

**EVALUTATION OF A HYBRID TREATMENT SYSTEM FOR FRACKING
WASTEWATER**

by

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ABSTRACT

The United States' pursuit of energy independence since the 1970s introduced a hydraulic fracturing (fracking) revolution for natural gas as a fuel source. Marcellus Shale in Pennsylvania has been the focal point as it is the largest known shale reserve in the U.S. and possibly the world, with approximately 77.2 trillion ft³ of natural gas production potential. Fracking presents significant issues for the communities associated with the process. The highly contaminated brine wastewater produced from fracking wells is not treatable in municipal treatment plants. Additionally, induced seismic activity in Youngstown, Ohio has been caused by the primary fracking wastewater disposal technique, deep-well injection. Characterizations have shown that the wastewater is composed of high levels of suspended solids, dissolved organics, salts, oils & greases, and naturally occurring radioactive material (NORM). To reduce the impacts of deep-well injection, comprehensive treatment of the wastewater has been proposed. Traditional treatment technologies explored include: coagulation and flocculation, granular media filtration, micro/ultra-filtration, reverse osmosis, forward osmosis, ion-exchange, activated carbon adsorption, distillation, and advanced oxidation processes. After analysis, a process was proposed using 3 treatment stages: (1) coagulation & flocculation and mixed-media rapid sand filtration to remove particulates and oil & greases, (2) forward osmosis desalination, and (3) advanced oxidation with ozone and hydrogen peroxide to degrade organic material. Design parameters were estimated for each stage to treat wastewater from 10 Marcellus Shale wells. An approximate cost analysis was also conducted to treat a loading of 10,000 m³/day, resulting in a total construction cost of \$56,900,000, and a total operation and maintenance cost of \$14,800,000.

Chapter 1

HYDRAULIC FRACTURING IN THE UNITED STATES

1.1 Energy in the U.S.

Energy independence has been a key interest of the U.S. since the energy crisis of the 1970s when oil became scarce in the nation. This led to decades of research and development of new energy production methods, as well as a search for new fuel sources. The search for new fuels has led to an increase in the use of natural gas as a fuel supply. Sources of natural gas fuel include drilling and hydraulic fracturing techniques in tight formations such as shale, sandstone, and carbonate. These rock formations usually contain large amounts of natural gas trapped in pore spaces throughout the rock. Shale gas is the largest of these sources, with the most potential for fuel production [1].

Large-scale production of natural gas from shale formations began in 2000, when Mitchell Energy and Development Corporation developed the technique of hydraulic fracturing to tap into Barnett Shale in Texas. Barnett Shale spurred efforts around the country with its success, producing 0.5 trillion ft³ of natural gas per year by 2005 [1]. The practice spread to newly discovered shale reserves across the U.S., with notable production in Arkansas, Texas, Louisiana, Oklahoma, and Pennsylvania [1].

1.2 Controversy Surrounding Hydraulic Fracturing

A common belief is that hydraulic fracturing, or fracking, is the cause of elevated induced seismicity (earthquake activity) throughout the U.S. over the past

decade. This is a misconception, explained effectively by studies on the well-known seismic activity in Oklahoma. The United States Geological Survey (USGS) explains that only 1-2% of induced earthquakes in OK can be attributed to fracking activities, while the remainder is due to a fracking wastewater disposal process known as deep-well injection [2]. Also contrary to popular belief, the wastewater produced from fracking contains little (around 10% or less) actual fracking fluid, which is the chemically enhanced water mixture injected in the drilled well during fracking [2]. The disposal wells, drilled in formations such as sandstone or limestone, thus prove to be a significant issue concerning the management of fracking wastewater [3]. While environmental concerns do exist, there are precautions against contamination of groundwater. The Underwater Injection Control (UIC) program from the U.S. EPA ensures that these wells are not abandoned and that injected fluids remain in the well and do not come in contact with other groundwater [3]. The oil and gas related wells are considered Class II by this program, which are primarily found in Texas, California, Oklahoma, and Kansas. The primary concern is seismic activity caused by deep-well injection, which translates the primary issue to fracking wastewater as this practice accounts for greater than 95% of natural gas related wastewater disposal in the U.S. [4].

Despite the controversy surrounding fracking and its subsequent consequences through deep-well injection, the practice is taking root in the U.S. economy as a major fuel source. The U.S. EIA's Annual Energy Outlook of 2018 predicts that natural gas production, consumption, and especially shale gas production are all expected to increase until 2050 [5]. In particular, "increased natural gas production is the result of continued development of shale gas and tight oil plays which account for more than

three quarters of natural gas production by 2050” [5]. Figure 1 below details the EIA’s projections, with the navy ‘Reference’ line representing the raw projection with no significant economic shifts; and Figure 2 depicts the projected dominance of shale in natural gas production.

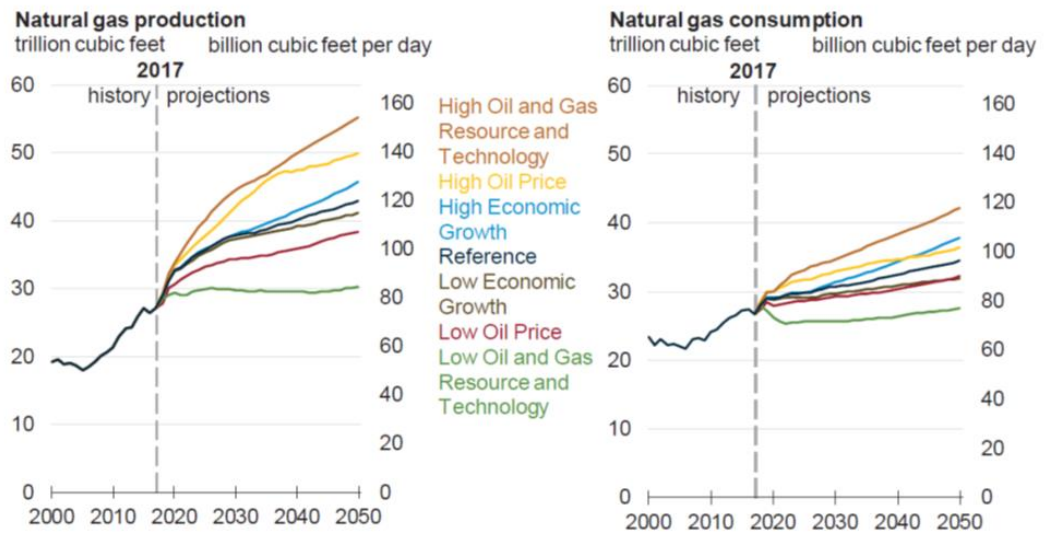


Figure 1: Projections until 2050 of natural gas production and consumption, from the U.S. Energy Information Administration Annual Energy Outlook 2018 [5]

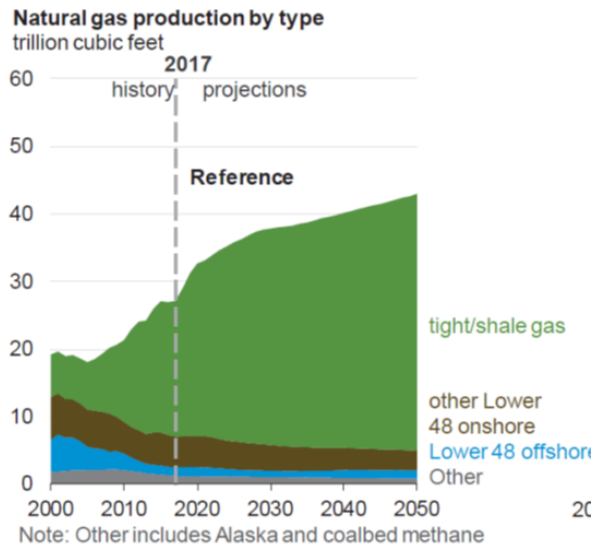


Figure 2: Projection until 2050 of the distribution of natural gas sources, from the U.S. Energy Information Administration Annual Energy Outlook 2018 [5]

1.3 The Marcellus Shale Formation

The focus of this study is on one of the most significant U.S. shale reserves, which is Marcellus Shale, spanning a total of 95,000 mi² across New York, Pennsylvania, Ohio, West Virginia, and Maryland [6]. The formation's boundaries are depicted in Figure 3.

