations, and it has proven challenging to treat to date. The aim of this study was to evaluate the feasibility of using forward osmosis as a remediation option for PW with high TDS levels from the Permian Basin using thin-film composite hollow fiber membranes. Trials consisted of a series of 5 experiments in order to evaluate the performance of the membrane. Three PW samples each from a different location were used to conduct the series of experiments and compare the performance of the membranes with TDS levels ranging from 16,000 to 210,000 mg/L. It can be concluded that FO can be used to extract water from high salinity oil field brines and PW. Flux decreased over the course of the trials due to a combination of membrane fouling, concentration polarization, and temperature fluctuations. The flux of the PW was similar to the flux measured for the PW mimic with small difference due to the influence of activity on the osmotic pressure. The flux was also influenced by temperature and the linear velocity of the feed solution and draw solution.

5.2 Introduction

Conventional and unconventional oil and gas operations are essential for meeting society's growing energy needs. Fossil fuels currently make up about 85% of the United States' energy consumption (Ground Water Protection Council and All Consulting, 2009). Water is vital to the process of obtaining the needed energy. As unconventional oil and gas (UOG) exploration and production have grown, so has public concerns about contamination of groundwater (Darrah et al., 2014; Fontenot et al., 2013; Hildenbrand et al., 2016b, 2016a, 2015), surface water (Drollette et al., 2015; Lauer et al., 2016), and air quality (Harriss et al., 2015; Hildenbrand et al., 2016b; Payne et al., 2017), as well as high water usage, frequently in arid and semiarid regions (Nicot et al., 2014), and the potential inducement of seismic activity (Wang et al., 2014).

The primary by-product of oil and gas operations is the wastewater stream formed from a combination of flow-back water (FBW) and produced water (PW) (Liden et al., 2017). Conventional oil and gas extraction and development tends to only use a moderate amount of water for well stimulation and the formations have high volumes of natural formation water relative to UOG wells (Veil, 2015). FBW is primarily considered the water-based fluid used for hydraulic stimulation. It is used to create pathways for the oil and gas to be recovered in a cost-effective manner, and it returns to the surface during the early stages of oil and gas recovery (Veil, 2015). PW can be found defined as the natural formation water (Coday et al., 2015; Veil et al., 2004). It has a similar chemical composition as the formation from which it came (Alessi et al., 2017; Mueller, 2017). The change in chemical composition of water returning to the wellhead is the basis for the distinction between the two components. However, when addressing UOG wastewater fractions, natural formation water is a minor component of returning water (Veil, 2015). The distinction for UOG operations can be defined as the point that the waste stream returns to the well comingled with the commodity (Liden et al., 2017; Veil, 2015). Therefore, a better definition of PW is water brought to the surface with the oil and gas (Veil, 2015). PW continues to be produced over the lifetime of the well; therefore, the FBW and PW are frequently referred to collectively as PW, as they will be for this study.

In recent years, there has been an exponential expansion in UOG extraction activities, and with it, an increase in PW generation. From 2000-2007, unconventional well production increased from 7% of the U.S. gas production to 46% (Perrin and Cook, 2016). By 2015, two-thirds of the U.S. natural gas output came from approximately 300,000 hydraulically stimulated wells, compared to the 26,000 wells, which existed in 2000 (Ground Water Protection Council and All Consulting, 2009; Perrin and Cook, 2016; Wang et al., 2014). During UOG extraction, approximately 10,000 to 20,000 bbls (bbl) (1 bbl= 42 gal) of water are injected into the individual horizontal operation stages (each stage is about 300 ft at an estimated rate of 70-100 bbl/min) over the course of several days (Liden et al., 2017). The cumulative total of the individual stages can comprise up to a 10,000 ft lateral stretch in the formation. The national median volumes for horizontal wells were 128,000 bbl and 163,000 bbl per oil and gas well, respectively in 2014 (Scanlon et al., 2014). From 2011-2014, 92% of oil and gas production growth was from UOG operations in seven key regions (U.S. Energy Information Administration, 2017). In 2011, 4.9 billion gallons of water was used for UOG production wells in Texas (Shaffer et al., 2013; U.S. Environmental Protection Agency, 2016a). While this only accounted for 1% of the state's water usage, these volumes are frequently localized to arid and semiarid regions, which can lead to notable cones of groundwater depletion. The most prolific contributor to the nation's oil production is the Permian Basin located in west Texas, where crude oil production increased from 850,000 bbl/day in 2007 to over 2.2 million bbl/day in 2012, due to advances in UOG development

(Budzik and Perrin, 2014; Collier, 2016; U.S. Energy Information Administration, 2017). The volume of PW has increased from 18 billion barrels (bbl) to 21.2 billion bbl generated in the U.S. annually from 1995-2012 (Veil, 2015).

The increase in the number of UOG wells, and the concomitant increase in PW, has led to a rise in the demand for wastewater disposal and treatment options (Clark and Veil, 2009). The method chosen is highly influenced by the cost, state regulations (Alessi et al., 2017), and available options which can vary from region to region (Thacker et al., 2015). Currently, approximately, 98% of PW in the U.S. was injected into Class II wells, which are used to inject non-hazardous fluids associated with oil and gas production for disposal or enhanced recovery (Arthur et al., 2008; Clark and Veil, 2009; U.S. Environmental Protection Agency, 2016b). PW disposal wells, also referred to as salt water disposal (SWD) wells due to the high total dissolved solids (TDS) found in PW, are typically considered the most cost-effective and manageable choice for PW disposal (Veil and Clark, 2011). However, concerns over increased seismic activity have grown along with the increasing volume of produced water being disposed of by injection into nonproductive subsurface formations (Hornbach et al., 2016). While, most of the seismicity associated with SWD well injection cannot be felt by the public, evidence indicates the volume of wastewater disposed of in some areas has triggered increased seismic activity (Elst et al., 2016; Gallegos et al., 2015; Hornbach et al., 2016, 2015; Magnani et al., 2017).

As local regulations become more stringent, disposal options decrease. A recent example can be seen in Oklahoma. In 2016, regulators called for a 40% reduction in the volume of salt water being injected in seismic active areas in response the 900 anthropologically induced earthquakes in 2015 with a magnitude of 3 or greater (Jula, 2016). The need to develop methods to reduce the volume of PW injected in to the ground, to treat and reuse, or recycle, PW becomes one of the biggest challenges associated with maintaining the favorable economics of UOG operations (Shaffer et al., 2013).

To date, treatment of PW has been challenging due to the complex nature of its composition (Estrada and Bhamidimarri, 2016), and its variation from formation to formation, or even within a given shale play (Arthur et al., 2008). When evaluating treatment options, the salinity is often a barrier that must be overcome. TDS levels of PW have been measured to range from a few thousand up to 400,000 mg/L (Otton and Mercier, n.d.). Reverse osmosis (RO) is a common desalination technique used in industry and community water supply systems, but it is limited to TDS levels of 40,000 mg/L (about the level of seawater) or lower (Gaudlip et al., 2008; Gregory et al., 2011). Notably, the Permian Basin has high salinity PW, which ranges from 8-12%, or around 2 to 3.5 times higher than seawater. Membrane distillation, mechanical vapor compression, or forward osmosis (FO) are better equipped to handle high TDS matrices (Shaffer et al., 2013). Even so, for membrane distillation and mechanical vapor compression, the liquid permeate is required to undergo a phase change during treatment. This is an energy intensive process that is not needed for FO treatment. Both RO and FO are membrane processes, with the primary difference being the driving force. For RO, hydraulic pressure is applied to overcome the osmotic pressure (π) induced on the feed source by the treated water. On the other hand, FO takes advantage of the osmotic pressure, and uses it as the primary driving force to move pure water across the membrane.

Osmotic pressure was first discovered by Nollet (Phuntsho et al., 2013). Later, van't Hoff derived a mathematical expression for dilute solutions as:

$$\pi = MRTi \qquad (1)$$

where M is the molar concentration, i is the number of particles, R is the ideal gas constant, and T is the temperature (in Kelvins) of the solution. Water flux (J_w) is created by permeate from the feed solution (FS) moving into the draw solution (DS) due to a difference in osmotic pressure across a semi-permeable membrane. It is represented as:

$$J_w = \frac{m}{A \times \Delta t \times \rho_w} \qquad (2)$$

where *m* is mass (mg), *A* is the surface area of the membrane (m^2), *t* is time (hr), and ρ_w is the density of water.

The concept of using FO as a desalination technique for PW has been evaluated by others, but primarily for low salinity UOG wastewaters (Chen et al., 2015; Coday et al., 2015; Minier-Matar et al., 2016). Two studies compared thin-film composite membranes versus cellulose triacetate flat sheets. Coday et al. investigated PW with TDS levels of 25,000 mg/L(Coday et al., 2015) and Chen et al. studied the potential of using FO for treating PW with TDS levels around 6,900 mg/L (Chen et al., 2015). A study by Minier-Matar et al. compared flat sheets versus hollow fiber thin-film composite membranes to evaluate the ability of FO to extract water from PW with TDS levels of 1,600 mg/L and seawater as the DS (Minier-Matar et al., 2016). The studies that have been previously conducted indicate that FO has the potential for full scale implantation for PW treatment. The results indicate that FO can facilitate high rejection of organic and inorganic contaminants (Coday et al., 2015). When comparing the polyamide thin-film composite membranes to cellulose triacetate flat sheets, the polyamide thin-film sheets outperformed its CTA counterpart in terms of pure water flux and reverse salt flux when synthetic brine was used as the FS (Chen et al., 2015).

The premise of this study was to evaluate FO as a remediation technique to concentrate the PW. The decreased volume of the concentrate would lower the volume of PW injected into the subsurface terrain. If the PW is reused the concentrate's condensed volume could reduce shipping cost thereby making it more economical to reuse the waste stream. The study began by building a bench system which was used to evaluate the proof of concept: could FO be used to effectively concentrate high salinity PW from the Permian Basin. The flux was compared at various flow rates of the FS and DS. Also, a NaCl (aq) mimic was used in lieu PW as the FS and run under the same condition in order to compare the performance of the flux. FO successfully decreased the volume of PW by extracting water from the FS. During this trial, all experiments were conducted in ALFS (active layer of the membrane in contact with the feed solution); however, future studies will need to test the other mode of operation, ALDS (active layer of the membrane in contact with the draw solution) and determine optimal conditions. Investigations leading to a fieldable process will have to be tested as well, which will begin by increasing the length of time the system is allowed to run.

5.3 Materials and Methods

5.3.1 Bench Top System

FO modules were provided by Asahi Kasei Corporation (Fuji, Japan). The module consisted of a bundle of 20 composite hollow fiber membranes each with a polyethersulfone support layer and a thin-film polyamide active layer, collectively encased in a plastic shell. The modules had a length of 105 mm and an outer diameter (OD) of 18 mm. Each fiber had an inner diameter (ID) of 0.7 mm.

The system used was custom built (Figure 1). Two variable speed Micropumps (Vancouver, WA) were used to regulate the velocity inside (GA-V21.CFS.A) and outside (GJ-N21.FF2S.A) the hollow fiber membrane; these were controlled with two GPD-2303S bench power supplies (GW Instek, New Taipei City, Taiwan). Two closed loop systems were created, one for the FS and the other for the DS, using primarily polyurethane tubing with a 6 mm OD. Silicon tubing approximately 5 cm long with a 6 mm OD was used as bridge from the polyurethane tubing to the module. The FS and DS were each stored in 1 L pots throughout the experiment. Changes in mass of the FS, monitored with a Shimadzu TX3202L digital balance, was used to determine the water flux (Shimadzu Scientific Instruments, Inc., Columbia MD, USA). Temperatures of the FS and DS were controlled using heat exchangers and a circulating water bath (Polyscience, Niles, IL). Temperatures were monitored with K type thermocouple probes and a GL240 data logger (Graphtec, Irvine, CA).

5.3.2 Feed solution and Draw solution

FO experiments consisted of a FS of either PW or sodium chloride mimics of PW prepared to exhibit the same conductivity of the PW. The DS consisted of NaCl (BDH ACS grade, VWR, Radnor, PA) solutions at least twice the estimated salt percentage of the FS when possible. Maximum concentration of DS was saturated NaCl or 26% (w/w). The salt percentage of the FS was estimated from a calibration of conductivity with prepared salt standards up to 10% NaCl (aq) or using a SW pen refractometer (Atago, Tokyo, Japan). The membrane performance was evaluated with the FS in contact with the active layer (AL-FS) inside of the hollow fiber. In principle, the modules can also be operated with the DS in contact with the active layer (AL-DS) inside of the hollow fiber, but that configuration was not evaluated during this study. It would be expected that AL-DS would yield similar results as was seen with AL-FS.

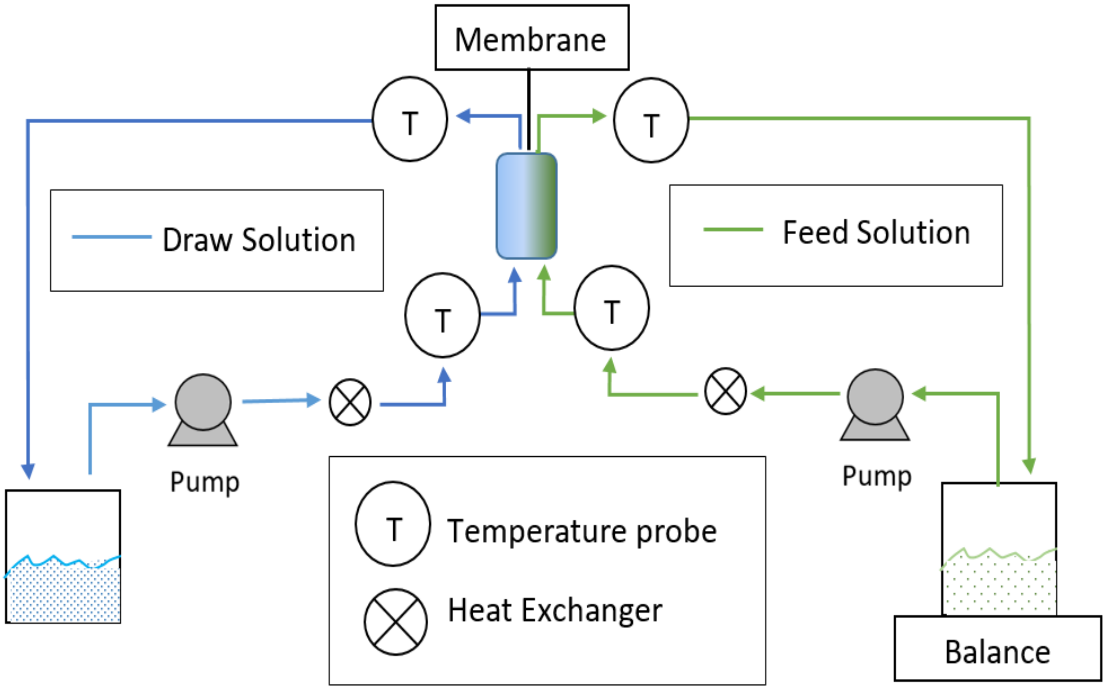

Figure 1. Forward osmosis benchtop system. The feed solution (on the right, in green) and the draw solution (on the left, in blue) were arranged in a recirculating configuration.

Each PW used was collected from the Permian Basin in west Texas (Figure 2). Nolan produced water (Nolan-PW) was from the Cline Shale formation of Nolan County. This sample was collected from an unconventional oil exploration on-site waste pit approximately 1 week after well completion. It possessed a conductivity near 20 mS/cm, equivalent to 0.85% salinity. This water would most likely be classified as FBW because of its age and chemical composition (Thacker et al., 2015).

Midland produced water (Midland-PW) was collected in Midland County from a saltwater disposal (SWD) well. This PW was a composite mixture, delivered to this specific SWD disposal site by six pipelines, as well as trucks purported to be from production sites up to 50 miles away. The PW is combined to form a composite mixture upon arriving at the community site. The Midland-PW was characterized by a conductivity of approximately 140 mS/cm, which is equivalent to approximately 10% salinity. Midland-PW contained more particulate than Nolan-PW, so vacuum filtration was used to remove the prominent oil layer and solids prior to treating with FO. Some oil remained suspended in solution, but was found to be sufficient for FO treatment assessment.

Dawson produced water (Dawson-PW) was collected in the region of Dawson County. This sample was collected from a community SWD well similar to Midland-PW; however, all the PW was brought to the site by truck. This was a mixture of produced water from multiple conventional and unconventional oil and gas wells delivered by trucks in close proximity to the SWD site. Dawson-PW had a conductivity of 150 mS/cm, equivalent to 11.25% NaCl (aq). This fluid had a prominent layer of oil on the surface, even after vacuum filtration with 25 µm filter paper.