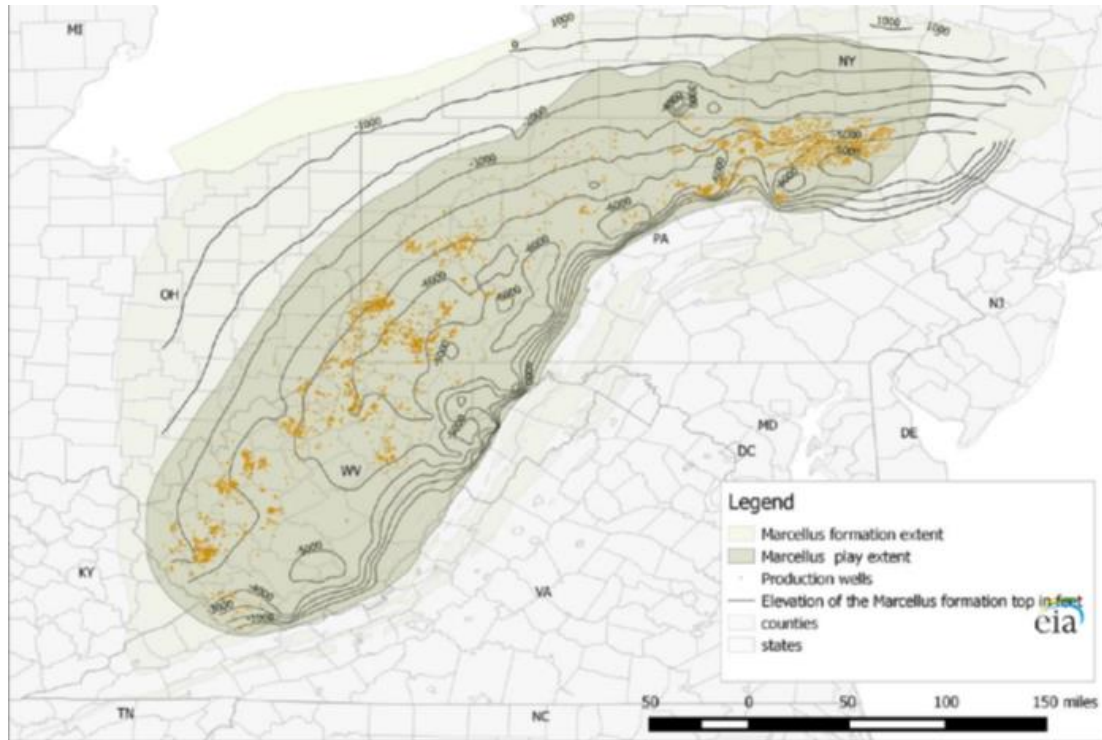


Figure 3: Map of the Marcellus Shale formation, taken from the Energy Information Administration Annual Energy Outlook 2018 [5]

Marcellus is currently reported to hold an estimate of 77.2 trillion ft³ of natural gas anywhere up to 9000 feet below the surface, making it one of the largest shale reserves in the U.S., and possibly the world [6]. While the formation was first drilled in 2003, significant production did not occur until 2008 when hydraulic fracturing was introduced. The practice also introduced a much larger water use, due to hydraulic fracturing techniques, and the formation's water use is currently regulated by the Pennsylvania Department of Environmental Protection along with both the Delaware River Basin Commission and the Susquehanna River Basin Commission. These organizations require fracturing companies to identify sources of water, as well as anticipated impacts to surrounding water sources [7].

Much of the brine wastewater produced in Marcellus Shale is transported and disposed in injection wells in Youngstown, Ohio [8]. The injection wells in this area are typically within sandstone layers with a depth of 2.2 km to 3.0 km, with pressures up to 2500 psi [8]. Drilling first began in 2010 and five wells were created, however only one was in operation from 2011 to 2013. Since operation began in 2010, small earthquakes have occurred and a total of 9 earthquakes with Mw (seismic moment, or the physical size of the earthquake) 1.8 to 2.8 were recorded. This was significant, as Youngstown, Ohio had no previous records of this scale of seismic activity before the operation of these wells [8]. The new seismic activity in deep-well injection sites across the country – and notably in Ohio – has been inextricably linked to the fracking wastewater disposal practice of deep well injection. As such, a different method of managing fracking wastewater can help reduce the need for this practice, therefore reducing the dangerous geological consequences.

1.4 Objectives

After understanding the state and current practices of hydraulic fracturing and associated wastewater management, a treatment process will be proposed to reduce impacts of fracking wastewater disposal through deep-well injection.

This goal is approached by first reviewing literature regarding fracking practices in the Marcellus Shale in Chapter 2. Wastewater production and management will be explored in Chapter 3, and viable treatment methods are discussed in Chapter 4. Chapter 5 presents the proposed treatment process developed from analysis of available methods.

Chapter 2

PROCESS OF HYDRAULIC FRACTURING

2.1 Drilling and Casing

In order to understand the issue of fracking wastewater generation, water use and the general fracking process must be understood. Overall, the process requires a total of 12 million liters per well in the Marcellus Shale [9]; but this water demand spans over several steps. The first step of this process involves drilling through the earth into the shale formation. Wells are drilled 5000 ft to 9000 ft vertically. Subsequent horizontal drilling, which was developed to reduce the number of vertical wells needed, can happen up to 10,000 ft across the formation [7]. In this process, drilling fluid is necessary to cool and lubricate the drill head [4]; reports state water use at 0.4 to 4 million liters of drilling fluid per well [10].

The well must be cased to protect the surrounding subsurface environment. As per EPA requirements in the Underground Injection Control (UIC) Program, a steel pipe is inserted into the borehole and cemented into place. As the well deepens, narrower casings are inserted inside the ones already in place. Once the casing is set, an electric current in a wire perforates the casing, going a little ways into the shale so that the fracturing process can work [7].

2.2 Fracking Fluid

After perforation, fracking fluid is sent into the well at high pressure, which enters the perforations and shatters the shale rock, releasing gas. The horizontal part of the well is fracked in steps, so that plugs are used to withhold fracking fluid until the desired section has been perforated [7]. The fracking fluid is typically 11.5 to 19 million liters of a chemically enhanced mixture of sand and water [10]. It consists of

88-90% freshwater (the rest being water recycled from previous fracking operations), which accounts for 86% of the total freshwater consumption in the life of a Marcellus Shale well [9]. The additives are usually proppants (sand or ceramic beads to hold fractures open for gas flow), biocides, anti-corrosives, viscosity correctors, and friction reducers, which all serve to improve the performance of the fluid [7]. Table 1 summarizes the types of additives, along with a summary of their purpose and possible substances used [10].

Table 1: Summary of Fracking Fluid Additives [10]

Constituent	Composition (% by volume)	Example Substances	Purpose
Water and sand	99.50	Sand suspension	“Proppant” sand grains hold fractures open
Acid	0.123	Hydrochloric acid, muriatic acid	Dissolves minerals and initiates cracks in the rock
Friction reducer	0.088	Polyacrylamide, mineral oil	Minimizes friction of the fluid in the pipe
Surfactants	0.085	Isopropanol	Increases viscosity
Salt	0.06	Potassium chloride	Creates a brine carrier fluid
Scale inhibitor	0.043	Ethylene glycol	Prevents scale deposits on pipes
pH-adjusting agent	0.011	Sodium carbonate, potassium carbonate	Maintains effectiveness of chemical additives
Iron control	0.004	Citric acid	Prevents precipitation of metal oxides
Corrosion inhibitor	0.002	n,n-dimethyl formamide	Prevents pipe corrosion
Biocide	0.001	Glutaraldehyde	Minimizes bacterial growth that produce corrosive and toxic by-product

After the well is fracked, gas flows through the cracks into the cased well and is collected at the surface. Marcellus Shale wells are known to produce much more gas than conventional wells but do require higher water use. Studies produced fuel production data averaged over 824 Marcellus Shale wells. On average, each well produced 11.2 billion liters in their first year as of 2013, compared to 198 million from conventional wells [4]. Over the lifetime of the well, Marcellus Shale wells produce 30 billion liters, while conventional wells only produce 1.1 billion liters [4]. Table 2 summarizes water use for a Marcellus Shale well. Lower versus higher water use can be attributed to the length of the well, such as the difference in drilling distance for a vertical well or a horizontal well.

Table 2: Summary of Total Water Use for a Marcellus Shale Well [4]

	Drilling (million liters)	Fracking Fluid (million liters)	Total (million liters)
Low	0.4	11.5	11.9
High	4	19	13
Average	2.2	15.3	17.5

Chapter 3

WASTEWATER PRODUCTION AND MANAGEMENT

3.1 Types of Wastewater

Throughout the life of a shale well, three types of wastewater are produced – drilling wastewater, flowback, and produced water. The first type that will be discussed is drilling wastewater. Shale wells require more drilling than conventional wells due to horizontal drilling and depth, so there is more water used and therefore higher wastewater production [4]. Specifically, Marcellus wells produce 0.654 million liters of drilling wastewater per well, while conventional wells produce 0.116 million liters which is six times less than shale [4].

The second type of wastewater is known as flowback, which mostly consists of fracking fluid that returns to the surface once gas production begins. However, much of the fracking fluid can be absorbed by shale rock below the water table so that on average, 10-70% of shale well fracking fluid returns. In Marcellus Shale only 10% to 30% of fracking fluid used in a single frack returns to the surface [7]. This flowback is often defined as wastewater produced by the well in the first 2 weeks to 1 month of gas production, and can return at a rate as high as 1000 m³/day for a single well [4], [10]. Marcellus Shale reportedly produces a total of 1.68 million liters of flowback per well, which represents 32.3% of the well's total wastewater generation. In comparison, conventional wells return only 0.107 million liters of flowback [4]. Flowback wastewater usually has an elevated level of salinity, as well as metals and possibly normally occurring radioactive material (NORM) [4].

The wastewater produced after the first month of production and then over the lifetime of the well is known as produced water. This is a subsurface brine originating

from the reservoir's rock formation, and contains much higher levels of metals, organics, and NORM than produced water, and sometimes residual fracking fluid [4]. The longer this wastewater takes to come to the surface, the more concentrated it is with contaminants from the shale rock [4], [11]. Throughout the well's life, wastewater production decreases over time so that produced water usually returns at a rate of 2 m³ to 8 m³ per day [10]. Also, while Marcellus wells produce 1.37 million liters of this brine in the first year, that dwindles to 0.105 million liters by year 4 of gas production [4]. This is still significantly higher than conventional wells, which produce 0.102 million liters in the first year which decreases to 0.042 million liters [4]. Produced water contributes most to the toxic condition of fracking wastewater. Studies have characterized this type of wastewater, revealing extremely high salinity and dissolved solids among other contaminants.

Overall, Marcellus Shale wells produce approximately 570% more wastewater than conventional wells in their first and second year of gas production, despite that Marcellus shale is considered a low-water forming shale. However, conventional wells do produce three times more wastewater than Marcellus wells per unit of gas produced; Marcellus shale produces about 3.3 to 27 m³ of wastewater per million cubic meter of gas [4].

3.2 Current Wastewater Management Practices

Studies conducted in 2013 and 2014 established Marcellus Shale's wastewater management practices. Overall, management involves a combination of three options: recycling, treatment, and deep-well injection.

3.2.1 Recycling

Recycling involves reusing the wastewater for fracking purposes, by diluting the wastewater or after minor on-site treatment (such as filtration and sedimentation) [7]. However, minor treatment is not sufficient to permit recycling on a large scale, since the wastewater still contains enough contaminants to interfere with fracking fluid performance [4], [7], [9]. In particular, ionic species can slow down gas flow once gas production begins, drawing out the life of the well [4]. Also, bacteria that may be present tend to produce corrosive by-products, reducing the integrity of the well casing; however, this issue is rare since fracking fluid often incorporates biocides for this purpose. Additionally, the wastewater's elevated salinity levels are known to cause shrinking and swelling of clay (a soil easily susceptible to such changes) within the formation, which can damage both the well-casing, and the integrity of the shale formation [4]. As such, before 2011, only 13% of total wastewater volume was actually recycled; but after further consideration and application of minor treatment processes, 56% of the wastewater volume was recycled after 2011. Most of this was flowback wastewater, which contains less contamination from the formation [4], [11]. The recycling process used in Marcellus Shale involved common primary treatments including settling and filtration, which costed 36-63 cents per cubic meter of wastewater [9].

A more comprehensive analysis by Jiang et al. in 2014 yielded the percentage of each wastewater that was able to be recycled in the years 2011 to 2013 [9]. Most of the drilling wastewater was recycled as it contained little contamination and additives, and even more flowback was recycled for the same reason. Little over 50% of the produced water, however, was recycled as it requires significant dilution to be used for other purposes [9].

3.2.2 Municipal Wastewater Treatment Plants

Small amounts of wastewater are sent to municipal wastewater treatment plants (MWTPs), and occasionally industrial treatment plants. MWTPs, per Pennsylvania law, are only allowed to accept 1% of their total daily load as fracking wastewater as it has been proven to cause issues with effluent quality [11]. In particular fracking wastewater has been proven to result in disinfection by-products, and they disrupt microbial activity during aerobic and anaerobic degradation processes. Effluent is often marked with increasing bromides both in its ionic form as well as in the form of disinfection by-products, and high TDS concentration in effluent discharged to surface waterways. The presence of disinfection by-products from fracking wastewater has promoted a shift from chloride to chloramine in many MWTPs [11].

Three treatment plants were examined by a study in 2013 to observe the effects of fracking wastewater on effluent quality [11]. First was the City of McKeesport publicly owned treatment plant that reported accepting, per PA law, 1% of their total daily load as fracking wastewater. Treatment methods included filtration, flocculation, aerobic degradation, and clarification. This rather traditional treatment process targets organic matter, but not soluble inorganics such as salts and heavy metals. The study found that the effluent consisted of 0.14-0.81% fracking wastewater with most contaminants still present [11], showing the MWTP only diluted the wastewater.

Another MWTP of Franklin Township Greene County, accepted 50,000 gallons per day of fracking wastewater. The process included filtration, flocculation, skimming, both anaerobic digestion and aerobic degradation, and clarification. Similar to the City of McKeesport, this process targets organics, but also oils and greases that

may coat the surface. Effluent was found to be 5.4% fracking wastewater, with contaminants again present but diluted [11].

One industrial treatment plant was also examined as a potential sink for fracking wastewater. The PA Brine Josephine commercially operated industrial facility that treats only oil and gas related wastewater. The process involves several steps to remove a larger variety of wastewater than MWTPs. It includes: debris removal in a spillway as well as settling, precipitation with Na_2SO_4 and polymer agents for alkaline earth metals, clarification with a fine lamellae screen, and a silicone defoamer agent. Solid waste resulting from the process is mechanically pressed and landfilled. While the process was able to dissolve cations and reduce the metal content, it still resulted on little to no impact on the total dissolved solids (TDS) concentration of fracking wastewater [11].

As shown in Table 3, little drilling and produced wastewater was treated through MWTPs or industrial treatment facilities, and almost no flowback [9]. This is likely because these treatment plants do little more than dilute the contaminant levels. While that is effective at meeting water quality standards, it still results in release of harmful compounds into the environment.

3.2.3 Deep-well Injection

The third method of wastewater management used in the Marcellus Shale is deep-well injection. As mentioned previously, this involves the wastewater being shipped to Youngstown, Ohio where wells have been drilled for this use, but also results in the aforementioned consequences: elevated induced seismicity [8]. While a relatively small percentage of each type of wastewater is disposed of in this manner, evidence of Youngstown's seismic activity [8] proves it is enough to produce these

dangerous effects. Produced water is wastewater with the largest percentage to be disposed of, consistent with its elevated contaminant levels that make it particularly difficult to treat. In 2014, the process of pumping the wastewater into the wells costed \$0.59 to \$13 per cubic meter, not including transportation costs [9].

Table 3 summarizes the percentages of each type of wastewater managed via recycling, transport to a treatment plant, and deep-well injection.

Table 3: Summary of Wastewater Production & Management in the Marcellus Shale

Type of Wastewater	Volume Produced (million liters) [4]	Recycling [9]	MWTP/treatment facility [9]	Deep-well injection [9]
Drilling	0.654	70.7-85%	15-19.8%	0-9.5%
Flowback	1.68	89-95%	5-6.8%	0-3.4%
Produced	1.37 in year 1* 0.102 in year 4*	55.7-56.9%	11.6-30.3%	12.2-32.7%

*year of gas production

3.3 Wastewater Characterization and Potential for Effective Treatment

In order to understand the difficulties surrounding fracking wastewater, it must be characterized. In a study by He et al. (2013) Marcellus wastewater was characterized to understand the contaminants of concern. Table 4 shows the contaminant levels reported [12]. Each average was taken over multiple wells where the reported data was available.

Table 4: Marcellus Shale Wastewater Characterization [12]

Parameter	Minimum (mg/L)	Maximum (mg/L)	Average (mg/L)
TDS	680	345,000	106,390
TSS	4	7,600	352

Oil and grease	4.6	802	74
COD	195	36,600	15,358
TOC	1.2	1,530	160
pH	5.1	8.42	6.56
Alkalinity	7.5	577	165
SO ₄	0	763	71
Cl	64.2	196,000	57,447
Br	0.2	1,990	511
Na	69.2	117,000	24,123
Ca	37.8	41,000	7,220
Mg	17.3	2,550	632
Ba	0.24	13,800	2,224
Sr	0.59	8,460	1,695
Fe dissolved	0.1	222	40.8
Fe total	2.6	321	76
Ra228 (pCi/L)	0	1,360	120
Ra226 (pCi/L)	2.75	9,280	623
U235 (pCi/L)	0	20	1
U238 (pCi/L)	0	497	42

From this table, the following categories of contaminants were determined: suspended solids, dissolved organics, salts, oils & greases, and NORM. Organics, specifically in the Marcellus Shale, usually consist of BTEX (benzene, toluene, ethylene, and xylene) and occasionally other naturally occurring organic material. Flowback water may contain chemicals added to fracking fluid including surfactants and friction reducers; however, the identities of these chemicals are not known. Of the four categories, the last contaminant, NORM, has been found to be inconsistent among other characterizations [10] and can possibly be dependent on the sampling location geology. Therefore, treatment is concentrated on the other four categories.

While suspended solids and dissolved organics can be removed via common treatment methods including filtration and biological degradation, the extremely high level of salinity provides an obstacle. Desalination methods such as distillation,

thermal crystallization, and reverse osmosis are known to have high costs and energy demands [10], [12]. Also as mentioned previously, the contaminant levels interfere with biological activity when MWTPs take as little as 1% of their daily load of fracking wastewater [11]. Evidently, these four main contaminant categories make treatment of fracking wastewater a difficult and complex issue. As such, this study was conducted to review traditional (and relatively common) treatment technologies and methods that may be feasible for the treatment of fracking wastewater. First, a literature review was conducted to understand the available treatment options, as summarized in Chapter 4. Chapter 5 will discuss the combination of certain selected methods to formulate a simple treatment process that can be applied to fracking wastewater from the Marcellus Shale.

Chapter 4

TREATMENT OPTIONS APPLICABLE TO FRACKING WASTEWATER

The following is a review of traditional methods of water treatment that may be used specifically for treating fracking wastewater. The main categories of pollutants being targeted are suspended solids, organic material, salinity, and oils and greases. For comparison purposes the costs for each process state construction and operation/maintenance separately. Design flow was considered for the total wastewater flow from 10 Marcellus Shale wells within a 10 square mile radius, which total approximately 10,000 m³/day (for details and calculations, see Appendix A) Also, costs are represented in 2008 U.S. dollars (2008 USD) unless otherwise specified. Cost calculations can be found in Appendix B.

4.1 Coagulation and Flocculation

Coagulation and flocculation treatment processes typically applied before filtration or sedimentation processes to make suspended solids and particulate removal more effective. It involves the addition of coagulants to wastewater, which destabilize particles and allow them to stick, forming flocs through aggregation [13]. Especially in oil-related wastewater treatment, coagulation and flocculation have been proven to (in conjunction with sedimentation or filtration) remove greater than 90% of suspended solids as well as oil and grease, however higher dosages were required (500 mg/L alum) [14]. Common coagulants are alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$), ferric chloride, and ferric sulfate. Polymer coagulants, such as polyaluminum chloride have also been proven to be effective, along with organic coagulants; however, these are typically not standardized and may not exhibit consistent results [15]. Regardless, the most effective coagulant depends on the composition of the wastewater being treated. The

most common coagulant, liquid alum, dosed at 500 mg/L results in a feed system that costs \$73,300 [16].