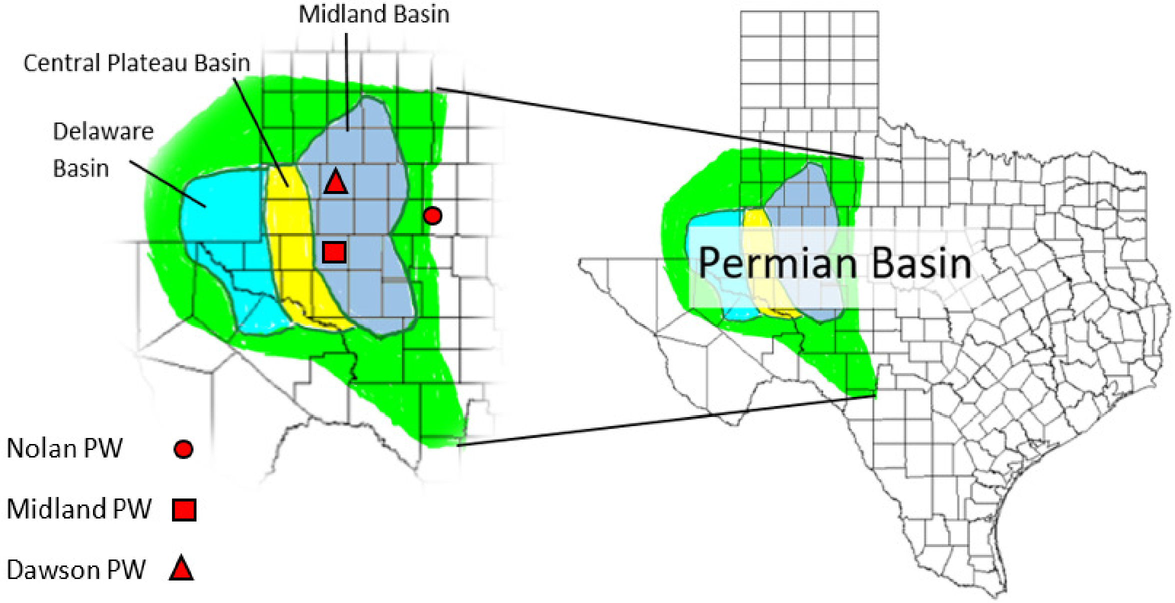

Figure 2 Collection point for the produced water samples are shown. Nolan-PW (circle) was collected from a waste pit in Nolan County. Midland-PW (square) was collected from a saltwater disposal site in Midland County. Dawson-PW (triangle) was collected at a salt water disposal site in Dawson County.

5.3.3 Analytical Instrumentation

Carbon content was measured through typical combustion techniques using the Shimadzu TOC-L Analyzer (Shimadzu Scientific Instruments, Inc.). Total carbon (TC) and inorganic carbon (IC) were measured. Total organic carbon (TOC) was determined by the difference of TC and IC. Total nitrogen (TN) was also measured with the same instrument using a TN module add-on (TNM-L, Shimadzu). Chemical speciation was performed using headspace sampling for gas chromatography with dual columns and dual flame ionization detectors (HS-GC-FID). Two columns were used simultaneously to increase confidence in analysis: BAC 1 Plus (30 m x 0.32 mm (ID) x 1.80 µm) and BAC 2 Plus (30 m x 0.32 mm (ID) x 0.60 µm) (Restek Corporation, Bellefonte, PA). The autosampler was an AOC-5000 plus coupled to a GC-2010 plus (Shimadzu

Scientific Instruments, Inc.). The injection volume was 1 mL of the HS. The injector was set at 225 °C with a split ratio of 10:1 and the dual column system was operated in constant linear velocity mode with a linear velocity (helium) of 50 cm/sec. The column oven was initially set to 35 °C (held for 4.5 min), then ramped at 30 °C/min to 205 °C (and held for 2.0 min). Both FIDs were set to 225 °C. Conductivity was measured with a Horiba LAQUA DS-70 (Kyoto, Japan). Elemental analysis was performed by inductively coupled plasma – optical emission spectroscopy (ICP-OES) using EPA method 200.7 an ICPE 9000 instrument from Shimadzu Scientific Instruments, Inc. Quantification of anions was completed using ion chromatography through an outside source, TTI Environmental Laboratories (Arlington, TX) as per the EPA methods 300.

5.3.4 Experimental Design

Three trials of a 5-part experimental series were conducted using salt water mimics and PW to evaluate the performance of the described FO membranes (Table 1). A new FO module containing fresh membranes was used with each trial, as well as a new PW. The FO module used in the trial with Nolan-PW was tested under all five experimental conditions. The FO modules used during trials with Midland and Dawson-PWs were tested with the first four experimental conditions. Experiment 5 was intended to evaluate the performance of the membrane with a high salinity FS. NaCl was added to Nolan-PW to increase the salinity by 10% and the DS was adjusted to a level that maintained approximately the same flux recorded in experiment 3. However, due to the high salinity initially of Midland and Dawson-PWs used in experiment 3, the DS was already near saturated or saturated and could not be increased further to perform experiment 5 for those samples.

The temperature was maintained near 25°C for Midland-PW and Dawson-PW for the FS and DS. For experiments using Nolan-PW, the temperature was not controlled and fluctuated with the room temperature and pumping speed.

Table 1 Experimental design of tests performed for the FO treatment of each PW and membrane tested.

Experiment	Purpose	FS Parameters	DS Parameters
1	Quality control to ensure the performance of the membrane had been maintained throughout storage.	Deionized (DI) water	3.5% NaCl
2	Surveyed various flow combinations between the FS and DS using PW as FS to evaluate the effect on flux.	Nolan-PW	10% NaCl
		Midland-P	25% NaCl
		Dawson-PW	26% NaCl
3	Replicated the same flow combinations used in experiment 2 using salt mimic as FS to the compare flux performance to those measure with PW. The conductivity of the salt mimic was the same as the PW.	Salt Mimic conductivity = Nolan-PW	10% NaCl
		Salt Mimic conductivity = Midland-PW	25% NaCl
		Salt Mimic conductivity = Dawson-PW	26% NaCl
4	A 10-part series of 5-hr sessions tested the durability and robustness of the membrane. PW was continuously recycled for 5 hr through the membrane. The module was washed* and stored in deionized (DI) water overnight then used the following day with fresh PW and DS.	Nolan-PW	10% NaCl
		Midland-P	25% NaCl
		Dawson-PW	26% NaCl
5	Evaluate FO systems' performance in a high salinity environment.	PW + required NaCl to increase salinity by 10%	Increased to required % salinity to maintain flux measured in experiment 3

*Washing: The membrane was washed before storing. 1L of DI water was used for the DS and FS. The system was turned on for 10 min at the experimental flow rate, and then both the DS and FS were replaced with fresh DI water, and the process was repeated 5 more times for a total of 60 min.

5.4 Results

5.4.1 Characterization of PW

The chemical composition of each PW was measured, and these data are summarized in Table 2. Various metals as well as TDS, TOC, and pH were measured. Nolan-PW which has the highest silicone to TDS ratio indicating it is possible an additive in the FBW as a defoamer (Borchardt, 1989). Nolan also contained the highest concentration of sulfate at 224 mg/L, Midland

PW TDS is composed of 7% group 2 cations which combined with alkalinity levels, 426 mg/L, which exceed reuse limits (Figure 3) present an increased scaling potential (Oetjen et al., 2018). The calcium levels in exceeds the limits for use in cement water prior to concentrating it with the FO system for all the waste streams and Midland PW exceeds the limits for reuse as well stimulation fluid (Figure 3). Therefore, reuse without treating the concentrate is not an option. Magnesium levels again indicate that the Midland and Dawson PW prior to concentration would not be acceptable for reuse as cement water for well development, however, the levels are significantly below the limits for reuse during well stimulation.

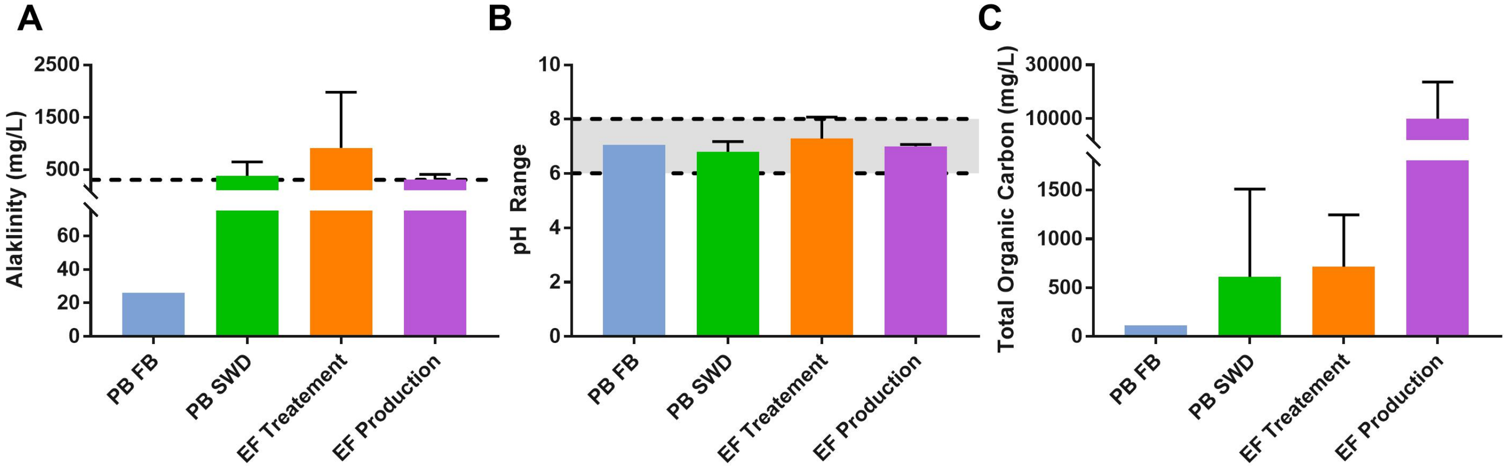

Figure 3 Bar graph of measured concentration of constituents of concern with respect to scaling. The dashed lines represent recommended water quality guidelines for the reuse of PW for production well stimulation made by Hildenbrand, King, and Oetjen et al (Hildenbrand et al., 2018; King, 2011; Oetjen et al., 2018).

Table 2. Chemical composition of selected constituents for the produced water samples studied in this work.

	Nolan-PW	Midland-PW	Dawson-PW
Component	mg/L	mg/L	mg/L
TDS	16,000 ± 3,000	180,000 ± 40,000	210,000 ± 30,000
B	6.65 ± 0.6	47 ± 7	37 ± 2
Ba	0.1 ± 0.2	2.7 ± 0.3	2.0 ± 0.2
Ca	1420 ± 90	2900 ± 200	1600 ± 100
Fe	4 ± 2	4 ± 2	7 ± 2
K	74 ± 4	450 ± 40	370 ± 30
Li	0.45 ± 0.7	18 ± 1	13 ± 1
Mg	109 ± 9	490 ± 36	330 ± 26
Mn	3 ± 1	0.1± 0.1	0.25 ± 0.9
Na	26,000 ± 2,000	43,000 ± 3,000	50,000 ± 3,000
Si	16 ± 0.9	15 ± 1	19 ± 1
Sr	18 ± 2	520 ± 40	390 ± 30
Cl^-	831	8470	8300
Br^-	<0.0260	67	60.9
NO_3^-	<0.0300	45.6	45.6
SO_4^-	224	33.1	49.4
F^-	0.939	2.37	2.48
TOC	116	1032	889
pH	7.05	6.45	7.12
Alkalinity (CO_3^{2-})	26	426	162

5.4.2 FO Trials

As a condition to progress to subsequent experiments, each FO module was checked during experiment 1 to assess appropriate performance relative to that specified on the label by the manufacturer. All the modules tested passed the quality control check.

During experiments 2 and 3, for tests involving all three PWs, flux increased as the flow rate of the DS was increased. An increased flow rate of the FS yielded a slight increase of the flux rate, but not as significant as when the DS flow rate was increased. The greatest flux was seen when both the DS and the FS had higher flow rates (180 mL/min for the FS and 1480 mL/min for the DS using Nolan PW). Flux measurements and experimental parameters are noted in Table 3.

Experiment 3 involved the use of a mimic salt solution prepared to exhibit equivalent conductivity as the PW for that system (i.e., Midland-PW had a conductivity of 135.4 mS/cm; for experiment 3, the FS was a 10% NaCl solution, which had a conductivity of 132.9 mS/cm). The model NaCl (aq) system for Nolan-PW yielded flux values slightly higher than those measured using PW with the same flow rate. For both Midland-PW and Dawson-PW salt water mimic solutions, the flux was lower than measured with the real PW at the same flow rate. During the trial using Dawson-PW, the maximum DS flow rate was set at 1200 mL/min rather than the 1480 mL/min used with Nolan- and Midland-PWs. This was because of the decrease in pump performance over time at the high voltages needed to reach higher flow rates.

During experiment 4, a 10-part series of 5-hr sessions, the flux decreased an average of 12% each day using Nolan-PW, as shown in Figure 4. Through each 5-hr segment using Midland-PW, the flux decreased each day an average of 36%. This flux decrease was nearly 3 times that observed for tests using Nolan-PW. During the 50-hour trial using Dawson-PW, a 30% average decrease was observed each day. In nearly all cases, the flux was restored after washing with DI

Table 3 Experimental parameters and measured flux.

PW	Expt	Feed Solution (FS)	Draw Solution (DS)	DS (% NaCl)	Flux (LMH)	FS Flow (mL/min) (cm/sec)	DS Flow (mL/min) (cm/sec)
Nolan	1	DI H_2O	NaCl	3.5	10.6	18 (3.9)	370 (2.5)
	2.1	PW	NaCl	10	11.3	18 (3.9)	370 (2.5)
	2.2	PW	NaCl	10	10.9	180 (39)	370 (2.5)
	2.3	PW	NaCl	10	14.0	180 (39)	1480 (10)
	2.4	PW	NaCl	10	13.3	18 (3.9)	1480 (10)
	3.1	0.85% NaCl	NaCl	10	12.2	18 (3.9)	370 (2.5)
	3.4	0.85% NaCl	NaCl	10	15.1	18 (3.9)	1480 (10)
Midland	1	DI H_2O	NaCl	3.5	12.0	18 (3.9)	370 (2.5)
	2.1	PW	NaCl	25	8.4	18 (3.9)	370 (2.5)
	2.2	PW	NaCl	25	10.8	180 (39)	370 (2.5)
	2.3	PW	NaCl	25	12.2	180 (39)	1480 (10)
	2.4	PW	NaCl	25	10.1	18 (3.9)	1480 (10)
	3.1	10% NaCl	NaCl	25	7.5	18 (3.9)	370 (2.5)
	3.4	10% NaCl	NaCl	25	7.4	18 (3.9)	1480 (10)
Dawson	1.1	DI H_2O	NaCl	3.5	14.7	18 (3.9)	370 (2.5)
	2.1	PW	NaCl	26	8.4	18 (3.9)	370 (2.5)
	2.2	PW	NaCl	26	14.0	180 (39)	370 (2.5)
	2.3	PW	NaCl	26	14.9	180 (39)	1200 (8.1)
	2.4	PW	NaCl	26	11.0	18 (3.9)	1200 (8.1)
	3.1	11.25% NaCl	NaCl	26	7.2	18 (3.9)	370 (2.5)
	3.4	11.25% NaCl	NaCl	26	10.5	18 (3.9)	1200 (8.1)

water and storing the membrane in DI water overnight. The beginning flux for the concluding two experiments (denoted experiments 4.09 and 4.10) using Nolan-PW averaged 13.3 LMH, while the preceding 40 hrs exhibited, on average, a beginning flux of 14.2 LMH. For experiments 4.09 and 4.10, using Midland-PW, the beginning flux averaged only 8.2 LMH, while the preceding 40 hrs exhibited an average beginning flux of 9.6 LMH. A summary of the measured flux for each time point for all three PWs is noted in the supplemental table (Table SI 1). It was observed through the duration of experiment 4 using Nolan-PW, that an increase in FS temperature had a positive influence on flux over the 300 min experimental series. The temperature was subsequently controlled in trials using Midland and Dawson-PW. Due to limited supply, the Nolan-PW could not be retested under temperature-controlled conditions.

Experiment 5 was used to evaluate the performance of the FO membrane with a high salinity matrix, as outlined in Table 4. The FS, Nolan-PW, was augmented with NaCl to increase the salinity by 10%. Consequently, the DS was adjusted to 25% salinity. As the salinity difference between the FS and DS was increased from a 9% difference for Nolan-PW to a 14% with the addition of NaCl, so the flux. Expt 2.2 and 2.3 had a flux of 11.3 and 13.3 LMH, respectively. While Expt 5.1 and 5.4 using the augmented Nolan-PW had a flux of 12.3 and 15.8 LMH, respectively.

Table 4. Summary of Experiment 5 flux for augmented salinity Nolan-PW.

PW	Expt	Feed Solution (FS)	Draw Solution (DS)	DS Conc.	Flux LMH	FS Flow (mL/min)	DS Flow (mL/min)
Nolan	5.1	PW + 10% NaCl	NaCl	25 %	12.3	18 (3.8)	370 (2.5)
	5.4	PW + 10% NaCl	NaCl	25 %	15.8	18 (3.8)	1480 (10)

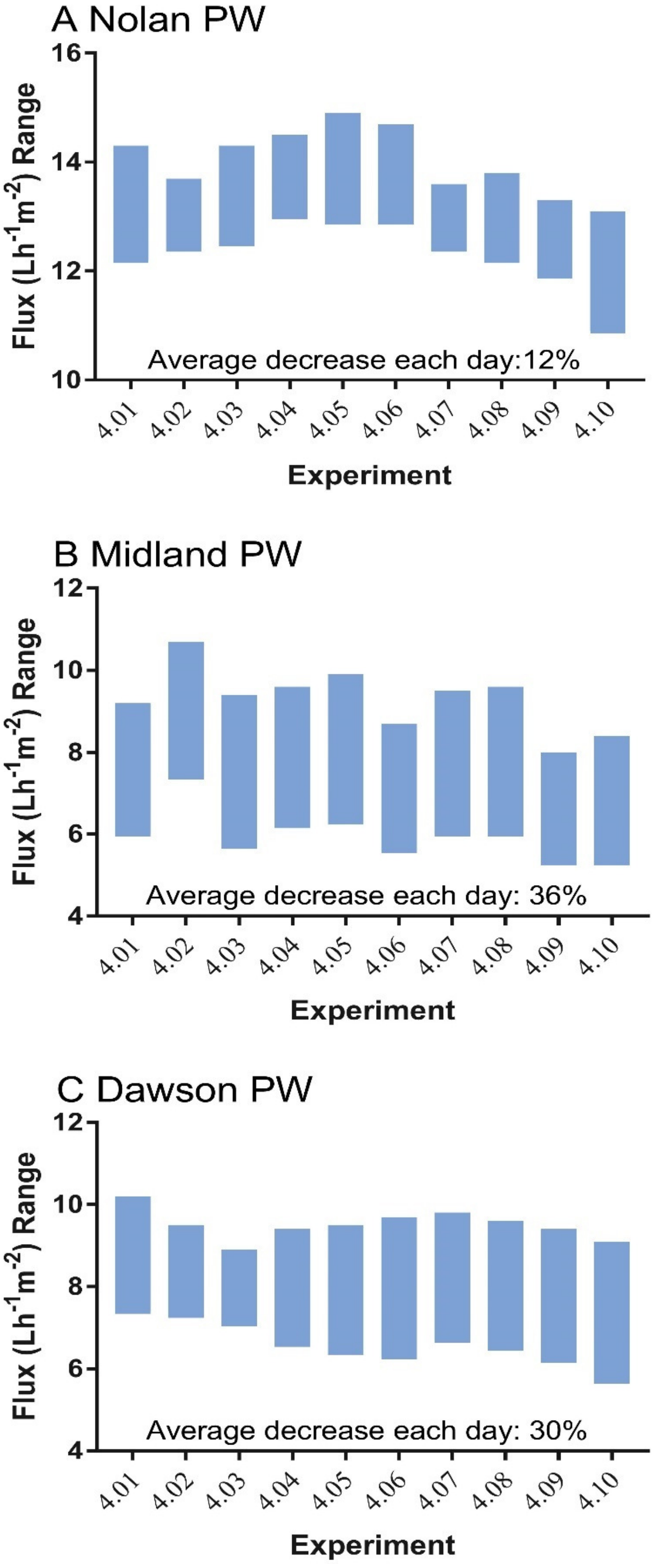

Figure 4 The range for initial and final flux for each day over the course of 10 days is plotted to represent the decrease in flux measured each day. ((a) Nolan-PW, (b) Midland-PW, and (c) Dawson-PW) The % decrease in the flux is listed at the top of each day.