4.2 Granular Media Filtration

Granular media filtration can be conducted as either slow sand filtration or rapid sand filtration. Slow filtration involves running water through a shallow depth (~1m) of silica sand at a low flow rate [17]. Due to the shallow depth, oxygen easily permeates the sand to allow microorganism activity at the sand-water interface. This allows removal of some organic contaminants in addition to the particulate matter, similar to trickling filters. However, the low flow rate (around 0.05 gal/ft²/min) requires either storage capability or a very large filter area to accommodate large volumes of wastewater [17]. For the design flow of 1000 m³/day, the required filter area would be over 36,000 ft² to treat wastewater from 10 wells. As all filters, slow sand filters require cleaning which usually involves scraping off the top layer of sand (which is where most matter becomes trapped) and washing it, or sometimes replacing it [17]. Cleaning frequency depends on the incoming water quality. With a TSS concentration of 352 mg/L, filtering fracking wastewater would require a high cleaning frequency. These disadvantages have made slow sand filtration extremely rare in the U.S. at this time [15].

In contrast, rapid sand filtration has a higher flow rate and smaller filter area requirement. A typical flow rate for a rapid filter consisting of silica sand is 5 gal/ft²/min, which can be higher depending on filter requirements [15], [17]. With a flow rate of 5 gal/ft²/min, a rapid sand filter would require 367 ft² of filter area to treat 10 wells' wastewater each day, which is 10% of the area required by a slow filter. The disadvantage to this faster process is that there is no room for the microbe community

to remove organics, and therefore this is a strictly particulate removal process. Also, there is a much higher depth of sand or granular media required as the filtered particles are carried much deeper into the media [17]. As such, the cleaning process is different as well since the top layer of sand cannot simply be shaved off. Backwashing is a process where water is pumped in the opposite direction of treatment at a much higher flow rate so that the trapped solids are released and cleaned out [15], [17]. The backwashing water is either pumped out or collected into troughs at the top of the filter, and the entire process can be automated to reduce labor requirements [15]. It is argued that faster flow forces the use of coagulants prior to filtration, however sources justify the use of direct filtration if backwashing is done correctly and frequently enough, and more so if dual media or mixed media setups are used. Dual and mixed media utilize granular media either more coarse or fine than silica sand in sequence to allow for more efficient filtration [15]. A multi-media filter plant has a construction cost of \$1,060,000 with an operation and maintenance cost of \$581,000 for the loading of 10 Marcellus wells [16].

4.3 Micro/Ultra-Filtration

Micro- and ultrafiltration (MF and UF respectively) processes make use of membranes with pore diameters on the micro-scale to filter out suspended solids, particulates, and occasionally very large molecules, bacteria, and algae [15], [18]. MF membranes typically have pore diameters of 0.05 μm to 2 μm , while UF membranes range from 0.1 μm to 0.001 μm [18], [19]. Water is pumped through the filter in two distinct ways: dead end (perpendicular to the membrane) or cross-flow (parallel, so that water permeates the membrane) [18]. While this process is effective in removing a huge range of particulates and usually results in high-quality effluent, it is a high-

maintenance process due to membrane fouling [15], [18]. The modes of fouling can vary. The most obvious involves large particulates clogging pores, but occasionally solutes adsorb onto the membrane [18], [19]. The process therefore involves backwashing or membrane replacement every 15-60 minutes, or more frequently depending on the quality of the feed water [18].

This process is not widely used, but has been applied to fracking wastewater in a study conducted by Q. Jiang et al. (2013) to determine if it is a feasible option. The experiment tested MF membranes with a flow rate of 300 mL/min and resulted in 100% TSS removal for the smallest pore size and 71% for the largest. However, they had negligible effect on other parameters such as organic content and TDS. Also, the permeability decreased drastically over the experiment and sometimes approached zero due to membrane fouling, especially complete pore blocking. This phenomenon increased with smaller pore sizes. The membranes were also tested in series, and it was determined that an MF-MF series was sufficient for 100% TSS removal, as opposed to MF-UF. A cost analysis was also provided and construction was stated to cost \$459,000 with operation and maintenance at \$30,400 per year in 2013 [19].

4.4 Reverse Osmosis

Another membrane-based treatment process is reverse osmosis, which involves water under pressure (known as permeate) passing through a semi-permeable membrane against a concentration gradient [10], [18]. This typically occurs in a pressurized vessel, and the membrane rejects solutes making the feed stream more concentrated as time passes [13]. General applications include desalination of seawater (currently the most common use), softening, and removal of specific contaminants to control disinfection by-products, and is marked by high solute rejection as opposed to

other filtration processes [13]. There are also reports of radium removal [15]. Reverse osmosis is not, however, capable of removing small, uncharged particles, especially dissolved gases [13], [18].

A typical configuration is a spiral-wound membrane, where the membrane is wrapped around a collection tube with spacers in between layers [13]. There are usually 4-7 of these elements in a series, each with 5-15% permeate recovery; and a full series reportedly has a 50% recovery rate for seawater, and 90% under low-pressure conditions [13]. The active membranes are usually 0.1 to 2 μm thick, and most commonly made of cellulose acetate or polyamide. Of the two, polyamide is more chemically and physically stable, with both higher flux and salt rejection. However the material is slightly hydrophobic making it more susceptible to fouling, and intolerant of free chlorine in the feed water [13]. Reverse osmosis is conducted continuously until the feed solution reaches a target concentration, so there is no periodic backwashing as in other filtration and membrane processes [13]. Since reverse osmosis requires mechanical energy to drive against a gradient, it has been deemed infeasible for waters with greater than 40,000 mg/L of TDS for economic reasons [10], [18]. For this study's assumed wastewater load, the cost of reverse osmosis was calculated as \$14,200,000 per year of operation, and an initial construction cost of \$54,700,000 [16]. Note that this cost does not account for the TDS of the wastewater in question.

4.5 Forward Osmosis

As the name implies, this process utilizes osmotic pressure differences to naturally drive water through a semi-permeable membrane down a concentration gradient, without the need for pumping or applied pressure [20], [21]. As such, it

theoretically has lower energy requirements and is less prone to membrane fouling than reverse osmosis [20]. This is done by using a draw solution, which contains a draw solute that results in a higher osmotic pressure than the feed solution, allowing water to pass through the membrane to dilute the draw solution [20], [21]. While there is evidence of forward osmosis studies as early as the 1960s, significant research on the topic as a wastewater treatment option has only begun in the past one to two decades, thus information and options are limited [20]. Despite this, it is a natural process with relatively simple operational parameters, so that research is focused on producing higher performance draw solutes and membranes specific to forward osmosis [20]–[22], as reverse osmosis membranes result in low fluxes [20]. There are few commercially available forward osmosis membranes, but one developed by Hydration Technology Inc. made with cellulose triacetate (CTA) has been used in multiple studies, including one with fracking wastewater [20], [21]. Draw solutions, on the other hand, have a wider variety. Studies have successfully used easily removable gases such as ammonia, sulfur dioxide, and carbon dioxide; precipitable salts such as aluminum sulfate; and more recently, magnetic draw solutes that are recoverable via a magnetic field [20], [22].

The ability of forward osmosis to produce water flow without applying pressure has led to the development of pressure-retarded osmosis. Since water flows to the permeate side, that side increases in volume and the expansion can be used to produce energy to drive other processes [20], [21]. This process was applied in a study by Atlaee and Hilal in 2014 to fracking wastewater. The study used two forward osmosis processes (with pressure-retarded osmosis in either the first or second phase) in series with a hypersaline solution and fracking wastewater. The hypersaline solution

acted as the draw solute, with fracking wastewater as the feed stream so that water was drawn into the saline solution, effectively diluting it. Salinities of the wastewater varied from 53,000 mg/L to 157,000 mg/L, and the experiment used a CTA membrane. The study found that both types of series were able to achieve the same dilution levels, but with different permeate fluxes [21]. The cost of a forward osmosis system has not yet been established since it is a relatively new process. Theoretically, the cost should be similar to reverse osmosis; however, the cost of pumping would be replaced with the cost of the draw solute/solution. Often, the issue arises of solute regeneration and in many cases this drives the cost of the process up drastically, since thermal distillation, reverse osmosis, or nanofiltration processes are required for that [22].

4.6 Ion-Exchange

Ion-exchange involves passing wastewater through a resin bed in a vessel consisting of a cationic medium, anionic medium, or both. In this process, the water passes through the resin and targeted ions are replaced with more desirable ions that have been loaded on the resin [18]. Most of the media are synthetically produced polymers, although naturally occurring ion-exchanging materials do exist [15], [18]. The synthetic resins are copolymers of divinylbenzene, styrene, or acrylic polymers [18]. The resins require regeneration, which is often done by backwashing and then rinsing with a regenerating agent – a water that can restore it to the desired ionic condition. Cationic resins, which have permanent negatively charged sites, function better when exchanging multivalent cations such as iron, magnesium, and calcium, and can be regenerated with sodium chloride brine [15], [18]. Anionic resins are usually effective at reducing a wide range of anions – even weak ones such as CO_2 –

and usually require higher regeneration dosages than expected; a common regenerating agent is a sodium hydroxide brine [18]. This process must be conducted in conditions where particulates have been removed as efficiently as possible, since this can plug the resins which are often in the form of beads of varying sizes [15], [18]. Also, ion-exchange produces its own wastewater from the brine used for regeneration that requires disposal [15].