5.4.3 Analytical Comparisons of TOC and TN in FS and DS

The compositions of the FS and DS were monitored at discrete points through experiment 4, a 10-part series of 5-hr FO treatment sessions. Samples of the FS and DS were collected on the first day, at the beginning and the end (times 0 and 5 hr, respectively). Another set of samples were again collected and analyzed on the fifth day, at the beginning and the end (times 20 and 25 hr, respectively). A final set of samples was collected for analysis on the tenth day, at the beginning and the end (times 45 and 50 hr, respectively).

5.4.3.1 Carbon, Nitrogen, and Metal Analysis

Both carbon and nitrogen compounds were lost from the FS throughout each experiment. An increase in carbon was measured in the DS; however, the loss measured from the FS was greater than the amount of carbon transferred to the DS. The tubing was stained an orange color by the end of the trials; therefore, the unaccounted-for loss of carbon and nitrogen was attributed to evaporation and adsorption to the lines and membrane.

Dawson-PW consistently lost approximately 33% of TOC at each of the 3 sets of collection points (0 to 5 hr, 20 to 25 hr, and 45 to 50 hr, respectively). There was a larger loss in TOC seen during the Nolan- and Midland-PW experiments, for the first set of collection points compared to the last two. For Nolan-PW, 40% was lost originally as compared to 12% and 5% decreases in TOC levels for the final collection points. There was a 29% decrease in the TOC mass for Midland-PW originally, compared to a decrease of 10% and 8% during the final 2 sets of collection points.

There were no detectable amounts of metals transferred to the DS. However, both nitrogen and carbon species increased in the DS after each experiment. TC lost from Nolan-PW, Midland-PW, and Dawson-PW was 92, 166, and 161 mg, respectively. This data is shown in table SI 2 of the Electronic Supplementary Information document prepared to accompany this article. Only 2.6, 1.8, and 5.8 mg were transferred to the DS for Nolan-, Midland-, and Dawson-PW, respectively. The majority of the lost components from the FS were not recovered in the DS, as represented in Figure 5.

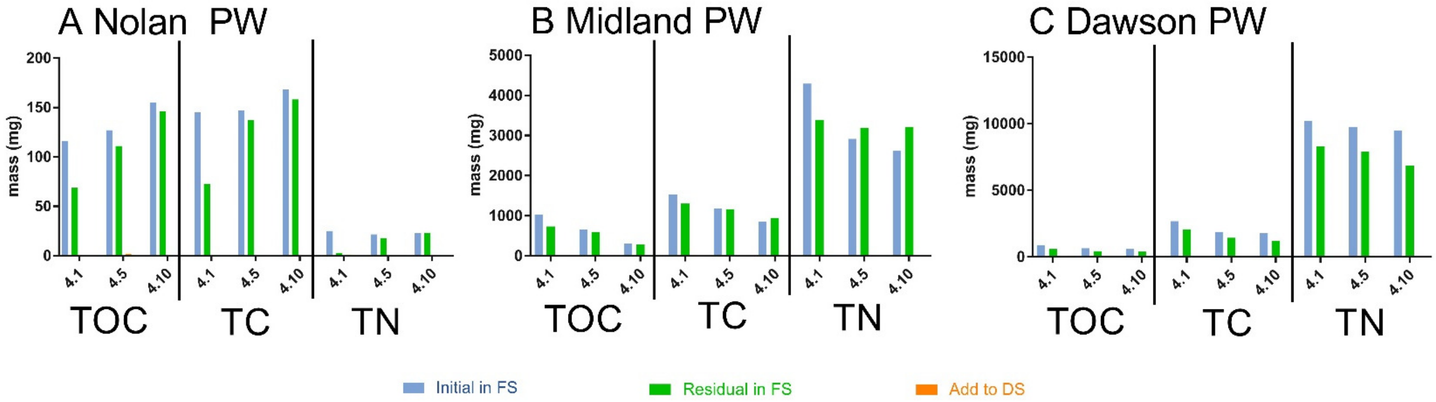

Figure 5 Initial mass of TOC and TN in each PW, Nolan, Midland, and Dawson PW are represented. The final PW concentrations and the amount transferred to the DS is represented as well.

5.4.3.2 Compound Identification using GC

Nitrogen-containing compounds were not detected in the FS or DS through GC experiments indicating that nitrogen containing compounds measured with the TNM-L were inorganic or non-volatile organics. Methanol, ethanol, acetone, and dichloromethane (DCM) were transferred to the DS in at least one experiment, as shown in Table 5. Isopropyl alcohol was detected in all three PWs, but it was not transferred to the DS in detectable quantities during the experiments. Propargyl alcohol was detected in Midland-PW and Dawson-PW, but it was not detected in the DS when each of these samples was treated. Ethyl acetate was detected in the FS for Nolan-PW, but did not appear to be transferred to the DS. Aromatic compounds, ethyl benzene, as well as *meta*-, *para*-, and *ortho*-xylenes, were detected in Dawson-PW, but they were not detected in the DS.

Table 5 Mass of organics measured in the FS and DS for compounds that were transferred across the membrane over the course of the 5 hr-10 part series experiments. ND indicates not detected.

Sample	Time Point (hr)	Methanol mg, FS	Methanol mg, DS	Ethanol mg, FS	Ethanol mg, DS	Acetone mg, FS	Acetone mg, DS	DCM mg, FS	DCM mg, DS
Nolan PW	**0**	3.7	ND	11.9	0.9	1.45	ND	5.7	ND
	5	2.6	1	12.9	1.1	1.68	0.04	3.3	0.2
	20	3.2	ND	9.8	ND	1.32	ND	7.8	ND
	25	3	0.5	10.5	0.2	2.12	0.05	4.4	0.2
	45	1.9	ND	11.7	0.4	1.54	ND	1.7	ND
	50	1.4	0.5	9.9	0.6	1.4	0.05	1	ND
Midland PW	**0**	35.4	0.2	ND	2.2	28.8	0.2	0.7	0.4
	5	19.4	6.5	ND	1.6	20	1.5	0.6	0.5
	20	17.5	0.1	ND	0.2	16.8	0	1.1	0.5
	25	15.2	3	0.8	0.3	17.9	0.9	0.5	0.4
	45	1.8	0	ND	ND	16.9	ND	0.8	0.4
	50	1.7	0.4	ND	0.3	21.5	1.3	0.6	0.6
Dawson PW	**0**	ND	ND	ND	ND	16 ± 2	ND	ND	ND
	5	ND	ND	ND	4.7 ± 0.3	12.2 ± 0.9	1.2 ± 0.1	ND	ND
	20	ND	ND	ND	ND	15 ± 1	0	ND	ND
	25	ND	ND	ND	2.2 ± 0.1	0.77 ± 0.05	1.03 ± 0.06	ND	ND
	45	ND	ND	ND	ND	13.3 ± 0.3	ND	ND	ND
	50	ND	ND	ND	0.30 ± 0.07	9.0 ± 0.6	0.87 ± 0.06	ND	ND

5.5 Discussion

Flux in an FO experiment can be influenced by the flow rate of the draw and feed solutions, as well as by the osmotic pressure (π). The influence of flux by the flow rate was demonstrated during experiments 2 and 3. However, the primary driving force for flux in FO can be considered as a difference in osmotic pressure between the FS and DS (Phuntsho et al., 2013). Equation 2 only holds true for ideal or very dilute solutions. As the TDS level increases, solute molar concentrations are not the primary factor affecting osmotic pressure. Activity (ɑ) and chemical potential (μ) play a role in the influence of the flux as well (Hamdan et al., 2015). The activity or "effective concentration" is affected by the ion's charge, concentration, and the diameter of the ion. Activity is represented as:

$$\{a\} = [M]\gamma \qquad (3)$$

Where [M] is the molar concentration and γ is the activity coefficient. The ionic strength (*I*) of the solution influences the activity coefficient and is represented as:

$$I = \frac{1}{2}\Sigma[M]_i z_i^2 \qquad (4)$$

Where z is the charge of the ion. For dilute solutions, the activity coefficient is generally considered to be unity, but as the solute concentration increases, the activity coefficient decreases ($\gamma \leq 1$).

Therefore, opposite trends were seen when comparing a low salinity system, Nolan-PW, to the NaCl mimic for that system, versus a high salinity system, Midland and Dawson-PW, to the NaCl mimics for each of those systems. The model NaCl(aq) system for Nolan-PW yielded flux values slightly higher (12.2 LMH at a flow rate of 18 mL/min for the FS and 370 mL/min for the DS) than those measured using real PW (11.3 LMH) with the same flow rate. It is clear that the NaCl (aq) mimic does not completely represent the PW. The salt water mimic was prepared to match the conductivity of the PW. Since the organic content in the Nolan-PW was not accounted for by the conductivity, the PW has a higher particle content than the mimic. Therefore, the osmotic pressure difference between the PW FS and the DS was less than the salt mimic FS and DS for Nolan-PW, as represented in Figure 6

For the Dawson- and Midland-PW systems, the opposite trend was observed. At a flow rate of 18 mL/min for the FS and 370 mL/min for the DS, the flux for the PW was higher than the flux measured for the NaCl mimics 8.4 LMH and 7.4 LMH, respectively. Based on the initial characterization, Midland- and Dawson-PWs resembled brine mixtures, whereas Nolan-PW was described previously as low salinity FBW (Thacker et al., 2015) Due to the combined high TDS levels and the organics, the activity or "effective concentration" of constituents in the Midland- and Dawson-PWs was less than that for the salt mimic.

During experiment 4, the decrease in initial flux over the time course was due to a combination of membrane fouling, concentration polarization, and temperature fluctuations (Minier-Matar et al., 2016; Phuntsho et al., 2012; You et al., 2012; Zhao and Zou, 2011). Using Nolan-PW, the average daily flux decrease of 12% was less than that for the other two systems. Throughout the experiments, it was noted that the temperature would increase through the course of the day. Flux across the FO membrane is temperature sensitive and could be increased by heating the solutions, a phenomenon that has been previously observed by others (Boo et al., 2013; Heo et al., 2016; Lay et al., 2012; Phuntsho et al., 2012; You et al., 2012; Zhao and Zou, 2011). The influence of temperature was eliminated by adding a temperature control bath during the remaining trials.

The average daily decrease of flux for Midland- and Dawson-PW trials were more comparable, at 36% and 30%, respectively. The decrease in flux each day for the last two trials was due to concentration polarization and fouling. Since the DS and the FS were cycled continuously for 5 hrs, the DS was diluted and the FS became more concentrated, thus decreasing the osmotic pressure. The effects of this driving force can clearly be seen by the flux recovery after overnight washing and replacing the FS and DS between each 5-hr session.

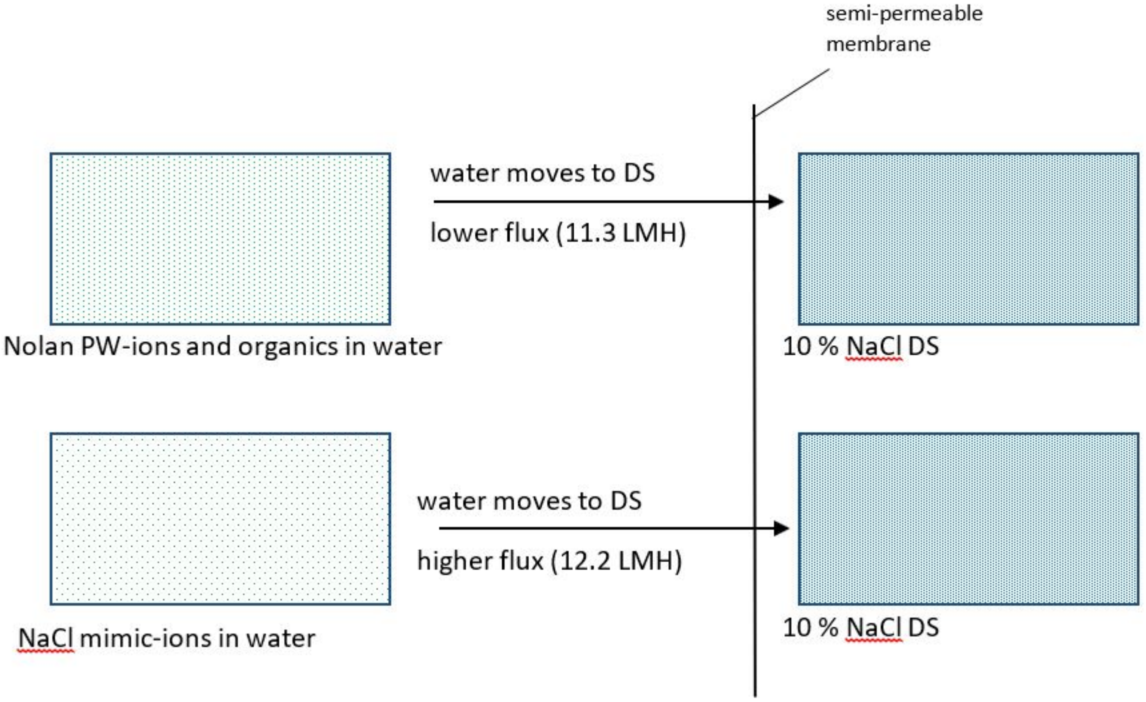

Figure 6a The flux difference from Nolan-PW (11.3 LMH) and NaCl mimic (12.2 LMH) at a flow rate of 18 ml/min and 370 mL/min for the FS and DS represents the osmotic pressure difference between the FS and DS. Nolan-PW, a low salinity system, has a smaller osmotic pressure difference between the FS and DS compared to the osmotic pressure difference between the FS and DS for the Nolan NaCl mimic. This is due a higher solute concentration because of the organics in the PW.

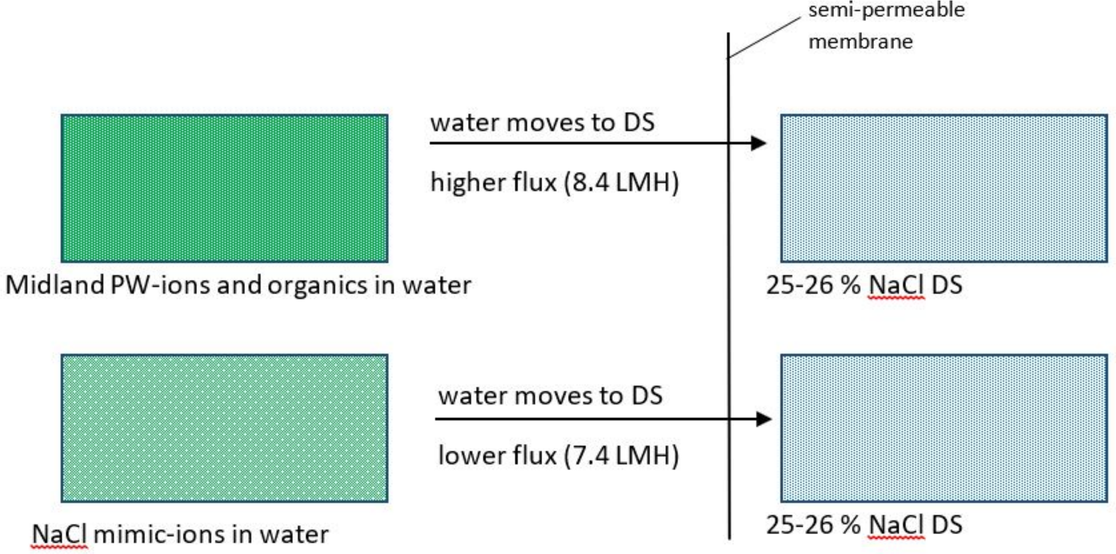

Figure 6b The flux difference from Midland-PW (8.4 LMH) and NaCl mimic (7.4 LMH) at a flow rate of 18 ml/min and 370 mL/min for the FS and DS represents the osmotic pressure difference between the FS and DS. Midland and Dawson-PW, a high salinity system, has a larger osmotic pressure between the FS and DS compared to the osmotic pressure difference between the FS and DS for the NaCl mimics for each system. This is due a higher solute concentration because of the organics in the PW decreasing the activity or "effective concentration".

While the flux was restored after washing, and even with storing the membrane in DI water overnight and replacing the FS and DS initially, toward the end of the 10 days, the starting flux of each day decreased. The starting solution temperature for experiments 4.09 and 4.10 using Nolan-PW was near the median temperature of the 10-part series, indicating temperature effects were not the source of the decreased starting flux on the last two days. For Midland- and Dawson-PWs, the temperature was controlled and the initial flux for experiments 4.09 and 4.10 dropped for both systems, indicating membrane fouling.

Nolan- and Midland-PW had high TOC levels and both measured a more significant decrease in flux on the last two days of the trials, indicating that organic constituents could be fouling the surface. Midland-PW had a higher concentration of group II cations, so scaling could also be contributing to the decrease in initial flux over time. While using Midland-PW, an orange scale accumulated over time along the silicone and polyurethane tubing during the various experiments. This did not occur for other trials. It is therefore, very possible that the scaling could also accumulate on the membrane surface and reduce flux.

5.6 Conclusions

Through these three trials, it can be concluded that FO can be used to extract water from high salinity oil field brines thereby reducing the volume of PW. This makes FO a feasible option for continued development as a viable remediation approach for high salinity PW matrices. Small organic compounds were transferred to the DS with water. This was a consistent result for all three modules when the compounds were present in the FS. It should be noted that modules are stored until initial use in 20% ethanol, which could be a plausible explanation for the increased ethanol levels found in both the FS and DS. More extensive initial membrane washing protocols will be investigated for subsequent experiments. Temperature influences the flux and thus, needs to be controlled throughout all experiments. While it is believed that AL-DS mode will behave similarly, future work should compare the module performance between AL-DS and AL-FS modes of operation.

The two most probable causes for flux loss were membrane fouling and concentration equilibration between the FS and DS. Future work will focus on maintaining a large conductivity difference between the FS and DS by preventing the DS from being diluted. It is highly probable that the unrecovered TOCs are adhering to the membrane surface, but analysis to determine the identity of the foulant should be completed in future work. Performance during fouling trials and the robustness of the membranes should be evaluated, as well. Future work should include operating for longer continuous spans. How best to clean the module after fouling should be considered. This can be accomplished by determining the degree of fouling at which the flux cannot be recovered after cleaning. Testing how frequently the membrane needs to be cleaned to maintain the flux, and how long the cleaning operations need to be performed (e.g. daily for one hour or every min for 10 sec, etc.) will be crucial to establishing a practical operation protocol for continued use. Further investigation is still needed to evaluate the optimal conditions for treatment of PW using this FO set-up, especially in the context of increasing throughput and applying the treatment system in the field.

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5.8 Supplementary Information

TableSI 1 Summary of Experiment 4 flux for Nolan-PW, Midland-PW, Dawson-PW.

PW	PW-Expt	Feed Solution (FS)	Draw Solution (DS)	DS Conc.	Flux, Begin $L\bullet h^{-1}\bullet m^{-2}$	Flux, End $L\bullet h^{-1}\bullet m^{-2}$
Nolan	4.01	PW	NaCl	10 %	14.3	12.2
	4.02	PW	NaCl	10 %	13.7	12.4
	4.03	PW	NaCl	10 %	14.3	12.5
	4.04	PW	NaCl	10 %	14.5	13.0
	4.05	PW	NaCl	10 %	14.9	12.9
	4.06	PW	NaCl	10 %	14.7	12.9
	4.07	PW	NaCl	10 %	13.6	12.4
	4.08	PW	NaCl	10 %	13.8	12.2
	4.09	PW	NaCl	10 %	13.3	11.9
	4.10	PW	NaCl	10 %	13.1	10.9
Midland	4.01	PW	NaCl	25 %	9.2	6.0
	4.02	PW	NaCl	25 %	10.7	7.4
	4.03	PW	NaCl	25 %	9.4	5.7
	4.04	PW	NaCl	25 %	9.6	6.2
	4.05	PW	NaCl	25 %	9.9	6.3
	4.06	PW	NaCl	25 %	8.7	5.6
	4.07	PW	NaCl	25 %	9.5	6.0
	4.08	PW	NaCl	25 %	9.6	6.0
	4.09	PW	NaCl	25 %	8.0	5.3
	4.10	PW	NaCl	25 %	8.4	5.3
Dawson	4.01	PW	NaCl	26 %	10.2	7.4
	4.02	PW	NaCl	26 %	9.5	7.3
	4.03	PW	NaCl	26 %	8.9	7.1
	4.04	PW	NaCl	26 %	9.4	6.6
	4.05	PW	NaCl	26 %	9.5	6.4
	4.06	PW	NaCl	26 %	9.7	6.3
	4.07	PW	NaCl	26 %	9.8	6.7
	4.08	PW	NaCl	26 %	9.6	6.5
	4.09	PW	NaCl	26 %	9.4	6.2
	4.10	PW	NaCl	26 %	9.1	5.7

TableSI 2 Total carbon and nitrogen mass lost from FS and increase in the DS for the over the course of the 50-hr experiment series.

Feed Solution	**TC lost from FS**	**TC added to DS**	**TN lost from FS**	**TN added to DS**
Nolan PW	92 mg	2.6 mg	26 mg	3.1 mg
Midland PW	166 mg	1.8 mg	50 mg	73 mg
Dawson PW	161 mg	5.9 mg	650 mg	123 mg

CHAPTER SIX

COMPARISON OF THE DEGREE OF FOULING AT VARIOUS FLUX RATES AND MODES OF OPERATIONS WHEN USING FORWARD OSMOSIS FOR REMEDIATION OF PRODUCED WATER FROM UNCONVENTIONAL OIL AND GAS EXPLORATION AND DEVELOPMENT

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Comparison of the Degree of Fouling at various Flux Rate and Modes of Operation when using Forward Osmosis for Remediation of Produced Water from Unconventional Oil and Gas Exploration and Development

Tiffany Liden[1], Doug D. Carlton Jr.[1,2], Shinji Miyazaki[3], Takehiko Otoyo[3], Kevin A. Schug[1,2*]

AUTHOR INFORMATION:

1. Department of Chemistry and Biochemistry, The University of Texas at Arlington, 700 Planetarium Place, Arlington, TX 76019, USA;
2. Affiliate of Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, USA;
3. Asahi Kasei Corporation, 2-1 Samejima, Fuji, Shizuoka 416-8501 Japan

*Correspondence should be addressed to: (email) kschug@uta.edu; Tel.: +1-817-272-3541; Fax: +1-817-272-3808

6.1 Abstract

Driven by increased energy demands and technological advancements, the energy landscape of the United States has been changed by the expansion of unconventional oil and gas extraction. Unconventional development requires well stimulation, which uses millions of gallons of water per well and generates billions of gallons of wastewater annually. The waste matrix, referred to as produced water, has proven to be challenging to treat due to the complex physical, chemical, and biological composition, which can change over the lifetime of a production well. Here, forward osmosis was used as a remediation technique to extract fresh water from produced water procured from the Permian Basin region of west Texas. The premise was to investigate the durability of thin-film hollow-fiber membranes by determining how quickly the membranes were irreversibly fouled at various flux rates, and during two modes of operation: a) active layer in contact with the draw solution (AL-DS); and b) active layer in contact with the feed solution (AL-FS). Membranes used in AL-DS mode fouled faster than their counterparts used in AL-FS mode. Additionally, membranes used with higher flux rates fouled more quickly than those used under low flux conditions.

KEYWORDS: forward osmosis, unconventional oil and gas, produced water remediation, active layer; hollow-fiber membranes

6.2 Introduction

Increasing energy demands and technological advancements in well development have led to the rapid expansion of unconventional oil and gas extraction (Ground Water Protection Council and All Consulting, 2009; Perrin and Cook, 2016; Wang et al., 2014). As the energy landscape of the United States has changed (Shaffer et al., 2013), concerns centered around potential human and environmental impacts have developed. In particular, the high-water usage required for unconventional development (UD), frequently in arid and semiarid regions, and the process of handling the ever-increasing volumes of wastewater being produced, have been the focus of a growing controversy. For example, in the Permian Basin, the most prolific oil production region in the U.S., up to 12 million gallons of water can be consumed during hydraulic stimulation of a well (Backstrom, 2018; Budzik and Perrin, 2014; Collier, 2016; Ewing et al., 2014; Liden et al., 2017; U.S. Energy Information Administration, 2017). The waste stream, referred to as produced water (PW), continues to be generated through the life of the production well and is comingled with the commodity (oil and/or natural gas) (Veil et al., 2004). One of the most significant challenges associated with maintaining the favorable economics of UD operations is managing the complex matrix of constituents in the waste stream, which can include: a wide range of metals and minerals, naturally occurring radioactive material (NORM), and scaling compounds; bacteria and biocides; and organics, such as residual hydrocarbons and surfactants (Estrada and Bhamidimarri, 2016; Gregory et al., 2011; Ground Water Protection Council and All Consulting, 2009; Shaffer et al., 2013). Currently, the primary disposal method for the billions of gallons of PW being generated annually is subsurface injection into saltwater disposal (SWD) wells (Liden et al., 2017; Veil, 2015). This process of handling the contaminated water removes water procured for well development from the water cycle and has been linked to induced seismic events (Elst et al., 2016; Hornbach et al., 2016, 2015; Shaffer et al., 2013; Walsh and Zoback, 2015; Wang et al., 2014). In an effort to facilitate more environmentally responsible practices, the interest in reusing PW has been growing. The feasibility of reusing PW ultimately hinges on the economics of the treatment process and the quality of treated water that can be generated (King, 2011; Oetjen et al., 2018; Tipton, 2013). Consistent water quality output is essential to be able to cost-effectively reuse PW, but this is difficult to achieve without pretreating the waste stream. As such, the development of cost-effective treatment technologies, which allow PW to be reused in an economical fashion, are being investigated.

Forward osmosis (FO) is one of the few approaches considered to be a viable option to treat PW solutions, which can have salinity levels up to 2.5 - 3.5 times than that of seawater (Blondes et al., 2016; Liden et al., 2018a; Shaffer et al., 2013). During the osmotically-driven process, pure water moves across a semi-permeable membrane from a feed solution (FS) to a draw solution (DS) (Ansari et al., 2016; Hickenbottom et al., 2013; Liden et al., 2018b; Zhao et al., 2012). One benefit of treating PW using FO is decreased waste volumes injected into formations, thus reducing concerns related to anthropologically induced seismic activity (Gallegos et al., 2015; Hornbach et al., 2016; Parker et al., 2014; Wang et al., 2014). Moreover, the osmotically diluted DS can be used as a brine for future well stimulation (Coday et al., 2014). In previous studies, which used FO as a remediation method for PW, fouling was an issue, or studies were conducted with PW characterized by significantly lower total dissolved solids (TDS), compared to PW that is representative of the Permian Basin (Chen et al., 2015; Coday et al., 2015; Liden et al., 2018b; Minier-Matar et al., 2016; Wang et al., 2011). Fouling hinders the transport of pure water across the surface of the membrane (Guo et al., 2012). This can result from biofilm formation, inorganic scaling, and the formation of a cake layer, due to organic constituents physically binding to the membrane surface and compromising its permeability.

Previous work by Liden *et al.* verified that water could be successfully extracted from the Permian Basin PW using FO with a composite thin-film, hollow fiber membrane (Liden et al., 2018b). Studies were conducted for 5 hours a day for 10 consecutive days. The FO module was stored in DI water overnight, and the FS and DS were replaced daily. Despite regenerating the initial conditions daily, the flux decreased over time.

The aim of this study was to determine if fouling was the culprit for the reduction in flux during previous studies. Current trials compared the fouling rate when the PW was in contact with the active layer (AL-FS) and when the DS was in contact with the active layer (AL-DS). Moreover, the rate of fouling was investigated at various flux rates. Through the course of the evaluation, the temperature was maintained near 25 °C, and the osmotic gradient was maintained. After the flux was determined to be less than 50% of the initial flux, the surface of the membrane was hydraulically cleaned to determine if the surface was irreversibly fouled. Clean membranes and fouled membrnaes were analyzed using scanning electron microscopy and energy dispersive X-ray spectroscopy, in addition to attenuated total reflectance-Fourier transform infrared spectroscopy.

6.3 Materials and Methods

6.3.1 Bench Top System

FO modules were provided by Asahi Kasei Corporation (Fuji, Japan). The module consisted of a bundle of 20 composite thin-film hollow fiber membranes, each with a polyethersulfone support layer and a thin-film polyamide active layer encased in a plastic shell. The modules had a length of 105 mm and an outer diameter (OD) of 18 mm. Each fiber had an inner diameter (ID) of 0.7 mm.

The design of the custom-built bench top system shown in Figure 1 was previously described by Liden *et al.* in more detail (Liden et al., 2018b). Briefly, two variable speed Micropumps (Vancouver, WA) were used to regulate the velocity of FS and DS. The FS and DS were attached to the module primarily using polyurethane tubing with a 6 mm OD. Silicon tubing approximately 5 cm long with a 6 mm OD was used as a bridge from the polyurethane tubing to the module. The FS container was a 2-L stainless steel pot while the DS container was a 20-L plastic bucket. Changes in mass of the FS were used to determine the water flux measured as liters per meter squared per hour (L/m^{2}h (LMH)). The water flux was determined by measuring the mass change for the FS. Temperatures of the solution were maintained near 25 °C.

6.3.2 Feed solution and Draw solution

FO experiments consisted of a FS of either oilfield PW or a sodium chloride mimic of the PW that exhibited the same conductivity. The DS was prepared using NaCl (BDH, ACS grade, VWR, Radnor, PA). The maximum concentration of DS was saturated NaCl or 26% (w/w). During trials conducted at high flux rates, saturation of the DS was maintained by suspending a natural cotton, porous pouch at the top of the DS, filled with approximately 250 g NaCl to prevent a decrease in flux due to osmotic dilution. The salt pouch was located at the surface where the sub-saturated water entered the DS to increase its contact with fresh and sub-saturated water. The salt percentage of the FS was estimated from a calibration of conductivity using prepared salt standards up to 10% NaCl (aq) or using a SW pen refractometer (Atago, Tokyo, Japan). The membrane performance was evaluated with the FS in contact with the active layer (AL-FS), inside of the hollow fiber, as well as with the DS in contact with the inside of the hollow fiber (AL-DS). To vary the flux from high flux to low flux conditions, the flux was reduced by decreasing the salinity of the DS to 10-11%. The DS salinity was monitored, and additional sodium chloride was added when required.

PW samples were collected from the Permian Basin in Midland County from a community SWD well. PW is brought to this specific SWD disposal site by trucks from production sites purportedly from up to 50 miles away or via six pipelines. The six pipelines connect to six fields, each of which has five to seven horizontal producing zones in the Wolfcamp formation. PW is combined to form a composite mixture upon arriving at the SWD site.

PW 1 exhibited a conductivity of approximately 127.0 mS/cm, equivalent to 10.2% NaCl(aq), and was collected in December of 2015 in 7.5 L HDPE buckets. PW 2, which was collected in March of 2016 in the same manner as PW 1, had a conductivity of approximately 113.0 mS/cm, equivalent to 8.5% NaCl(aq).

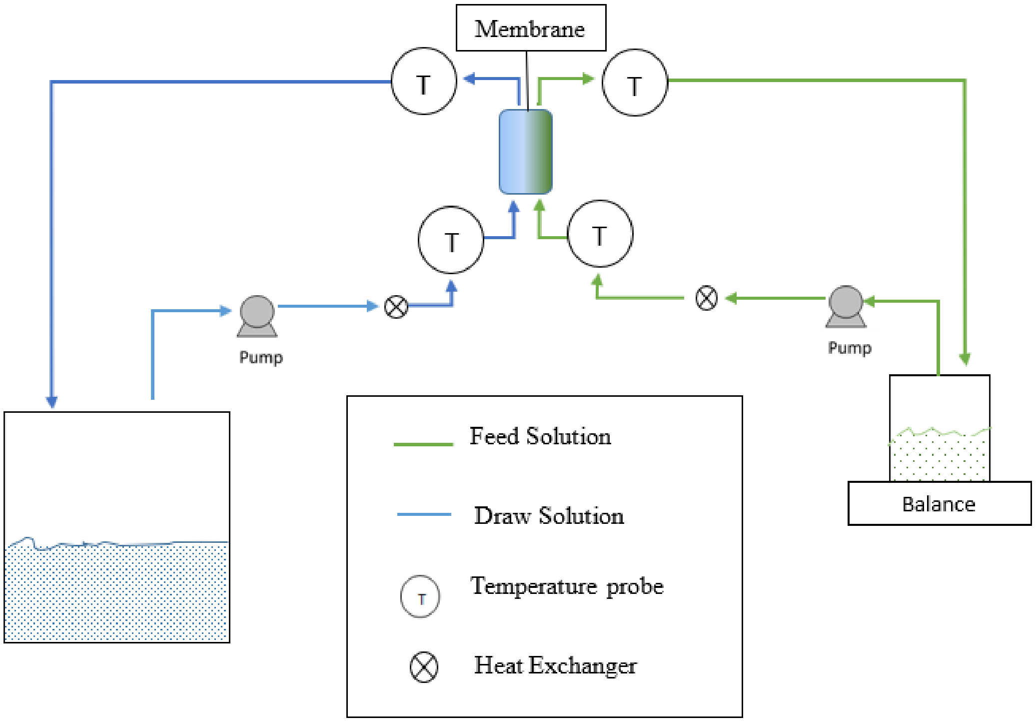

Figure 1 Forward Osmosis benchtop system. Depiction adapted from Liden et al. (Liden et al., 2018b).