The study by Q. Jiang et al. (2013) mentioned above also tested fracking wastewater with ion-exchange. The issue of particulate removal was resolved by using effluent from the MF-MF process as the feed water in the experiment. The resin bed was a mixed bed of both a cationic and anionic resin evenly spread throughout a column, and water was pumped through at a rate of 20 mL/min. Ion-exchange, in the context of this study, was used to remove TDS content of the wastewater. Characterization of the effluent showed that all ions except Na and Cl were reduced to below 1 mg/L, while the other two were still reduced by 99%. The TOC content was also reduced by 90%. While it effectively removed dissolved content of the wastewater, it was not found to be a cost-effective process, as the process used in this study was found to cost \$76,800 per year of operation with a construction cost of \$1,330,000 in 2013. Also, this cost increases drastically with higher TDS concentrations TDS [19].

4.7 Activated Carbon Adsorption

While adsorption can be performed with a variety of materials (e.g., aforementioned ion-exchange), activated carbon is one of the least expensive of the materials making it the most commonly used adsorbent medium [13]. Most synthetic media have small pore sizes, making them difficult to use with large molecules such as

organic compounds [13]. Activated removes a large range of contaminants due to a highly varied pore size, including some organic compounds such as BTEX and most naturally occurring organics, and some heavy metals [13], [15]. Typically, the beds are composed of granular activated carbon, and water is filtered through it while the material captures contaminants through adsorption [13]. The beds become saturated with chemicals starting at the front end (where water first enters), and are usually kept until the entire bed is used up, at which point it has to be either regenerated or replaced [13]. This often does not happen for months or even years, but this depends on the quality of the feed water [13]. Fracking wastewater's heavily concentrated nature would require more frequent regeneration/replacement than usual wastewater applications.

A study by Butkovskiy et al. in 2017 discussed activated carbon adsorption as a solution to organics removal for Marcellus Shale wastewater. The study considered it a polishing step, as opposed to solution since the activated carbon beds easily get overloaded with organics, especially at the high concentrations at which they are present in this wastewater [23]. There is also evidence that some organics such as phthalates are not effectively removed. Additionally, while salinity is traditionally known to increase adsorption since it decreases their solubility in water, there are also reports that high salinity can reduce adsorption of other compounds [23]. Therefore, this method is marked by uncertainty in its ability to reduce organic content of this wastewater. For cost, the lowest flow rate available at 10 MGD (million gallons per day) for a 20 ft diameter tank required 31,400 ft³ of carbon in total. The cost of construction of the steel gravity contactor and fluid bed system (for regeneration) is

\$37,600,000. Operation and maintenance, including regeneration, costs \$3,620,000 [16].

4.8 Distillation

Distillation processes involve separating water molecules (usually via phase changes) from all other contaminants to achieve total purification of the water [15]. Distillation that has been examined for fracking wastewater treatment primarily includes thermal distillation and crystallization. Membrane distillation has also been considered, however it is researched as a desalination procedure and has not been applied to fracking wastewater [24]. Membrane distillation utilizes the vapor pressure of water with a hydrophobic membrane, so that liquid-vapor interfaces form at pore entrances and only water vapor can pass through for subsequent condensation [24].

Thermal distillation and crystallization involves evaporation to separate water from dissolved content. The vapor produced is then passed through a heat exchanger which condenses it into purified water [10]. This process has been shown to remove 99.5% of dissolved material (including TDS up to 125,000 mg/L), however it is very energy intensive and costly, since heat is needed to evaporate all of the wastewater, and then additional energy to condense it [10]. Also, it has low flow rates of about 300 m³/day, meaning periods with high flowback (as mentioned previously, up to 1000 m³/day) would require storage [10]. This process, if used to treat Marcellus Shale wastewater to PA surface discharge quality, is reported by M. Jiang et al. (2014) to cost \$53-74/m³ [9]. For comparison to other processes, the cost of mechanical vapor compression distillation, which is a process used for flows below 10 MGD as this wastewater is, was calculated. Construction cost was found to be \$36,900,000, with operation and maintenance at \$7,770,000 [16].

4.9 Advanced Oxidation Processes

The basic principle of advanced oxidation (AO) involves producing hydroxyl radicals ($\text{HO}\cdot$) in solution which then oxidizes virtually all reduced species [13], [25]. These hydroxyl radicals are extremely reactive and nonselective, as any reduced species in the water can be targeted. Since organic chemicals always have carbon in a reduced form (especially synthetic ones), AO is widely used to remove these from wastewater [13]. Because hydroxyl radicals are so reactive, if a process is given enough reaction time, compounds are almost always completely destroyed. Additionally, other processes using adsorption (e.g., ion-exchange, activated carbon) result in simply moving the contaminants to another phase which need to be dealt with afterwards, but AO breaks down the compounds into precipitates that can be easily filtered or removed through sedimentation [13], [25]. The process can be done either in a reactor vessel, or as an in-situ process since it fundamentally only involves addition of chemicals to produce the radicals [25]. AO is known to effectively and safely break down naturally occurring organic compounds, including BTEX [13], [25].

An important consideration is the quantity of oxidant that is needed to fully destroy organic matter in the target wastewater. Full-scale processes, according to Howe et al. usually generate hydroxyl radicals at concentrations between 10^{-11} and 10^{-9} mol/L, but this can also be determined by understanding the concentrations of organic material in the wastewater. One significant issue in AO processes is scavenging, which is defined as background reactions that use up hydroxyl radicals by reacting with material that is not being targeted. Known scavengers are HCO_3^- and CO_3^{2-} , as well as some reduced metal ions. Naturally occurring organics are sometimes considered scavengers [13], possibly when the target compound is synthetic, but with fracking wastewater these compounds are among the list of targets.

The most common method to produce hydroxyl radicals is with the addition of hydrogen peroxide with ozone, which is ideal in high pH conditions that allow ozone to oxidize material as well [13], [25]. Also possible is UV-based AO, which usually involves the addition of a catalyst such as TiO_2 and may be used to enhance hydroxyl radical yield of other methods [25]. The Fenton process uses hydrogen peroxide activated by ferrous ions to generate the appropriate reactive species, and is desirable in acidic conditions [25]. Some newer/less common approaches involve the use of ultrasound or electronic-beam irradiation to split water molecules, or the use of a sulfate radical, where $\text{S}_2\text{O}_8^{2-}$ is activated by heat or UV [25].

The total costs of advanced oxidation processes are difficult to estimate since each method involves different materials (e.g. energy for UV radiation or chemical costs). However, a contact chamber's construction costs can be estimated for a 40,000 gallon chamber at \$82,200 [16]. Biological digestion is a common method for organics removal, however as described previously, municipal treatment plants that utilize this technique experience difficulties with fracking wastewater as it disrupts the microbial activity [11].

The methods discussed throughout Chapter 4 are summarized in Table 5. Construction (C) and operation and maintenance (O&M) costs are stated separately.

Table 5: Summary of Wastewater Treatment Processes

Process	Purpose	Advantages	Disadvantages	Cost
Coagulation & Flocculation	Addition of chemicals forms flocs of suspended material and oils and greases	Effective filtration pretreatment with low construction cost	Periodic cost of coagulant feed; and flocculation time requirement	C: \$73,300
Granular Media Filtration	Remove particulates	High flow rates and relatively low costs to remove particulates and suspended material	Backwashing requirements may increase with lower quality feed stream	C: \$1,060,000 O&M: \$581,000
Micro/Ultra-Filtration	Use of membranes to filter particulates	High quality effluent with 99% particulate removal	Slow flow rate and clogging issues require frequent washing; costly	C: \$459,000 O&M: \$30,400
Reverse Osmosis	Desalination by pumping feed stream through a membrane	Effective desalination with small residual concentrated waste	Infeasible for TDS greater than 40,000 mg/L due to pumping requirements;	C: \$54,700,000 O&M: \$14,200,000
Forward Osmosis	Desalination using osmotic pressure of solutions to promote flow through a membrane	Flexibility in flow rate and level of desalination required; no pumping/energy requirement; potential for energy production	Cost of draw solute and preparing draw solution; new technology with limited supply options; draw solute regeneration	See Reverse Osmosis

Ion-exchange	Removal of ionic compounds through adsorption onto charged resin bed	Effectively removes all ionic compounds by 99%, and reduces TOC	Expensive and slow flow rates	C: \$1,330,000 O&M: \$76,800
Activated Carbon Adsorption	Organic material adsorbs to activated carbon bed	Low-cost adsorption media; effective BTEX removal	Not effective for certain organic materials; regeneration requirements increase with lower feed quality	C: \$37,600,000 O&M: \$3,620,000
Distillation	Use of thermal or membrane processes to obtain pure water	Removes all contaminants, resulting in pure water effluent	Expensive; potential for over-treatment	C: \$36,900,000 O&M: \$7,770,000
Advanced Oxidation Processes	Addition of chemicals to produce hydroxyl radicals in solution that break down organic matter	Non-selective organic removal with little operation costs outside of chemical addition	Contact time can vary for effective removal; potential for by-products if contact time is insufficient; pH and alkalinity must be monitored	C: \$82,200

Chapter 5

DESIGN OF PROPOSED FRACKING WASTEWATER TREATMENT SYSTEM

The concentrations that need to be treated are assumed to be the ‘average’ amounts reported in Table 4 above. The design flow rate of wastewater considered is the worst-case stated by Lutz et al. (2013) for flowback water – 1000 m³/day/well. The most recent estimate for the number of wells in the Marcellus Shale reported by the EIA was in 2016 at 153,696 wells [26]. That yielded approximately 1 well per square mile, and if 10 wells are assumed to be treated in one 10 square mile unit, the total flow rate for one unit is 10,000 m³/day, or 2.64 million gallons per day (MGD).