6.3.3 Analytical Instrumentation

Total carbon (TC) and inorganic carbon (IC) content was measured using typical combustion techniques with the Shimadzu TOC-L Analyzer (Shimadzu Scientific Instruments, Inc., Columbia, MD). Total organic carbon (TOC) was determined by the difference of TC and IC. Total nitrogen (TN) was also measured with the same instrument using a TN module add-on (TNM-L, Shimadzu). Conductivity was measured with a Horiba LAQUA DS-70 (Kyoto, Japan). Metal analysis was completed using a Shimadzu ICPE-9000, based on Environmental Protection Agency (EPA) method 200.7. Standard solutions for the metals were from High-Purity Standards (North Charleston SC). Ion chromatography (IC) and titration were used to quantify pertinent anions, as per EPA methods 300 and 310.1 performed by TTI Environmental Laboratories (Arlington, TX). Surface analysis of the membrane was completed using a Hitachi S-3000N scanning electron microscope (SEM) (Krefeld Germany) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrophotometry using a IR Prestige-21 (Shimadzu).

6.4 Experimental Design

Each trial consisted of an 8-part experimental series. Saltwater mimics and PW were used as FS to evaluate the performance of the FO membranes (Table 1). A quality control trial was performed to assess the module performance, using a 3.5% sodium chloride DS and DI water for the FS. After ensuring shipping and storage had not damage the module, a series of experiments were conducted using saltwater mimics and prodcued water as the FS . When using PW 1, a 10.2% sodium chloride water solution was used for the FS to mimic the PW, in conjunction with a saturated solution of sodium chloride DS, to determine a performance baseline. The PW was used as the FS at a flow rate of 18 mL/min, until the flux was less than 50% of the original flux; a saturated solution of sodium chloride was used as DS (AL-FS 3). To confirm the flux was below

50% of the initial flux due to fouling, a 10.2% sodium chloride water solution was used for the FS with a saturated sodium chloride DS (AL-FS 4(1)). After confirming the module flux was less than half of the initial flux, two hours of hydraulic cleaning at an increased flow rate was completed (180 mL/min on the inside of the fibers and 1,200 mL/min on the outside of the fibers). The module performance was re-evaluated using a 10.2% sodium chloride PW mimic as the FS, and a saturated sodium chloride solution as the DS, to assess the effectiveness of the cleaning technique. This process was then repeated a second time.

The flow rates were reversed for AL-DS trials (Table SI 1) (i.e. FS 370 mL/min and DS 18 mL/min). A new FO module was used with each trial. In all experiments, the FS was replaced daily, and the temperature was maintained near 25 °C for the FS and DS. During tests using PW 2, the saltwater mimic was prepared to have a salinity of 8.5%; the initial flux measured was near 2-3 LMH. The reduced flux was achieved by decreasing the salinity of the DS to 11% NaCl. The DS was monitored daily to maintain a constant salinity, and additional NaCl was added when required.

Table 1. AL-FS experimental series design using PW 1.

Expt No	Draw Solutions Parameters			Feed Solutions Parameters			
	Solution	Flow Rate (mL/min)	Volume (L)	Solution	Flow Rate (mL/min)	Volume (L)	Time (h)
AL-FS-1	3.5% NaCl	370	1	DI Water	18	1	0.5
AL-FS-2	26% NaCl	370	1	10.2% NaCl	18	1	0.5
AL-FS-3	26% NaCl	370	2	PW	18	2	24
AL-FS-4(1)	26% NaCl	370	1	10.2% NaCl	18	1	0.5
Hydraulic Cleaning	DI water	1200	1	DI Water	180	1	2
AL-FS-4(2)	26% NaCl	370	1	10.2% NaCl	18	1	0.5
Hydraulic Cleaning	DI water	1200	1	DI Water	180	1	2
AL-FS-4(3)	26% NaCl	370	1	10.2% NaCl	18	1	0.5

6.5 Results and Discussion

6.5.1 Characterization of PW

Based on published reuse guidelines, it was determined that direct reuse of the PW from the Permian Basin would not be feasible for subsequent production well development without treatment (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018c; Oetjen et al., 2018). The levels of total suspended solids (TSS) observed in PW 1 and 2 (5,400 and 4,950 mg/L, respectively) exceeded the reuse limit of 500 mg/L by an order of magnitude (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018c; Oetjen et al., 2018). TOC values were 46 and 51 mg/L for PW 1 and 2, respectively, which more than doubled the suggested limit of 20 mg/L (Table 2) (Liden et al., 2018c).

Pertinent metals of concern are those that cause scaling and those that can potentially interfere with crosslinker efficiencies (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018c; Oetjen et al., 2018). Barium, calcium, magnesium, and strontium are generally the largest contributors to the formation scale (Hu et al., 2016). Barium was determined to have a concentration of 2.1 ± 0.3 mg/L for PW 1 and 2.7 ± 0.3 mg/L for PW 2, which was below the prerequisite limit of 20 mg/L (Table 2) (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018c; Oetjen et al., 2018). The reuse limit for calcium has been reported as 2,000 mg/L (Hildenbrand et al., 2018; King, 2011; Liden et al., 2018c; Oetjen et al., 2018), which PW 1 exceeded by 1,000 mg/L and PW 2 surpassed by 350 mg/L (Table 2). The magnesium reuse limit of 2,000 mg/L was not surpassed by either of the samples. The authors could not find reported limits for strontium, but the concentration of 510 ± 40 mg/L for PW 1 and 420 ± 30 mg/ for PW 2 were elevated compared to PW from other regions (Liden et al., 2018a).

Other metals of interest regarding reusability of PW include boron, iron, titanium, and zirconium (Esmaeilirad et al., 2016; Montgomery, 2013). Elevated concentrations of these ions in stimulation fluids can cause overcrosslinking, which can negatively impact gel viscosity, temperature stability, and proppant dispersion (Esmaeilirad et al., 2016; Oetjen et al., 2018; Wasylishen and Fulton, 2012). The boron levels for the untreated PW well exceeded the suggested reuse value of 10 mg/L (47 ± 3 and 45 ± 2 mg/L for PW 1 and PW 2, respectively) (Hildenbrand et al., 2018; Liden et al., 2018c; Tipton, 2013). On the other hand, iron was below the reuse limit of 10 mg/L in both PWs (Hildenbrand et al., 2018; Liden et al., 2018c; Tipton, 2013). Titanium and zirconium were not detected in the samples.

When evaluating the reusability water quality, carbonate and sulfate are also problematic due to their affinity to form insoluble precipitates (scale) with group II metals such as barium, calcium, and strontium (Zielinski and Otton, 1999). Carbonate exceeded the reuse limits of 500 mg/L for PW 2 with a value of 841 mg/L, while PW 1 exhibited a significantly lower carbonate concentration of 73.7 mg/L. Sulfate levels were below the published limit of 300 mg/L. Sulfate-reducing bacteria can obtain energy by reducing sulfate as well as other oxygenated sulfur compounds to form hydrogen sulfide (H_2S) (Liden et al., 2018c). This toxin is the main cause of costly product quality degradation, referred to as souring, and biocorrosion of metal infrastructure that potentially can lead to casing failure and environmental contamination (Liden et al., 2018c). The proliferation of problematic bacteria is also pertinent to the treatment of PW as the occurrence of biofouling can significantly impede the effectiveness of membrane separations, such as RO (Jiang et al., 2017).

Table 2 Initial characterization of PW samples relative to published hydraulic fracturing reuse guidelines.

Component	**PW 1 (mg/L)**	**PW 2 (mg/L)**	**Reuse Guidelines** (Hildenbrand et al., 2018; Liden et al., 2018c) **(mg/L)**
Total Alkalinity ($CaCO_3$)	73.7	841	
TDS	147,000	118,000	
TSS	5,400	4,950	500
TOC	46	51	20
B	47 ± 3	45 ± 2	10
Ba	2.1 ± 0.3	2.7 ± 0.3	20
Ca	3,000 ± 100	2,350 ± 9	2,000
Fe	5.0 ± 0.4	1.0 ± 0.4	10
K	460 ± 30	410 ± 40	
Li	18 ± 1	15 ± 1	
Mg	460 ± 30	390 ± 30	2,000
Mn	2.4 ± 13	1.0 ± 0.1	
Na	34,000 ± 2,000	33,000 ± 3,000	
Sr	510 ± 40	420 ± 30	
Silica	10.5 ± 0.8	26 ± 2	
Bromide	58.7	58.1	
Chloride	75,000	70,000	
Fluoride	2.24	2.15	
Nitrate	46.6	46.4	
Sulfate	77.1	2.22	500
pH	6.72	6.49	6.5 – 8.5

6.5.2 FO Trials Results

6.5.2.1 PW 1 Active Layer Feed Solution (AL-FS)

During the AL-FS trials using PW 1, the flux was 11.6 LMH (AL-FS 2) when the saltwater mimic was used as the FS. An initial flux of 10.1 LMH was measured when using PW 1 as the FS (AL-FS 3). A flux, 5.8 LMH, was calculated to be 50% of the module's performance based on the flux of the salt water mimic. Figure 2 shows the flux decreased daily as the FS was concentrated, thereby reducing the osmotic gradient. However, when the FS was replaced every 24 hours, the flux increased due to the increased osmotic gradient. The sodium chloride mimic was used to confirm fouling after the flux was reduced to less than 50% of the initial flux . After the module was washed with distilled water, the flux decreased to 40% of the original performance (Table 3). The flux did not improve when the module was hydraulically cleaned a second time.

Table 3 AL-FS Module performance evaluation during AL-FS trial using PW.

	AL-FS-2	**AL-FS-4(1)**	**AL-FS-4(2)**	**AL-FS-4(3)**
Flux (LMH)	11.6	5.4	4.6	4.6
Module Performance	100%	45%	40%	40%

6.5.2.2 PW 1 Active Layer Draw Solution (AL-DS)

The initial flux was 10.2 LMH for AL-DS trials using PW 1. Half of the module performance was calculated to be 5.1 LMH when using the saltwater mimic as the FS during AL-DS trials using PW 1 (Table 4). The initial flux using the PW as the FS was 9.4 LMH, as shown in Figure 2. Similar to AL-FS mode, the flux decreased daily, but increased with the addition of fresh PW increasing the osmotic gradient. The flux decreased to less than the initial flux after 24 hours, but the trial was continued for 72 hours to monitor the progression of the decrease in flux. When AL-DS using PW 1 trial was stopped, module performance was 42% of the initial sodium chloride mimic (AL-DS 4(1)). After the first 2-hour hydraulic cleaning, module performance improved to 65% of the initial performance using the salt water mimic for the FS. When the module was hydraulicly cleaned a second time, the flux improved again, reaching 79% of the initial flux (Table 4).

Table 4 Module performance evaluation during AL-DS trial using PW 1.

	AL-DS-2	**AL-DS-4(1)**	**AL-DS-5(2)**	**AL-DS-5(3)**
Flux (LMH)	10.2	4.3	6.6	8.1
Module Performance	100%	42%	65%	79%

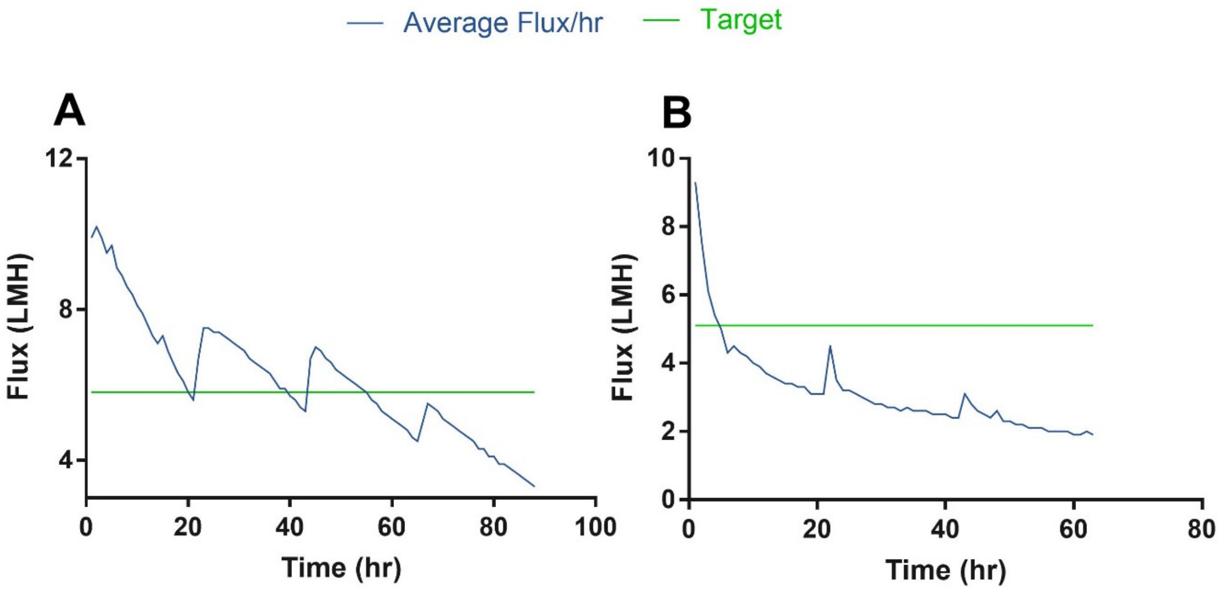

Figure 2 Flux of FO system using PW 1 as the FS which was replaced daily. AL-FS mode (A) performed for 4 days total with the FS replaced with fresh PW daily. Half module performance was determined to be 5.8 LMH. Half of the module performance was 5.1 LMH for the trial evaluated in AL-DS mode (B). The FS was replaced daily and allowed to continue for 3 days total.

6.5.2.4 PW 2 Active Layer Feed Solution (AL-FS)

PW 2 was used for AL-FS experiments at a decreased flux rate. The sodium chloride solution which mimicked the salinity of PW 2 yielded an initial flux of 2.6 LMH (AL-FS 2) (Table 5). The initial flux of 1.7 LMH measured for the PW FS (AL-FS 3). Half module performance, based on the salt water mimic, was determined to be 1.3 LMH. Figure 3 shows that the flux decreased daily as the FS was concentrated, thereby reducing the osmotic gradient. However, the flux was regenerated above 50% of the initial performance level daily when the concentrated FS solution was replaced with fresh FS. The trial was stopped after 11 days when the available fresh PW was consumed. After the 11th day, module performance was determined to be 62% (1.6 LMH) of the initial performance, when it was reevaluated with the saltwater mimic. The module was hydraulically cleaned for two hours, followed by a subsequent evaluation of module performance using a saltwater mimic that yielded a flux of 0.8 LMH or 31% of the module's initial performance. After washing with distilled water a second time, the flux decreased further to 15% of baseline module performance (Table 5).

Table 5. Module performance evaluation during AL-FS trial using PW 2.

	AL-FS-2	AL-FS-4(1)	AL-FS-5(2)	AL-FS-5(3)
Flux (LMH)	2.6	1.6	0.8	0.4
Module Performance	100%	62%	31%	15%

6.5.2.5 PW 2 Active Layer Draw Solution (AL-DS)

Trials using PW 2 as the FS were operated at reduced flux to determine the impact of fouling. When operating in AL-DS mode, the initial flux was 3.4 LMH, with the flux for the saltwater mimic recorded to be 3.1 LMH (Table 6). A flux of 1.5 LMH was determined to be 50% of module performance, based on the salt water solution used as the PW mimic. The trial was stopped after 3 days when the flux was not successfully regenerated upon replacing the FS to restore the original osmotic gradient (Figure 3). Once the trial was completed, module performance was measured to be 42% of the initial performance, using a sodium chloride mimic. After the first two hours of hydraulic cleaning, module performance decreased to 0.8 LMH (26%).The flux improved after hydraulic cleaning reaching 45% of the initial flux (Table 6).

Table 6. Module performance evaluation during AL-DS trial using PW 2.

	AL-DS-2	AL-DS-4(1)	AL-DS-5(2)	AL-DS-5(3)
Flux (LMH)	3.1	1.3	0.8	1.4
Module Performance	100%	42%	26%	45%

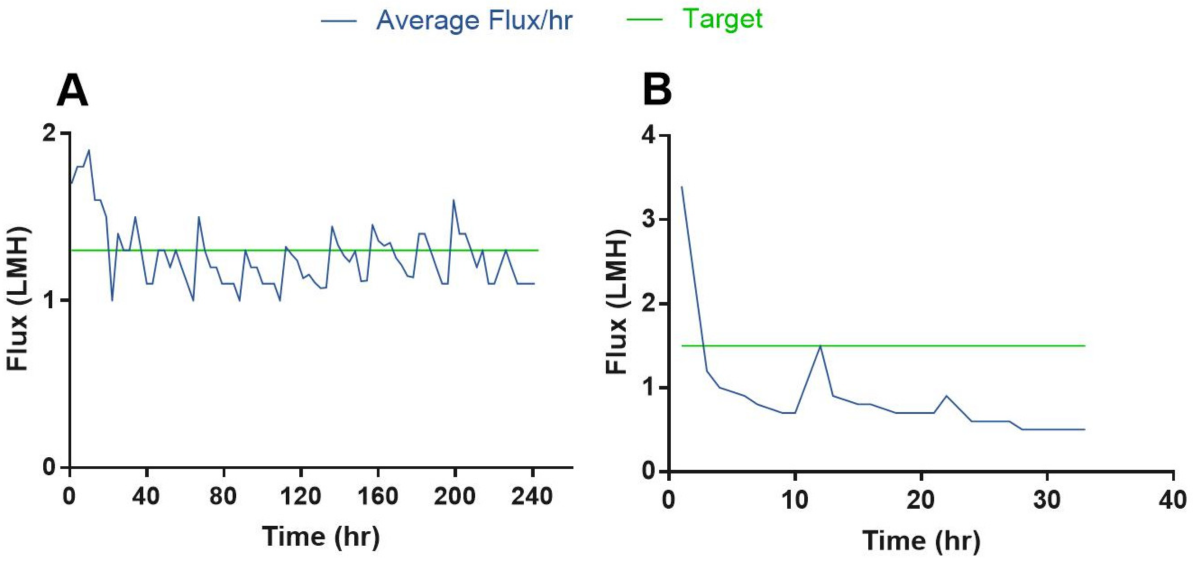

Figure 3. The flux of FO system using PW 2 as the FS. The flow rate was reduced to 2-3 LMH by decreasing the salinity of the DS. AL-FS mode (A) ran for 11 days total with the FS replaced with fresh PW daily. Half of the module's performance was determined to be 1.3 LMH. Half of the module performance was 1.5 LMH for the trial evaluated in AL-DS mode (B). The FS was replaced daily and allowed to continue for 3 days total.