The construction costs were determined separately from operation and maintenance, which was done on a yearly basis.

All calculations are shown in the Appendices.

5.1 Stage 1 – Coagulation, Flocculation, and Filtration

The first stage of the proposed water treatment process targets suspended solids and particulates to prevent fouling of equipment, as well as prepare the wastewater for subsequent stages. While several filtration processes can achieve this, many are expensive with slow flow rates; however, rapid sand filtration proves to be both quick and relatively less costly. Filtration is rarely done without prior coagulation and flocculation, and since this wastewater has a very high TSS content, this step is applied before granular filtration.

Coagulation and flocculation play the part of preparing water for filtration by forming larger flocs of particulates and suspended material [15]. This involves the addition of a coagulant, and while many are commercially available (see Section 4.1),

the most effective coagulant and dosage should be determined through a jar test [13], [15]. A suggested coagulant is polyaluminum chloride (PAC) at 300 mg/L, as this has been shown to be effective in treating high TSS (348 mg/L) oil/gas-related wastewaters [14]. While mixing is usually required for flocculation, this can be avoided with hydraulic flocculation which simply involves allowing the water to flow through baffles, and results in large, fluffy flocs with minimal energy and construction costs [13]. The configuration is shown in Figure 4, from *Principles of Water Treatment* [13].

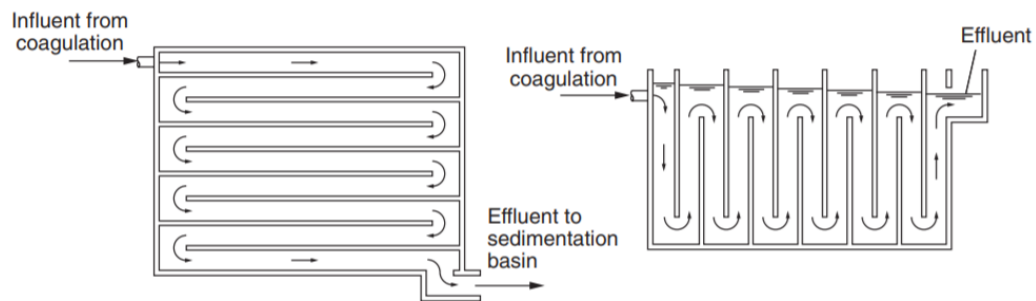


Figure 4: Flocculation configurations using hydraulic flocculation [13]

Rapid granular filtration can use several different types of media. Most common is the use of silica sand, however this can be applied as: a single sand layer, dual media with silica sand and a layer of anthracite, or mixed media, which incorporates the use of anthracite, sand, and a layer of garnet [15], [17]. Of the three, mixed-media filters allow higher quality effluent at higher flow rates, reducing the need for storage and also allow for longer run times, reducing backwashing frequency

[15]. Therefore, a mixed-media filter was selected for this design with the following order from top to bottom of the filter: anthracite, silica sand, and garnet.

Recommended media depth for this type of filter varies between sources [15], [17], [27]. Definitive depths were found in *Estimating Water Treatment Costs, Vol. 2* [27] that fall within acceptable ranges and are shown in the stage summary in Table 6.

Recommended wastewater flow rates are in the range of 7-10 gpm/ft² [17] and at 5-6 gpm/ft² [15]. A relatively slower flow rate (which can ensure high quality effluent) of 6 gpm/ft² was selected for the filter design, since this can also account for worst-cases where TSS is very high (slower flow rates yield higher quality effluent [13]). Given the wastewater flow of 10,000 m³/day, it was determined that 2 filters with an area of 153 ft² each (or 13 ft width) would be required to treat this loading.

Backwashing is necessary to clean the filter between filter runs (12-72 hours long) [15]. The process involves pumping water up through the filter bed (against the direction of filtration) which expands the bed and washes out the trapped particulates [13], [15]. It is often automated, and takes from 3 to 15 minutes [15]. The backwashing flow rate recommended by the Hach Company for a mixed-media filter is 15 gpm/ft², which falls within the AWWA and ASCE recommended range of 15-23 gpm/ft². This rate is selected with a pumping head of 50 ft, 70% motor efficiency, with a frequency of twice a day for 10 minutes each [27]. While backwashing clears the filter media of trapped particulates, the backwashing water is collected in troughs over top the media and then recirculated through the system. When dealing with high TSS waters such as fracking wastewater, a concern is that recirculation causes a very high amount of particulates to accumulate in the filter media, and therefore reduce effluent

quality. When this occurs, the filter media is usually replaced, and the used media is de-watered (often through filter-pressing) and landfilled [13], [17].

After analysis, the cost of the filtration system with coagulation and flocculation was determined. Construction costs for the filtration system are much higher than the coagulant feed system. Costs are summarized in Table 6, along with other design parameters of this stage. Figure 5 shows a schematic of rapid granular filtration. The figure depicts a dual media filter, but a mixed-media filter will only differ in that the sand layer will also have a layer of garnet underneath.

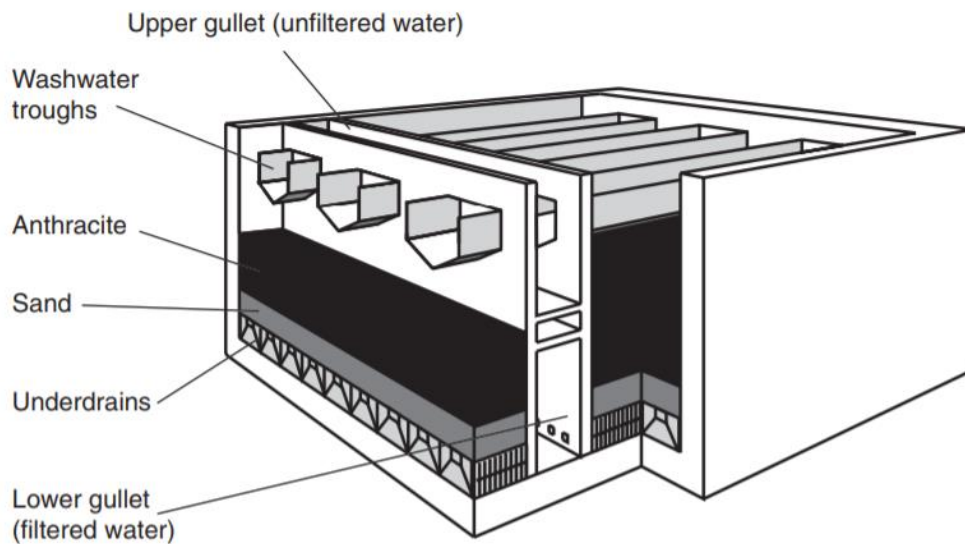


Figure 5: Schematic of a common dual-media filter [13]

Table 6: Summary of Stage 1 – Coagulation, Flocculation, and Filtration

Design Parameter	Recommendation	Reference
Coagulation	300 mg/L of PAC	[14]
Flocculation	Hydraulic flocculation with baffles	[13]

Rapid Granular Filtration:		
Media Type	Mixed-media	[15], [17]
Loading	6 gpm/ft ²	[15], [17]
Filter Area	2 filters; 306 ft ² total area	
Media Depths:		[27]
Anthracite	16.5 in	
Silica sand	9 in	
Garnet	4.5 in	
Backwashing	15 gpm/ft ²	[17]
Cost:	In 2008 USD	
Filtration		
Construction	\$1,064,000	[16]
Operation & Maintenance	\$581,000 per year	[27]
Coagulation & Flocculation		
Feed System Construction	\$44,700	[16]
Total Construction	\$1,110,000	
Total Operation & Maintenance	\$581,000 per year	

5.2 Stage 2 – Forward Osmosis Desalination

After Stage 1, the wastewater should be free of particulates, thus dissolved contaminants are targeted for Stage 2. This step is meant to desalinate the wastewater. Two common desalination techniques, reverse osmosis and ion-exchange, are not economically feasible since both require high amounts of pumping, especially with concentrated wastewater such as fracking wastewater. However, forward osmosis utilizes no pumping, and draw solutions can be modified to increase flow rates as needed. Due to this flexibility in procedure paired with cheaper costs, forward osmosis was selected as the desalination method for this stage.

In order to determine the requirements for this process (e.g., draw solution characteristics), the osmotic pressure of the wastewater is necessary. Literature review yielded no information on the osmotic pressure of this wastewater – which is usually measured with various devices – however the characterization is available with the

concentrations of most ions found in solution, as well as the TDS content. A simple way of calculating osmotic pressure of a solution is to use the van't Hoff equation for each solute and sum their resulting pressures. The solutes in the characterization did not sum to the total TDS in solution (11% lower). Also, when the van't Hoff equation is applied to highly saline solutions a correction factor, ϕ , is applied, but this information for the solutes of concern was not found. To account for these, the calculated osmotic pressure from the solutes was increased by 10% as a contingency. The osmotic pressure of this wastewater was calculated as approximately 7.90 MPa, or 79.0 bar.