6.5.2.6 FO Trial Comparison

Trials operated in AL-DS mode had a rapid decrease in flux when compared to experiments conducted in AL-FS under the same conditions. When working at a lower flux rate, the fouling rate decreased. The lack of ability to fully recover the initial flux after hydraulic cleaning in both AL-DS and AL-FS modes of operation indicated the memebrane is being irreversible fouled during trials. Irreversible fouling was more prevalent for the AL-FS trials, 40% and 15.4% for PW 1 and 2, respectively (Tables 3 and 5). Comparatively, trials operated in AL-DS mode yielded a flux of 79% and 45% after hydraulic cleaning for PW 1 and 2, respectively represented in Tables 4 and 6. When hydraulically cleaned, experiments operated in AL-DS mode had an improved flux compared to their counterpart operated in AL-FS mode.

6.5.3 Surface Analysis using ATR-FTIR and SEM-EDS

The active and support layer of a clean membrane were analyzed along with the fouled membrane surfaces using ATR-FTIR from 700 - 4,000 cm^{-1}. Figure 4 (A-D) plots signals from 800 - 2,400 cm^{-1}. Figure 4 A and C compare the active layer of the clean membrane to the fouled surfaces of the membranes used with PW 1 and 2, respectively, in AL-FS mode. Figure 4 B represents the spectrum for the fouled support layer that was in contact with the FS during the AL-DS trial using PW 1, and Figure 4 D represents the spectrum of the membrane used with PW 2. Infrared likely penetrated the thin-film polyamide when analyzing the active layer resulting in detection of the polyethersulfone support layer. The opposite can be inferred when analyzing the support layer as well. Peaks are assigned to amide groups (1650 cm^{-1}), aromatic groups (835 cm^{-1}, 872 cm^{-1}, 1110 cm^{-1}, and 1580 cm^{-1}), and ether groups (1240 cm^{-1}). Signals at 1070 cm^{-1} and 1292 cm^{-1} from sulfone groups were similar to observations from previous studies (Riley et al., 2018; Xu and Drewes, 2006). Analysis of the fouled membranes revealed that the aforementioned peaks were weakened. The amide peak at 1650 cm^{-} is no longer visible in the active layer of the membrane used for AL-FS experiments with PW 1. The significant reduction in signal and/or elimination could indicate that the amide is being chemically reduced or that the signal is perhaps reduced due to fouling impeding penetration of the IR. Additionally, peaks were detected for all of the fouled membranes at 1,410 cm^{-1} and 2,330 cm^{-1}. Both regions can be indicative of boron derivatives. If intact viscosifiers used in stimulation fluid, composed of boron functioning as crosslinkers of starch-based compounds were fouling the surface, then a significant change in the spectra around 3,000 cm^{-1} would have been expected. The lack of increased signals around 3,000 cm^{-1} indicated that the viscosifiers have been degraded (Liden et al., 2018c; Tayal et al., 1997). Therefore, it is suspected that free boron in the form of boric acid interacts with the surface. The high levels of boron identified in the PW solutions further indicated that residual viscosifying agents could have been in the PW solutions.

SEM images of the membrane surface are shown in Figure 5 (A-F). The clean membranes revealed carbon and sulfur as the primary components, as expected due to the presence of the polyethersulfone support layer and the polyamide active layer. The active layer of the clean surface, imaged in Figure 5A, was visibly rough, while the support layer appeared to be a smoother surface (Figure 5D). However, the active layer of the membrane used in the AL-FS experimental series with PW 1 was not visible due to a layer of foulant on the surface of the membrane when using PW 1 during the AL-FS experimental series. Calcium, chloride, copper, iron, magnesium, manganese, nickel, silicon, strontium, were identified on the surface of the membrane, in addition to elevated levels of oxygen. Less fouling is visible on the surface the membrane used with PW 2 in AL-FS mode; however, fewer elements were identified (chloride, chromium, iron, magnesium, nickel, and silicon) in comparison to the membrane used in AL-FS mode with PW 1 (Figure 5C). Interestingly, this was the experimental design that lasted 11 days at a decreased flux rate.

The membrane used with PW 1 in AL-DS mode at increased flux rates again showed a significant buildup of foulant, with the same elements detected for PW 1 in AL-FS mode (Figure 5E). When operating in AL-DS mode with PW 2, the surface appears to possibly have some foulant that smoothed the surface. Additionally, there appears to be a secondary contaminate, perhaps in the form of an inorganic precipitate or a biofilm. The same elements previously seen with PW 2 (Figure 5F) were detected. During the FO trials, the 2-L stainless steel pot began to corrode, due to the elevated salinity; therefore, levels of chromium and nickel detected on the surface of the membranes, and in part, some of the iron observed can be attributed to corrosion.

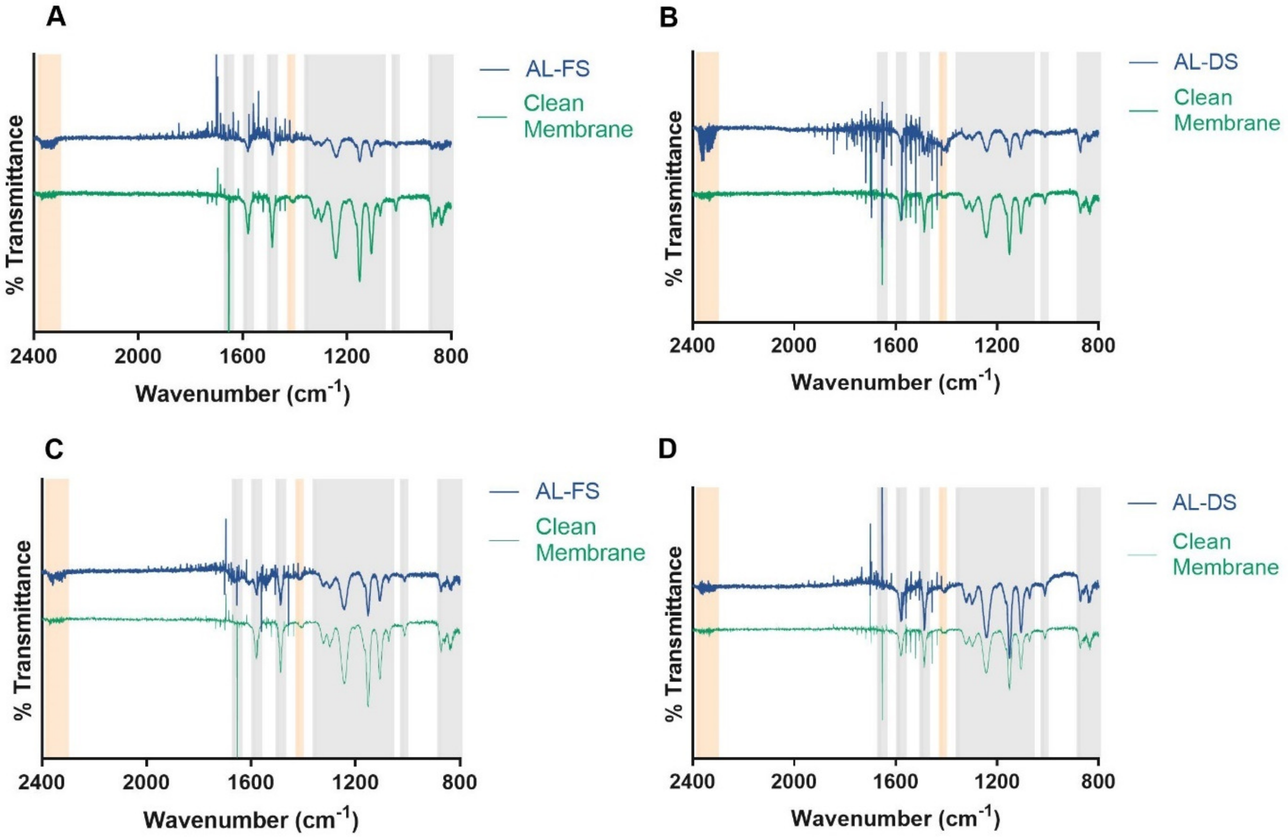

Figure 4. ATR-FTIR spectra of clean and fouled membrane surfaces are represented for the active layers analyzed when using AL-FS mode with (A) PW 1 and (C) PW 2. Whereas the support layer was evaluated for experiments operated in AL-DS using (B) PW 1 and (D) PW 2.

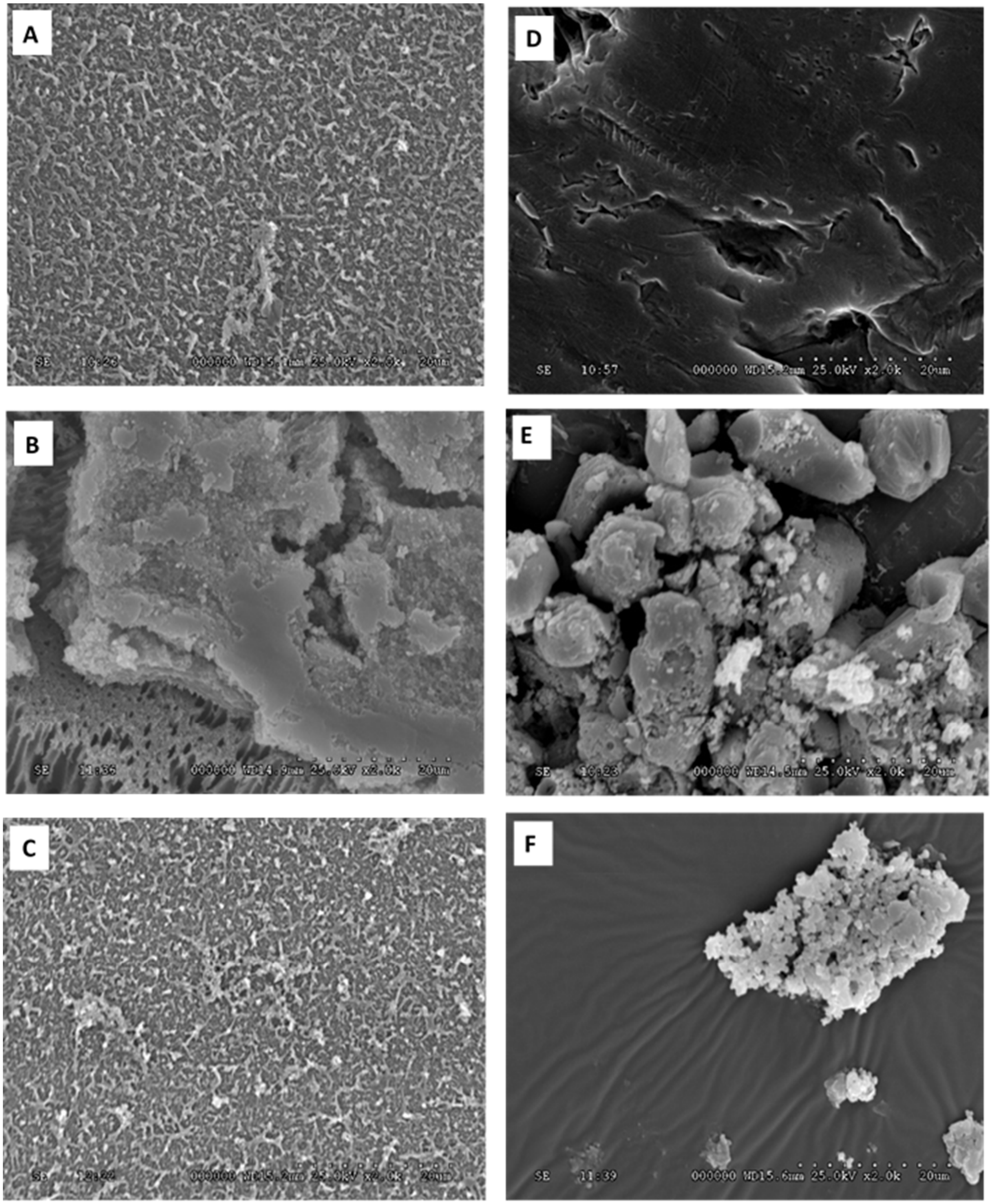

Figure 5. SEM images of a clean (A) active layer and (D) support layer to compare to fouled membrane surfaces. For AL-FS experiments, the active layers for the FSs (B) PW 1 and (C) PW 2 were captured. The support layer was evaluated for (E) PW 1 and (F) PW 2 when operated in AL-DS mode.

6.6 Conclusion

Irreversible fouling occurred throughout trials using PW from the Permian Basin as a FS. Membrane properties, such as roughness, surface charge, and hydrophobicity, are known to be critical factors that drive membrane performance (Riley et al., 2018; Xu and Drewes, 2006). When membranes that were used in AL-FS mode with the rougher surface were hydraulically cleaned, the performance was decreased. As such, these results are indicative that the surface morphology likely impacts membrane fouling. Moreover, the quality of the feed solution has an effect on the fouling. The water quality can influence the membrane's properties and the membrane-foulant interactions (Riley et al., 2018; Xu and Drewes, 2006). Therefore, pretreating PW and/or the membrane surface with anti-scaling agents could be beneficial to sustain module performance (Riley et al., 2018). Moreover, future work could include similar experiments with a decreased flow during hydraulic cleaning to determine if the increased flow rate used in this experimental series impacted fouling. Additionally, more aggressive cleaning strategies using chemical-based solution would be beneficial to test.

Acknowledgments

Support for this work was provided by Asahi Kasei Corporation and the Collaborative Laboratories for Environmental Analysis and Remediation at The University of Texas at Arlington. Solaris Water Midstream is also gratefully acknowledged for providing PW samples. We would also like to thank Dr. Zacariah Hildenbrand for donating his time and effort to proof-read content and to provide valuable feedback on earlier drafts of this work. Additionally, we thank Dr. Frank Foss Jr for his help interpreting the ATR-FTIR data.

6.7 References

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6.8 Supplemental Information

TableSI 1 AL-DS experimental series design using PW 2.

Exp No	**Draw Solutions Parameters**			**Feed Solutions Parameters**			
	Solution	**Flow Rate (mL/min)**	**Volume (L)**	**Solution**	**Flow Rate (mL/min)**	**Volume (L)**	**Time (h)**
AL-DS-1 (baseline)	3.5% NaCl	18	1	DI Water	370	1	0.5
AL-DS-2	26% NaCl	18	1	10.2% NaCl	370	1	0.5
AL-DS-3	26% NaCl	18	2	PW	370	2	24
AL-DS-4(1)	26% NaCl	18	1	10.2% NaCl	370	1	0.5
Hydraulic Cleaning	DI water	180	1	DI Water	1200	1	2
AL-DS-4(2)	26% NaCl	18	1	10.2% NaCl	370	1	0.5
Hydraulic Cleaning	DI water	180	1	DI Water	1200	1	2
AL-DS-4(3)	26% NaCl	18	1	10.2% NaCl	370	1	0.5

TableSI 2 Summary of fouling experiments.

Feed Solution	**Mode**	**Initial Flux (x-2)**	**Duration (days)**	**% Module Performance After Two 2-hour Hydraulic Cleanings**
PW 5	AL-FS	11.6	4	40
PW 5	AL-DS	10.2	3	79
PW 6	AL-FS	2.6	11	15.4
PW 6	AL-DS	3.1	3	45.2

CHAPTER SEVEN

PRETREATMENT TECHNIQUIES FOR PRODUCED WATER REMEDIATION USING FORWARD OSMOSIS

Tiffany Liden, Doug D. Calton Jr, Youchiro Ide, Takehiko Otoyo, Zacariah L. Hildenbrand, Kevin A. Schug, Pretreatment Techniques for Produced Water Remediation using Forward Osmosis, Sci Tot Environ, 2018, in preparation.

Pretreatment Techniques for Produced Water with Subsequent Forward Osmosis Remediation

Tiffany Liden[1], Youchiro Ide[2], Doug D. Calton Jr.[3], Takehiko Otoyo[2],
Zacariah L. Hildenbrand[3,4], Kevin A. Schug[1,3*]

Author Information

4. Department of Chemistry and Biochemistry, The University of Texas at Arlington, 700 Planetarium Place, Arlington, TX 76019, USA;
5. Asahi Kasei Corporation, 2-1 Samejima, Fuji, Shizuoka 416-8501 Japan

3. Affiliate of Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, USA;

4. Inform Environmental, LLC, 6060 N. Central Expressway, Suite 500, Dallas, TX 75206

Correspondence should be addressed to: 700 Planetarium Pl.; Box 19065; Arlington, TX 76019-0065 (email) kschug@uta.edu; Tel.: +1-817-272-3541; Fax: +1-817-272-3808

Keywords: Pretreatment, Forward osmosis, Produced water, Unconventional development

7.1 Abstract

Unconventional oil and gas extraction is on the rise across the United States and comprises an integral component in meeting the nation's energy needs. The primary by-product of this industrious process is produced water, which is a challenging matrix to remediate because of its complex physical and chemical composition, and the fact that the composition can change over the lifetime of a production well. Forward osmosis is one of the few approaches considered to be a viable option to treat high salinity produced water; however, fouling has been an issue. This study aimed to treat produced water before using forward osmosis as a remediation option. Trials consisted of a series of five experiments in order to evaluate the performance of the membrane. Samples were treated by centrifugation, activated carbon, filtration, ferric chloride, as well as coagulants and a polymer. It can be concluded that forward osmosis can be used to extract water from high salinity oil field brines and produced water, and that pretreating the produced water decreased the tendency for fouling. The pretreatment with the overall best performance was activated carbon, which also yielded the lowest total organic carbon concentrations. Forward osmosis water flux for pre-treated produced water held steady, with minimal losses, over the course of the 7-hour trials.

7.2 Introduction

Unconventional oil and gas development (UD), which involves horizontal drilling and hydraulic fracturing, has vastly changed the energy landscape of the United States and the world [1]. Concerns centered around the potential environmental impacts have primary focused on the contamination of groundwater [2–5], surface water [6,7], and air quality [8–10]; as well as high water usage, frequently in arid and semiarid regions [11]. Following the use of up to 12 million gallons of water per well for hydraulic stimulation in some regions, such as the Permian Basin [12,13], only a fraction of the water is retrieved. The resurfaced water, referred to as produced water (PW), is the largest waste stream throughout the life of the well [14].

The majority of the billions of gallons of PW generated annually are disposed of using salt water disposal (SWD) wells [15,16], which remove the contaminated water from the water cycle but have been linked to induced seismic events [1,17–21]. Growing restrictions on this disposal option have left an increased need to treat PW. This would allow the reuse of PW in subsequent oil and gas development, which would inherently reduce the volume disposed of in injection wells [22–24]. Additional PW treatment could be used to return water to the water cycle. Cost-effective treatment options need to be developed to treat the complex matrix of constituents, which can include naturally occurring radioactive material (NORM), scaling compounds, bacteria, biocides, and other organics, such as residual oil and gas hydrocarbons, as well as surfactants [25]. For reuse, the total concentration of petroleum hydrocarbons needs to be less than 20 mg/L; whereas all bacteria, algae, and fungi must be eliminated, and solids must be reduced to less than 20 µm [15]. Total dissolved solids (TDS) are not particularly problematic with respect to the reuse of PW, as long as pertinent ions (barium, boron, calcium, iron, and strontium), which can cause scaling or negatively impact the solution chemistry used for well development, are reduced to acceptable levels [13,26–29]. However, it is necessary to meet more stringent water quality parameters when considering the recycling of PW for use in other industries, which will require desalination [30]. Forward osmosis (FO) is one of the few approaches considered to be a viable option to treat the high salinity of PW solutions [1].

FO is an osmotically-driven process that moves pure water across a semi-permeable membrane from a feed solution (FS) to a draw solution (DS) [31–34]. Desalination can be achieved through a two-step process, which includes osmotic dilution of the DS and freshwater extracted from the diluted DS [32,34]. Regeneration of the DS has been suggested through several techniques such as reverse osmosis and membrane distillation [34]. When osmotic dilution of the DS is used independently, it can serve a dual purpose to decrease the volume of PW (the FS) injected into formations, thus reducing concerns related to seismic activity. The diluted DS provides a brine solution, which can be used or further processed for future well stimulation [35]. However, when paired with a desalination technique to extract the pure water, this process could potentially be used to recycle PW for use in other anthropological activities (i.e., irrigation, agriculture, etc). Moreover, based on the water quality of the extracted water, it could potentially be discharged providing an opportunity to recharge depleted aquifers. Previous studies have evaluated the use of FO as a remediation method for PW; however, fouling was an issue [31,36,37]. Fouling hinders the transport of pure water across the membrane's surface [38]. This can result from biofilm formation, inorganic scaling, and the formation of a cake layer due to organic constituents physically binding to the membrane's surface and block the pores. When PW is used as the FS for FO, fouling has been specifically attributed to polyacrylamide, which is commonly used as a friction reducer to enhance oil and gas recovery [36,39,40].

The goal of this study was to characterize PW and evaluate various pretreatment options, including centrifugation, adsorption on activated carbon, filtration, coagulation, and flocculation. Five pretreatment options were selected based on the total organic carbon (TOC) and the turbidity. Each of the selected modalities was used to pretreat 20 L of PW. The treated PW was used as FS during FO to evaluate the performance of the module

7.3 Methods and Material

7.3.1 Bench Top System

FO modules provided by Asahi Kasei Corporation (Fuji, Japan) consisted of a bundle of 20 composite hollow fiber membranes, each with a polyethersulfone support layer and a thin-film polyamide active layer, collectively encased in a plastic shell. The modules were described in more detail in a previous work [31].

The system, which was custom built (Figure 1), used two variable speed Micropumps (Vancouver WA) to regulate the velocity inside (GA-V21.CFS.A) and outside (GJ-N21.FF2S.A) the hollow fiber membrane. Pumps were controlled with two GPD-2303S bench power supplies (GW Instek, New Taipei City, Taiwan). As with previous trials [31], the DS was a closed loop system; in contrast to previous trials, the FS was designed here to operate as a single pass system. Therefore, the FS only came into contact with the membrane surface once, prior to being discarded as waste, as illustrated in Figure 1. The tubing used to connect the FS and DS to the module was primarily polyurethane tubing with a 6 mm OD; however, silicon tubing approximately 5 cm long with a 6 mm OD was used as a bridge from the polyurethane tubing to the module. The FS and DS were each stored in 20 L plastic buckets throughout the experiment. The flux, measured as liters per square meter per hour ((L/m^2hr) LMH), was determined by monitoring the change in mass of the DS with a Shimadzu BX32KS digital balance (Shimadzu Scientific Instruments, Inc., Columbia MD). Temperatures of the FS and DS were controlled using heat exchangers and a circulating water bath (Polyscience, Niles IL). Temperatures were monitored with K-type thermocouple probes and a GL240 data logger (Graphtec, Irvine CA).

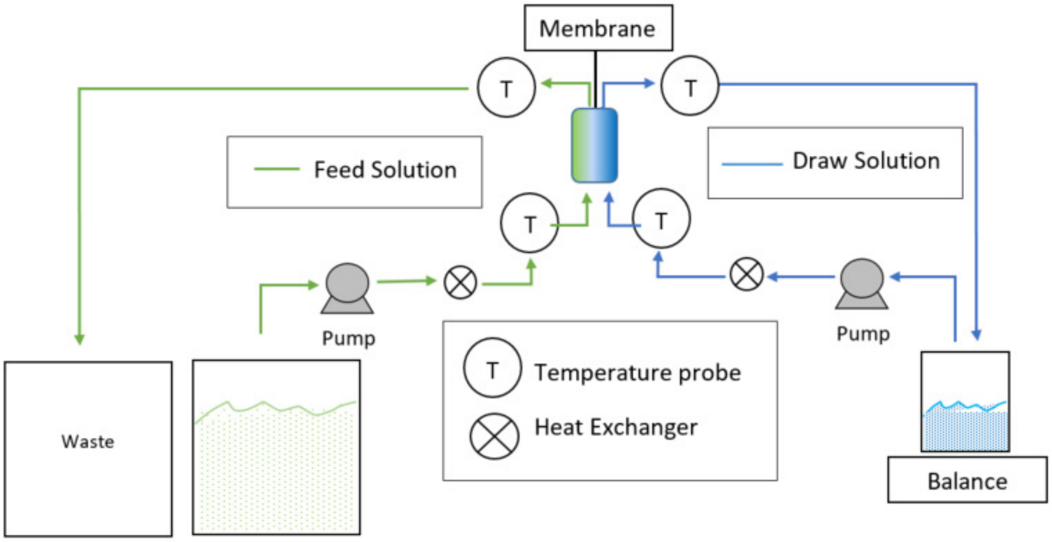

Figure 1. Forward Osmosis bench top design. DS is a closed loop system while the FS is a single pass design.

Two hundred liters of PW was collected to use as the FS. PW was collected from a saltwater disposal site in Midland County of the Permian Basin, as previously described [29,31], in an HDPE barrel. Saturated DS was prepared using ACS-grade magnesium chloride hexahydrate (VWR, Radnor PA). Previous works [31,37] used sodium chloride to prepare the DS; however, the DS was switched to magnesium chloride to increase the osmotic pressure [41]. Saturation was maintained throughout the course of each trial by suspending a porous cotton pouch at the top of the solution filled with 540 g of anhydrous magnesium chloride (Alfa Aesar, Haverhill MA).

7.3.2 Analytical Instrumentation and Chemicals

Carbon content was measured through typical combustion techniques using the Shimadzu TOC-L Analyzer (Shimadzu Scientific Instruments, Inc.). Total suspended solids were quantified using gravimetric analysis for PW samples were filtered using Ahlstrom 1 µm Glass Microfiber

Paper (Leominster, Ma) that were dried overnight at 90 °C. Polyaluminum chloride (PAC) was provided by GEO Specialty Chemicals, Water Treatment Chemicals Division, Ambler PA. Centrifuges used were a IEC Clinical Rotor 809 (Chattanooga TN) for 15-mL centrifuge vials and a Beckman-Coulter Avanti J-E (Indianapolis IN) for 500-mL bottles. DARCO© activated carbon used was from Sigma Aldrich. Anhydrous ferric chloride was produced by EMD Millipore Corporation (Billerica MA). Thermogravimetric analysis (TGA) was performed using a Shimadzu TGS 50.

7.4 Experimental Conditions

In previous experiments using untreated PW as the FS, significant variations were seen in fouling rates. Therefore, PW was manually homogenized using a plastic rod for 30 min before collecting representative samples for each treatment evaluation. Eight treatment techniques were tested using 100 mL of PW, as described in Table 1. These were centrifugation, adsorption on activated charcoal, filtration, addition of ferric chloride, addition of three different polyaluminum chlorides (UltraPAC 261, 2346, and 1145), addition of an amine polymer (UltraPAC 560CV), and a addition of a combination of UltraPAC 261 and the polymer. The supernatant layer was collected for analysis.

It was determined in previous work that the decrease in flux during FO trials using PW as the FS could be attributed to membrane fouling and edge blocking [37]. Membrane fouling is characterized as the formation of a cake layer that leads to irreversible fouling, while edge blocking was caused by particulates blocking the inlet of the hollow fiber. Since it is thought that TOC relates to the formation of the cake layer and particulates were responsible for edge blocking, the focus of the pretreatment methods used for the FO trials was to reduce TOC and turbidity. Turbidity measurements provide insight about the smaller constituents in PW, generally less than

Table 1. Experimental Conditions for Treating Produced Water.

Component	**Conditions**
Centrifugation	Speed 3, estimated to be 2485 rpm, 30 min → supernatant extracted
Activated Carbon	1% (wt), 1 h of stirring → 25 µm vacuum filtration
Filtration	25 µm then 1 µm vacuum filtration
$FeCl_3$	1000 mg, mixed for 5 min stirring on low → supernatant extracted
UltraPAC 261	1000 ppm, mix high 15 sec, low for 15 min → 25 µm vacuum filtration
UltraPAC 2346	1000 ppm, mix high 15 sec, low for 15 min → 25 µm vacuum filtration
UltraPAC 1145	1000 ppm, mix high 15 sec, low for 15 min → 25 µm vacuum filtration
UltraPAC 560 CV	1000 ppm, mix high 15 sec, low for 15 min → 25 µm vacuum filtration
UltraPAC 261 & UltraPAC 560CV	1000 ppm of each coagulant, mix high 15 sec, low for 15 min → 25 µm vacuum filtration

1 µm, including dissolved solids, colloids, and bacteria [27]. pH was also monitored during the pretreatment trials in order to ensure that the FO membrane surface would not be adversely affected in subsequent experiments.

The membrane performance during FO trials was evaluated with the FS in contact with the active layer (AL-FS) inside of the hollow fiber, based on previous work [37]. The temperature was also maintained near 25 °C for the FS and DS [31]. Five, 5-part experimental series were conducted using treated PW to evaluate the performance of the FO membranes (Table 2). A new FO module containing fresh membranes was used with each trial. The process began with a baseline measurement to ensure the module was performing as expected. Next, the module performance was evaluated by measuring flux over a period of 7 h. Baseline conditions were repeated after the 7 h trial, and after washing the membrane with deionized (DI) water for 1 h, to compare the performance of the membrane to the initial baseline. Flow rates were maintained at 12 mL/min for the FS and 370 mL/min for the DS through each part of the FO trials. The module performance was determined using Equation 1 after the FO trial, and the standardized fouling index (SFI) was calculated using Equation 2 after washing with DI water.

Table 2. Experimental conditions for the 5-part experiment series to evaluate the performance of the FO membranes.

	FS	**DS**	**Time**
Baseline	DI water	3.5% (wt) NaCl	30 min
FO Trial	Treated PW	54% (wt) $MgCl_2$	7 hours
Baseline after trail	DI water	3.5% (wt) NaCl	30 min
Washing	DI Water	DI Water	1 hr
Baseline after washing	DI water	3.5% (wt) NaCl	30 min

Equation 1 for Module Performance:

$$Module\ Performance = \frac{baseline\ flux\ after\ FO\ trial}{initial\ baseline\ flux} \times 100$$

Equation 2 for Standardized Fouling Index (SFI):

$$Standardized\ fouling\ index = 1 - \left(\frac{baseline\ flux\ after\ washing}{inital\ baseline\ flux}\right) \times 100$$

7.5 Results and Discussion

7.5.1 Raw PW Characterization

The PW from Midland saltwater disposal had a black hue, due to the distributed particles, with a specific gravity of 1.05 ± 0.01. The only constituents of concern in this sample that were above the direct reuse limit were TOC, calcium, and boron; however, significant compositional variability can exist in PWs from a given region [29], which further substantiates the need for pretreatment to maintain a cost-effective and reproducible reuse practice. The PW exhibited a TOC concentration of 147.2 ± 0.3 mg/L and a neutral pH (Table 3). Calcium was 1.5 times greater than the 2,000 mg/L reuse limit with a value of 3,018 mg/L, while magnesium at a concentration of 432 mg/L was not a scaling concern [13,27,28,42]. Calcium and magnesium, along with other group II cations, are generally the largest contributors to the formation of scale [43]; whereas elevated levels of boron, iron, titanium, and zirconium [44,45], which are metals used as crosslinkers to increase molecular weight of fracturing fluid, can reduce gel viscosity, alter temperature stability, and reduce the efficiency of proppant dispersion [46]. The boron levels for the untreated PW exceeded the suggested reuse value of 10 mg/L (49.05 mg/L) [13,26,27]; however, iron was below the reuse limit of 10 mg/L [13,26,27]. Other common metals used as crosslinkers were not detected in the sample. TSS were below the reuse limit of 500 mg/L, with a concentration of 300 mg/L [13,27,28,42].

The particles in the solution were also analyzed, and the relevant data are shown in Figure 2. The particles were determined to be oil-wetted solids, which can be categorized into four groups: Volatile organics; nonvolatile organics; decomposable inorganics; and thermally stable inorganics. The outer layer represented in Figure 3 for a 1 μm particle is composed of organic outer layer, which surrounds an inner inorganic core.

Upon sitting it was determined that the PW separated into three layers, each presenting their own different properties. They all had a pH near neutral, but the pH of the bottom layer was slightly more acidic (6.59) than the top (7.36) and middle (7.49) layers. The top layer had a TOC of 24.5 ± 0.8 mg/L. The middle layer, which was the clearest based on visual inspection, has a TOC of 13.7 ± 0.8 mg/L. The bottom layer had the highest particulate concentration and exhibited a TOC value of 180.6 ± 0.3 mg/L.

Table 3 Analytical parameters measured for the raw PW.

Parameter (mg/L)	
Total Alkalinity $CaCO_3$	208
TDS	112,000
TSS	300
TOC	147.2 ± 0.3
pH	7.06
Specific Gravity	1.05 ± 0.01
Bromide	429
Chloride	77,000
Fluoride	<0.034
Nitrate	<0.06
Sulfate	416
B	49 ± 2
Ba	2.4 ± 0.2
Ca	3,000 ± 200
Fe	1.7 ± 0.3
K	460 ± 20
Li	16.8 ± 0.8
Mg	430 ± 20
Mn	1.9 ± 0.1
Na	37,00 ± 3,000
Si	15 ± 1
Sr	430 ± 30

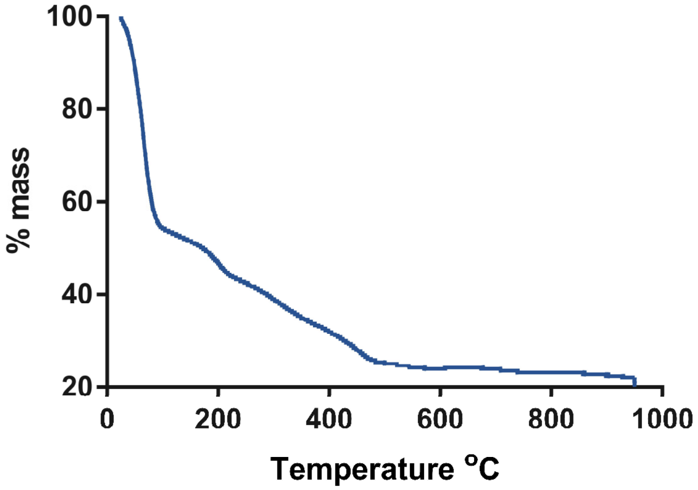

Figure 2. Thermogravimetric analysis of PW particles. Four distinct groupings were determined: 1) Loss of water and volatile organics until 100 °C, 2) loss of larger organic molecules such as gas and diesel range compounds up to 500 °C, 3) primarily the loss of decomposing inorganics, such as calcium carbonate, above 500°C, and 4) residual inorganics, such as iron oxides and dirt.

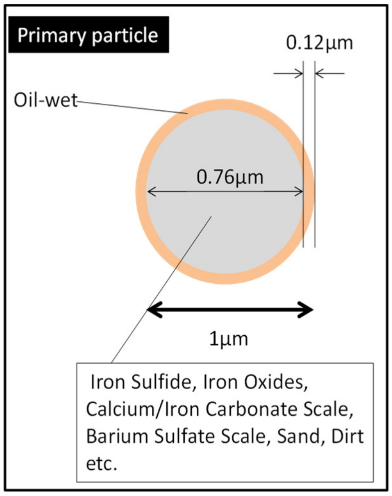

Figure 3. Representation of the predicted layers of a PW particle based on the mass percentage ration from thermogravimetric analysis.