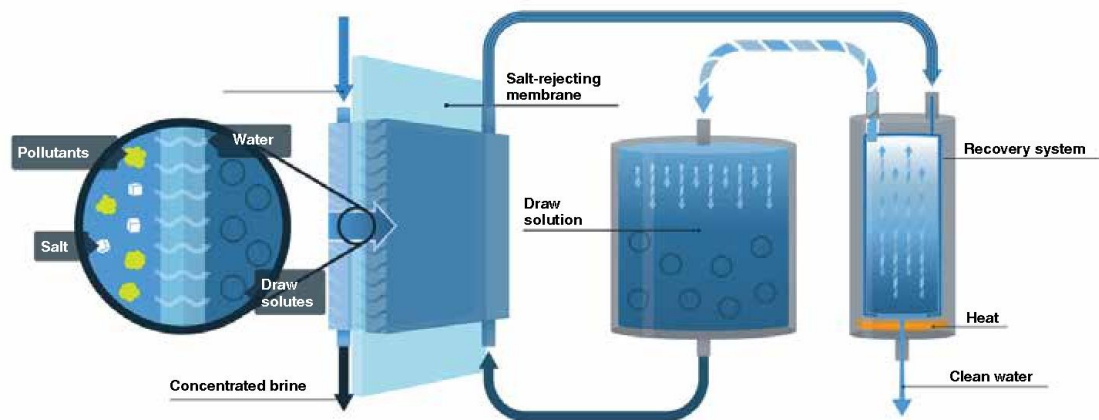
Next, a draw solute was selected. Inorganic salts such as NaCl and KCl are commonly used in the draw solution as they are cheap and effective ways of increasing osmotic pressure, desalination is the goal of this process and using a salt would be counter-productive. Other options include organic salts (e.g. EDTA), hydrogels, magnetic nanoparticles, and quantum dots, but these are very expensive and/or not commercially available for use [22]. Simple organics such as sucrose, glucose, and fructose, are also relatively less costly at \$14.39 per kg and have high solubility, however they have a low osmotic pressure in solution [22]. Volatile gases can also be used as draw solutes, and one such solute is NH_4HCO_3 [22]. Regeneration involves heating, however since the compound is volatile, there is not a high energy requirement. Preferably, a very high osmotic pressure draw solute would be used such as switchable polarity solvents (up to 32 MPa), however these are typically not commercially available for this process [22]. A membrane specifically for forward osmosis was also selected. As discussed previously, a CTA membrane was used successfully with fracking wastewater, and is the most common commercially

available forward osmosis membrane; therefore, this was selected. It reportedly has a water permeability coefficient, A_w , of 0.79 L/m³-h-bar [21].

The wastewater's pressure is estimated as 79.0 bar, and these organic sugars are known to have an osmotic pressure of 4.8 MPa at 1.1M in solution [22]. Since the van't Hoff equation shows osmotic pressure is directly related to molarity of solution (if all other variables are held constant), a 10.0M draw solution of organic sugars with 436 bar pressure should be sufficient to create enough osmotic pressure differential for water flow. The 10.0M draw solution with flow through the CTA membrane results in a theoretical flux, J_w , of 4.71 kg/min (or L/min) of water. This converts to 6.78 m³/day. As mentioned, the daily load that needs to be treated is 10,000 m³/day which means storage will be necessary with the desalination process. With further study, however, this flow rate can be increased. The surface area of the membrane is assumed to be 1 m² for this calculation, however membrane areas are typically much larger. Common forward osmosis membrane sizes are unknown, which is the reason that the 1 m² area was kept for this study.

It is possible to use the treated wastewater in the draw solution after the first full treatment cycle, so the cost of water for this purpose was omitted. Since membrane and osmotic treatment processes usually have a limited (~80%) water recovery rate, the process results in a concentrated wastewater at the end. Forward osmosis will likely result in a very concentrated brine at the end of the process. If treated with advanced oxidation or another form of organics removal, this brine can be re-sold or re-used in other forward osmosis process. One such possibility is to use it in industrial sludge de-watering.

The draw solution, with the given requirement for solute, costs \$8.75 per liter of solution. Costs for construction and operation of the forward osmosis process are not available since it is not widely used. Since it is very similar to reverse osmosis – the primary difference being a lack of pumping – the construction costs and operation and management were calculated from those of reverse osmosis, with 80% water recovery [27]. While this process does not involve pumping, it does involve heating to remove the volatile draw solute and therefore it was assumed that the pumping cost can be replaced with the heating cost. The costs calculated may be an overestimation it was done using data from 1979 – better construction practices have developed since then. Table 7 summarizes the parameters and costs calculated for Stage 2, and Figure 6 depicts a common forward osmosis process schematic.



© Oasys Water Inc.
FO—forward osmosis

Figure 6: Schematic of the forward osmosis process. (Source: Oasys Water Inc.)

Table 7: Summary of Stage 2 – Forward Osmosis Desalination

Design Parameter	Recommendation	Reference
Draw Solute	NH ₄ HCO ₃ ; 4.80 MPa/1.1 M	[22]
Membrane	Cellulose triacetate; A _w = 0.79 L/m ² -h-bar	[21]
Estimated Osmotic Pressure of Wastewater	7.90 MPa or 79.0 bar	
Draw Solution Concentration	10.0 M	
Water Flux	4.71 L/min of wastewater	
Draw Solute Requirement	0.791 kg/L draw solution	
Cost:	In 2008 USD	
Draw Solute	\$6.92 per L draw solution	[22]
Construction	\$54,700,000	[27]
Operation & Maintenance	\$14,200,000 per year	[27]

5.3 Stage 3 – Advanced Oxidation for Organics Removal

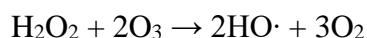
The previous treatment processes have dealt with all contaminants except for organic material. The use of activated carbon was previously discussed, and it was concluded that it is not ideal as it involves high costs and questionable organic material reduction. Also, biological degradation is not considered since it is a very slow process. As such, advanced oxidation is still available as an option with relatively lower maintenance and quick, non-selective organics removal.

As discussed previously, there are several different methods for advanced oxidation treatment. After literature review, it was found that the combination of hydrogen peroxide (H₂O₂) and ozone (O₃) is best. It allows for very effective hydroxyl radical production at pH's around neutral, and this wastewater's pH is reported as 6.56 [12], [13]. UV is often used to bolster the process, however it is energy intensive and therefore raises costs [25]. Also, another mechanism exists when treating this wastewater with advanced oxidation. There is iron already present in this wastewater,

therefore, the Fenton process can increase hydroxyl production if the H₂O₂ dosage is increased accordingly with the ferrous ion concentration. However, the ferrous content (as opposed to total iron content) is unknown so this will have to be determined through experimentation.

Chemical dosage for this process varies greatly with wastewater conditions such as alkalinity, pH, and target organic concentration, and is typically determined through laboratory testing [13], [28]. However, a rule of thumb is that 1-2 mg/L of O₃ be added per mg/L of dissolved organic carbon (DOC) [28]. Since the alkalinity of this wastewater is relatively high (165 mg/L as CaCO₃), the higher end of this range was used [28]. Also, DOC content of the wastewater is unknown, however its determination involves determining the TOC content; hence, the values tend to be numerically similar, and so the TOC can be used as an approximation. This process is modeled to take place after the forward osmosis process, however the draw solute should have been removed during regeneration with a thermal process, leaving the wastewater with generally the same organic properties as before.

This yielded an O₃ dosage of 320 mg/L or 0.00667 mol/L. The stoichiometric ratio of H₂O₂ to O₃ can be found in the overall reaction, given as



This results in a ratio of 1:2, so that the H₂O₂ dosage is 0.00333 mol/L, or 113 mg/L.

The full mechanism of reactions occurring in the addition of these chemicals to water involves several intermediate steps and up to four other radicals (HO₃[·], O₃^{·-}, HO₂[·], and O₂^{·-}). However, around a neutral pH, these radicals react so quickly that a net zero rate of formation can be assumed, resulting in a pseudo-steady-state approximation [13]. This assumption allows a system of equations from the full

reaction mechanism to be condensed to solve for the initial pseudo-steady-state HO· concentration, $[\text{HO}\cdot]_{\text{ss},0}$. Calculations result in a $[\text{HO}\cdot]_{\text{ss},0}$ of 3.96×10^{-10} mol/L. Since the identities of organic compounds are unknown, it was assumed that the compounds can be cumulatively categorized as naturally occurring organic matter. Using this information, the pseudo-steady-state rate constant, k_R is 0.0554 s^{-1} , and the rate of destruction of the target compounds is r_R is 7.38×10^{-4} mol/L/s. The half-life of the compound in a reactor is calculated to be 12.5 seconds, with a total contact time for 95% removal of 51.4 seconds. All parameters calculated are reported in Table 8.

The cost for an ozone or hydrogen peroxide feed system was not found and were therefore omitted, however the cost of an ozone contact chamber was available. While the overall flow rate of the preceding forward osmosis process is highly variable, it is assumed that there is 80% recovery of the water volume. Therefore, the flow rate used was $8000 \text{ m}^3/\text{day}$, or 2.11 MGD. Figure 7 depicts a schematic of APTWater's HiPOx advanced oxidation reactor. While this is not a conventional contact chamber, it serves the same purpose of injecting hydrogen peroxide and ozone at intervals to treat the wastewater flowing through the pipes.