7.5.2 Analytical Results for Pretreated PW

Ultimately, the pretreatment options that were selected to produce FS for the FO experiments were centrifugation, activated carbon, filtration, UltraPAC 2346, and the UltraPAC combination 261 and 560CV based on analytical parameters listed in Table SI 1. Twenty liters of homogenized PW was collected and treated using the predetermined conditions. Following centrifugation, the resulting TOC concentration was 16.5 ± 0.5 mg/L with TSS and turbidity values of 360 ± 60 and 46.9 ± 0.6 NTU, respectively (Table 5). The addition of activated carbon followed by 25 µm filtration lead to the best conditions with a TOC value of 1.9 ± 0.1 mg/L. The TSS and the turbidity were also the lowest among the treatment options used. Filtration with a 1 µm pore size had a residual TOC level of 12 ± 1 mg/L with an unexpectedly high TSS value of 220 ± 20 mg/L represented in Table 5. The addition of the coagulant alone had a lower TOC value (7.9 ± 0.4 mg/L) than when the combination of a coagulant and polymer was used (12.9 ± 1 mg/L). However, the coagulant alone had higher TSS (300 ± 200 mg/L) and turbidity (21 ± 6 NTU). Metals measured in the untreated PW were not influenced by pretreatment methodologies.

Table 4 Analytical Parameters for the 20 L of treated PW used as FS.

Treated PW FS	TOC (mg/L)	TSS (mg/L)	Turbidity (NTU)
Centrifugation	16.5 ± 0.5	360 ± 60	46.9 ± 0.6
Activated Carbon	1.9 ± 0.1	70 ± 20	26 ± 1
Filtration	12. ± 1	220 ±20	65 ± 3
UltraPAC 2346	7.0 ± 0.4	300 ± 200	54.3 ± 0.9
UltraPAC 261 & Ultra PAC560CV	12.9 ± 0.5	200 ± 100	21 ± 6

7.5.3 Forward Osmosis with Pretreated PW

Over the 7-hour trial, the 20 L of PW that was centrifuged to remove particulates had a decrease in the flux of 12% (Table SI 2). During the trial using the centrifuged FS, no edge blocking was visible, and fouling was not indicated based on the module performance of 115%, which showed improved flux compared to the baseline. Overall, the FS that was pretreated with activated carbon, which had the lowest TOC and TSS, performed the best. During the 7-hour trial, the flux decreased by 14% as shown in Figure 5. However, there was an improvement in module performance after the FO trial, 114%, and no fouling occurred during trial based on the standard fouling index (SFI) of with DI water for a when compared to the baseline flux (Table SI 2). Filtered PW with no additional treatment had the worst performance. A build-up of particles at the inlet FO module occurred rapidly, which lead to a decrease in the flux of 79% during the 7-hour trial (Figure 5). Notably, the PW pretreated with filtration alone had the highest turbidity. The module performance after the FO trial was -16% indicating that the flux was reversed so that the pure water was being extracted from the DS because of the high particulate concentration at the inlet of the hollow fiber tube and possibly inside the membranes. After washing for one hour with DI water, the SFI revealed an increase in the flux of 5%, when compared to the baseline, showing that the membrane's surface was not permanently fouled. The flux decreased the least over the course of

7 hours for both trials where the PW was pretreated with UltraPAC. The FS treated with the UltraPAC 2346 exhibited a 2% decrease in flux, while a 4% decrease was calculated for the FS treated with a combination of UltraPAC 261 and 560CV. The high SFI, 25% for the polyaluminum chloride trial and 31% for the combination trial, was unexpected based on the minimal decrease in flux over the course of the 7-hour trial. When a solution with a neutral pH is utilized as the FS, the membrane has a slightly negative charge, while the coagulant and polymer have a residual positive charge. When the high-salinity PW was used as the FS, the coagulant and polymer remain in solution. However, the lines were not drained prior to replacing the FS of treated PW with DI water to replicated baseline conditions. Instead, the flow was controlled by directional knobs to change the FS and DS. Once the FS and DS were changed the fluid was discarded until the new fluid filled the module and tubing. Once FS became diluted because of the influx of DI water, it is believed that the positively charged additives preferentially interact with the membrane, leading to fouling. The polymer, with the long hydrophobic tail, would potentially have an increased propensity for the adhering the membranes surface, which is reflected by the lower module performance compared to the coagulant alone. Furthermore, the increase SFI for the coagulant/polymer combination indicates that the polymer has an impact on the membrane fouling

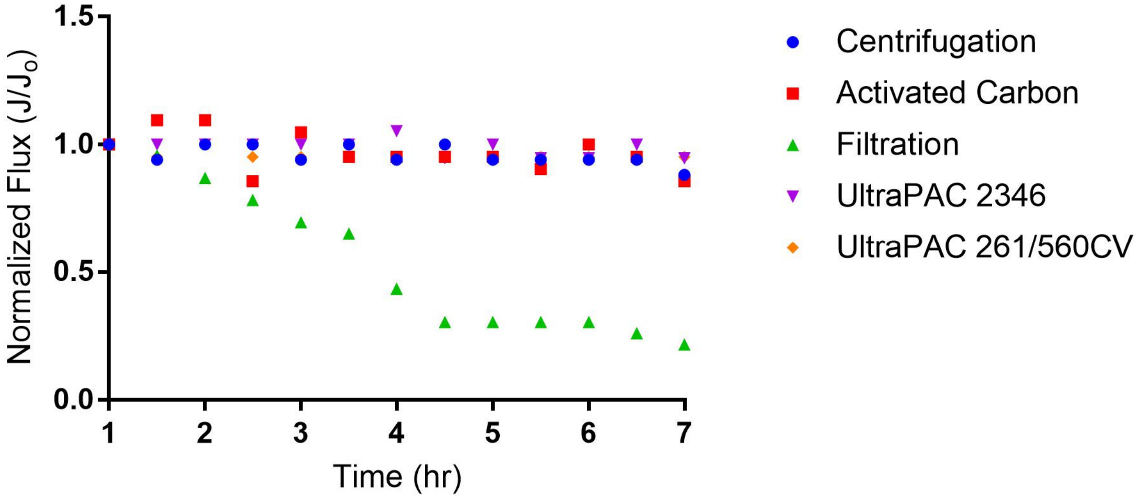

Figure 4. Normalized flux of the five pretreated produced water samples used for a FS for the FO trials.

7.6 Conclusions

Current methodology for handling PW through the use of subsurface injection is not environmentally sustainable, due to the massive loses of water from the water cycle and the induction of seismic event. Consequently, there is a growing need for cost-effective treatment options for large-scale operations that can process 500,000 gal of PW/day and even up to 1,000,000 gal of PW per day [15]. FO is a promising technique for treating high-salinity PW for reuse in subsequent well development and when paired with a desalination method can be used to reintroduce previously contaminated water back into the water cycle. FO has been evaluated in several studies including The Green Machine pilot plant being operated in the Haynesville Shale [1,33,41,47,48] with membrane fouling has been the most significan opposition to widely successful implementation. Cost-effective pretreatment methods are required to be able to consistently and reproducibly use FO as a remediation method. Chemical treatment is a favorable approach as seen by the limited decrease in flux using the coagulant UltraPac 2346 and the combination of coagulant and polymer, UltraPAC 261/560CV. However, when treated PW FS was replaced with DI water to replicate the baseline conditions, an unexpected drop in the modules performance was measured. It is believed that the decrease in flux was due to residual levels of the PAC and polymer remained in the FS; studies have indicated that residual levels of coagulants and polymers can induced membrane fouling [49,50]. Future work optimizing the coagulant/flocculant ratio should be considered. Moreover, studies that focus on the effects of sedimentation time and prefiltration as a secondary step would be valuable.

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7.8 Supplemental Information

TableSI 1 Analytical parameters measured for the treated PW.

Component	TOC (mg/L)	pH	Turbidity (NTU)
Centrifuge	16.9 ± 0.4	7.00	24 ± 2
Activated Carbon	1.6 ± 0.4	7.28	17.4 ± 0.4
Filtration	17.1 ± 0.6	7.46	85 ± 7
$FeCl_3$	10.4 ± 0.2	1.68	530 ± 70
UltraPAC 261	16.3 ± 0.4	5.19	67 ± 17
UltraPAC 2346	15.4 ± 0.5	6.79	56 ± 4
UltraPAC 1145	14.9 ± 0.2	3.95	74 ± 3
UltraPAC 560 CV	25 ± 1	7.06	40± 10
UltraPAC 261 & Ultra PAC560CV	18.5 ± 0.7	7.11	24.9 ± 0.6

TableSI 7-2 The initial baseline flux, baseline after FO trials. and baseline after washing module for 1 hr with DI water. The module performance and standard fouling index is also provided for FO trial using pretreated PW as the FS.

Component	Baseline Flux (LMH)	Baseline Flux after FO Trial (LMH)	Baseline Flux after Washing (LMH)	% Flux Decrease over 7 hr Trial	Module Performance After FO Trial	Standardized Fouling Index (SFI)*
Centrifuge	11.6	13.3	11	12%	115%	5%
Activated Carbon	12.0	13.7	12.6	14%	114%	-5%
Filtration	14.6	-2.4	15.4	79%	-16%	-5%
UltraPAC 2346	12.2	2.2	9.2	2%	18%	25%
UltraPAC 261 & UltraPAC 560CV	13.3	1.2	9.2	4%	9%	31%

*Negative SFI indicates an improvement in module performance.

Summary and Future Work

Unconventional development recovers sequestered hydrocarbons from shale and tight sands, which were previously considered uneconomical.[1,2] The rapid expansion of unconventional oil and gas extraction has changed the energy landscape nationally and globally.[1,3,4] The process requires advanced technologies to extract oil and gas from low porosity formations, such as hydraulic fracturing and horizontal drilling.[5–7] During well stimulation with hydraulic fracturing, millions of gallons of freshwater resources can be used which are mixed with proppants and chemical additives; [8–10] once complete, millions of gallons of highly variable, chemically-rich wastewater is produced daily. This waste stream can contain a mixture of organic and inorganic additives, transformation products, as well as inorganic and organic substances from the formation. [11] Significant knowledge gaps exist because of the limited requirements to report water usage, the protection of proprietary chemical additive information, in addition to the lack of validated and approved analytical methods from U.S. regulatory agencies for evaluating produced water. Collectively, these gaps have led to an inadequate understanding of the environmental and human impacts of unconventional development. This has incited concern among the citizens of this nation. Concerns are centered around high-water usage required for unconventional development, frequently in arid and semiarid regions,[12] and the process of handling the ever-increasing volumes of wastewater being produced. Furthermore, the unknown implications from human and environmental exposure during contamination events is an issue, due to the lack of knowledge. To mitigate these concerns, it is necessary to understand the lifecycle of water in oil and gas development (conventional and unconventional) and the constituents in produced water.

The volumes of water used and waste produced was evaluated for each phase of unconventional development: drilling, stimulation, and production. Additionally, current waste management strategies and challenges, as well as the widespread implications of the varying forms of waste management and reusability were addressed. Ultimately, it was determined that the feasibility of reusing produced water hinges on the water quality.[13–15] Additionally, the primary disposal practice of injecting the waste stream into subsurface, non-productive stratum has proven to not be environmentally sustainable due to induced seismic events[1,16,17] and loss of water from the water cycle.

Through the pursuit of a deeper understanding of the chemicals which could be present in the waste stream implications of potential exposure and contamination remediation can be addressed. This can be accomplished through the review of current analytical methods applied to the evaluation of produced water, the development of new methods, and the validation of methods. Additionally, filling these knowledge gaps equips engineers and scientists with the ability to discern if direct reuse is an option, and to provide valuable insight into how to test the water quality of the waste stream. One can also determine the variability of produced water over time within or between a given set of regions.

Twenty-four unconventional development wastewater samples were evaluated from South and West Texas to characterize their variability and to assess the feasibility for direct reuse without treatment.[18] Analytical methods were used to assess bulk measurements, including total organic carbon, total nitrogen, as well as total dissolved and suspended solids; additionally, pertinent inorganics were quantified and compared to reuse thresholds. Significant variations were not only seen between the regions evaluated but among samples collected from the same region. For example, the average total organic carbon for Eagle Ford samples collected was 700 ± 500 mg/L, while samples collected from the Permian Basin measured 600 ± 900 mg/L. The high standard deviation for the Permian Basin total organic carbon was indicative of the variability of samples with values of 1,032 mg/L, 889 mg/L, 38 mg/L, 46 mg/L, 51 mg/L, 147 mg/L, 73 mg/L, and 2,600 mg/L. The total dissolved solids levels had the same variability between regions with an average value for Eagle Ford 20,000 ± 10,000 mg/L and the Permian Basin value was 150,000 ± 40,000 mg/L. Based on published reuse guidelines, the direct reuse of untreated produced water for subsequent well development is not a suitable option. Furthermore, consistent water quality output is essential to cost-effectively reuse produced water, and this is difficult to achieve without pretreating the waste stream.

In order to maintain responsible practices, the development of cost-effective treatment technologies, which allow produced water to be reused in an economical fashion, are essential.[19] A study of various treatment options currently utilized in shale energy basins was conducted.[20] Focus centered around the key parameters of concern, including organic, inorganic, and biological constituents, as well as naturally occurring radioactive material. Advancements in water treatment technologies have improved the efficacy and financial viability of produced water recycling for beneficial reuse in the oil and gas sector. However, the complex and highly variable biogeochemical composition requires a series of technologies to effectively treat produced water.[21,22] Viable options need to be inexpensive, modular in design, have a low tendency for fouling, and handle significant throughput (up to 20,000 barrels a day or 840,000 gal). If recycling for other industrial applications is the ultimate objective, then efficient desalination of the effluent is also required.

Forward osmosis, an osmotically-driven process, is one of the few approaches considered to be a viable option to treat produced water solutions, which can have a salinity up to 2.5 to 3.5 times higher than seawater.[21] The process osmotically dilutes the draw solution by moving pure water across a semi-permeable membrane from a feed solution.[23–26] When paired with techniques to regenerate the draw solution, such as reverse osmosis and membrane distillation, desalination can be achieved.[24,26] The two-step process, osmotic dilution and freshwater extraction from the diluted draw solution, can serve a dual purpose. First, it can decrease the volume of PW injected into formations, thus reducing concern related to seismic activity, and it can provide a brine solution for future well stimulation. Second, when paired with a desalination technique to extract the pure water, this process could potentially be used to recycle produced water for use in other anthropological activities (i.e., irrigations, agricultural, etc.). It could also provide an opportunity to recharge depleted aquifers. Three studies were conducted to determine if remediation of high salinity produced water from the Permian Basin with total dissolved solids ranging from 16,000 to 210,000 mg/L was a viable option. Analytical methods were used (and developed, where necessary) to validate the effectiveness of the using forward osmosis for the remediation of produced water.

The first study tested the fundamental concept of forward osmosis with thin-film composite hollow fiber membranes, which proved to be successful. Water was successfully extracted from Permian Basin produced water. Minimal levels of total organic carbon transferred to the draw solution, in the form of small organic compounds, during the experimental series. Through this process, it was determined that flux was influenced by the osmotic gradients, temperature, and fouling. When the temperature was maintained during forward osmosis trials, a decrease in flux was still seen. The two most probable causes for flux loss were membrane fouling, and concentration equilibration between the feed and draw solution. Membrane fouling hinders the transport of pure water across the membrane's surface. The osmotic pressure was the primary driving force for the flux.

A second study determined the cause of the decrease in flux. Through the course of the evaluation, the temperature was maintained near 25 °C, and adecrease in the osmotic pressure difference wasinhibited. The prevent osmotic dilution of the draw solution, saturation was maintained by suspending a cotton, porous pouch from the surface, and the feed solution was replenished daily. During the study, irreversible fouling occurred on the membrane’s surface, which was determined using a scanning electron microscope to be primarily organic in nature. Insoluble precipitates of calcium, magnesium, silicon, and strontium were a contributing factor, as well. Additionally, it was determined that there was a decreased propensity for fouling when working at lower flux rates.

The third study investigated the treatment of produced water prior to using forward osmosis as a remediation option. Samples were treated by centrifugation, activated carbon, filtration, ferric chloride, as well as coagulants and a polymer. It was concluded that pretreating the produced water prior to forward osmosis decreased the tendency for fouling. Flux had a minimal reduction over the course of the 7-hr trials.

The aim of future work should be centered around the optimization of the pretreatment process. This should include developing an optimized series of treatment methodologies. For example, based on the findings it was determined that a combination of coagulation and polymerization was effective at removing foulants, but upon washing, they caused a decrease in flux. Therefore, the inclusion of a clarifying tank to allow residual additives to settle out of solution could prove beneficial. Additionally, absorption on activated carbon was the most successful pretreatment method to reduced total organic carbon levels. As such, the addition of active carbon either before or after forward osmosis could help to eliminate small organics, such as methanol, that were detected crossing the semi-permeable membrane with water. Evaluating additional methods to alternative methods to clean the membrane’s surface would be beneficial, as well as pairing forward osmosis with a desalination technique.

Ultimately, the goal would be to scale up the lab-based system for field application. However, the cost would be the primary driving force behind the success of the system. In 2015, approximately 40-55% of UD operational costs were associated with produced water management and disposal comprising a $12.6 billion industry.[2728] The cost of transporting and disposing of PW in SWD well ranges from $1.00/bbl to $8.00/bbl.[27] Current treatment options tend to be a more expensive alternative to SWD disposal, and can range from $5.00/bbl to $14.00/bbl.[29] For a treatment option to be competitive in the oil and gas industry, it need to be able to process approximately 20,000 bbl/day and be competitive with SWD operations. Given the expenses associated with transporting and disposing of produced water, reusing it for subsequent hydraulic fracturing operations could theoretically lower water costs by approximately 45% per well,[27] while also reducing the reliance on freshwater resources.

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