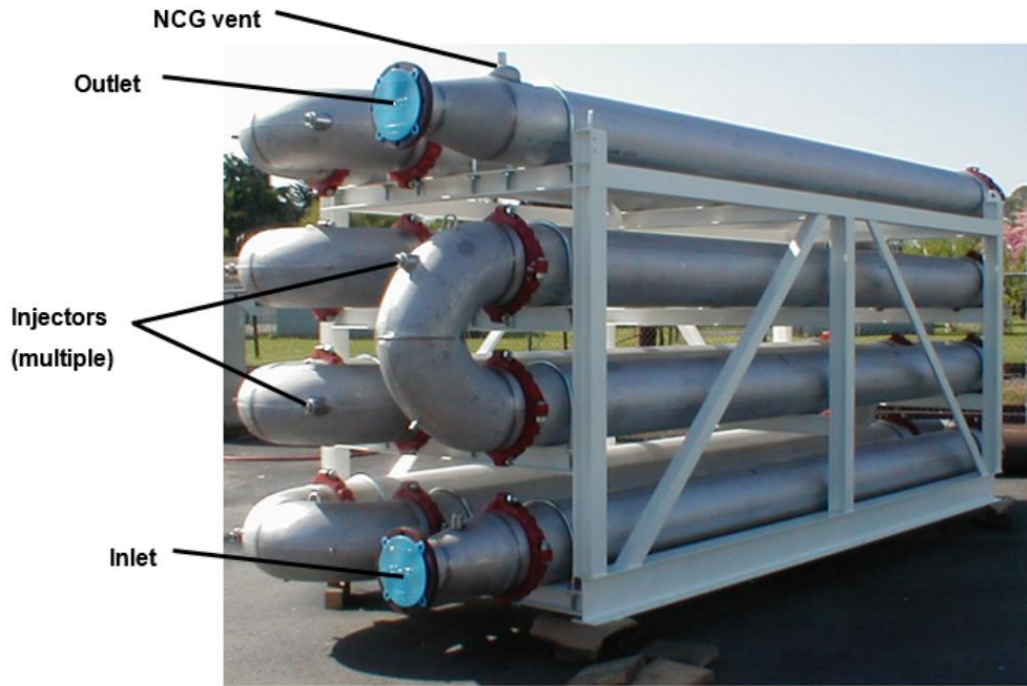


Figure 7: Hydrogen peroxide and ozone contactor for advanced oxidation water treatment (Source: APTWater HiPOx Treatment System)

Table 8: Summary of Stage 3 – Advanced Oxidation for Organics Removal

Design Parameter	Recommendation	Reference
Radical Production Method	H ₂ O ₂ /O ₃ addition	[13]
Target Compound	Natural organic material	[4], [12], [13]
Approximate TOC	160 mg/L or 0.0133 mol/L	[12]
Approximate O ₃ dosage	320 mg/L or 0.00667 mol/L	
Approximate H ₂ O ₂ dosage	113 mg/L or 0.00333 mol/L	
[HO•] _{SS,0}	3.69×10 ⁻¹⁰ mol/L	
k _R	0.0554 s ⁻¹	
r _R	7.38×10 ⁻⁴ mol/L/s	
Approximate Contact Time	51.4 s	
Cost:	In 2008 USD	[16]
Contact Chamber Construction	\$1,059,000	

5.4 Treatment and Cost Summary

Table 9 presents a summary of the proposed treatment process and costs associated with each step. The details presented assume a wastewater loading of 2.64 MGD. The residence times are meant to account for the time required for each treatment process to treat the entire loading of wastewater. The filtration process was designed to handle the daily loading in a 24-hour period. The forward osmosis process, however, has a much more variable time depending on the draw solution characteristics. While the draw solution discussed in this study has a relatively slow flow rate, this can be increased drastically with more effective draw solutes (such as the previously discussed switchable polarity solvents). Finally, theoretical calculations for the advanced oxidation process only yields the contact time required to treat 1 L of the wastewater. This time changes non-linearly with higher volumes of wastewater, and therefore must be accurately determined through live testing.

Table 9: Summary of Treatment Process and Costs

	Stage 1	Stage 2	Stage 3
Treatment Method	Coagulation, Flocculation, and Rapid Sand Filtration	Forward Osmosis Desalination	Advanced Oxidation
Description	Remove oils & greases and suspended material by adding a coagulant to form flocs, and filtering the wastewater in a multi-media filter.	Desalinate through a membrane using osmotic pressure differences as the driving mechanism.	Generate hydroxyl radicals in the water that will non-selectively react with and break down organic material.
Residence Time:	24 hours	variable	51.4 s for 1 L wastewater

Basic Parameters:	Coagulant: PAC Flocculation: hydraulic flocculation with baffles Media type: mixed-media (anthracite, silica sand, and garnet) Filter loading: 6 gpm/ft ² Filter area: 306 ft ² Backwashing: 15 gpm/ft ²	Draw solute: NH ₄ HCO ₃ Membrane: CTA Estimated osmotic pressure of wastewater: 79.0 bar Draw solution concentration: 10.0M Water Flux: 4.71 L/min	Method: H ₂ O ₂ /O ₃ TOC: 160 mg/L O ₃ dosage: 320 mg/L H ₂ O ₂ dosage: 113 mg/L k _R = 0.0554 s ⁻¹ r _R = 7.38×10 ⁻⁴ mol/L/s
Construction Cost:	\$1,110,000	\$54,700,000	\$1,059,000
Operation & Maintenance Cost:	\$581,000	\$14,200,000	Not available
Other Costs:	-	Draw solute: \$6.92/L draw solution	-

Figure 8 is a process-flow diagram that illustrates the movement of the wastewater through each stage with potential by-products from each stage. As mentioned previously, filter media in Stage 1 may need to be replaced when the particulate concentration of the backwash water being cycled through the process is too high and interferes with effluent quality. The filter media is usually filter-pressed and landfilled. In Stage 2, the forward osmosis desalination process discussed is assumed to recover 80% of the wastewater volume. The remaining 20% is a highly concentrated brine that can be treated with advanced oxidation to remove organics and then re-used as a draw solution in other industrial forward osmosis processes (e.g., sludge de-watering). The oxidation reactions in Stage 3 may produce some

precipitates that are usually settled out, and subsequently removed and disposed of through methods such as landfilling.

While the wastewater is being produced daily, it is ideal if the wastewater passes through each stage per day. This means that the first 10,000 m³ of wastewater would ideally be filtered in the first day. The second and third days would involve forward osmosis treatment and advanced oxidation. In those second and third days, the wastewater produced would enter the treatment process with filtration so that each day, a new batch of wastewater is being filtered. This is an ideal scenario, however, and will require testing and optimization to achieve.

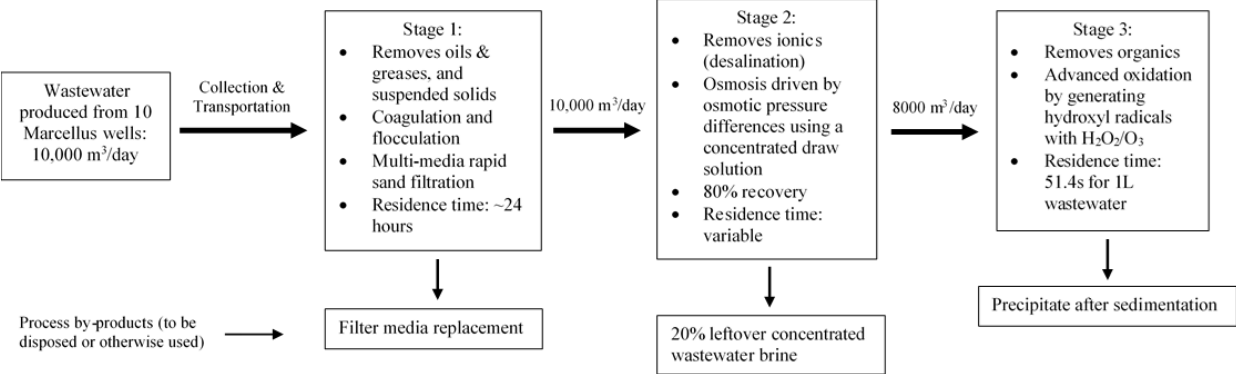


Figure 8: Process-flow diagram of proposed treatment process

Chapter 6

CONCLUSIONS AND FUTURE WORK

While hydraulic fracturing is a controversial practice from many environmental standpoints, the particular concern of wastewater production is an issue that can be feasibly dealt with using available technologies. Literature review revealed several different methods that can be applied, but after careful analysis of advantages and disadvantages, and cost, a three-stage system was formulated and proposed. Marcellus wastewater was targeted, characterized by high TSS, salinity, organics, and oils and greases. Each of these contaminants are targeted in the system illustrated in Chapter 5: (1) mixed-media rapid sand filtration with coagulation and flocculation; (2) forward osmosis desalination; and (3) advanced oxidation with ozone and hydrogen peroxide.

Stage 1 involves using coagulation and flocculation with PAC at a certain dosage, as well as mixed-media filtration in a 306 ft² filter area with a flow of 6 gpm/ft². However, this is only a theoretical set-up and testing is required to understand if this is effective. A jar test is necessary to understand what the most effective coagulant would be at what dosage, and a sample of wastewater should be filtered to understand if effluent suspended solids content is acceptable at this flow rate.

Stage 2 uses a relatively new process known as forward osmosis. An NH_4HCO_3 draw solute has been proposed since it has a high osmotic pressure and simple regeneration process, however it is possible that this is not the most effective draw solute. Others should be tested and analyzed to understand which would provide the best performance at acceptable costs.

Stage 3 induces oxidation reactions with hydroxyl radicals and organic compounds by adding hydrogen peroxide and ozone to the wastewater. While a dosage was estimated, a proper dosage (and effectiveness of method) should be established through testing, which can also yield an accurate contact time.

The testing proposed above can also yield parameters that can subsequently be optimized to reduce costs. A theoretical cost analysis was performed in this study, resulting in a construction cost of \$56,900,000, and a yearly operation and maintenance cost of \$14,800,000. These values were determined using outdated sources so they are likely to be overestimations since better practices have been developed over time. However, testing and optimization can also drastically reduce the costs. By doing so, the process can be translated into small, economical treatment plants throughout the Marcellus Shale that can take an applied loading of Marcellus wastewater and produce a usable (e.g., recyclable) or dischargeable effluent. To this end, testing should apply target effluent concentrations of surface discharge levels.

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Appendix A

DETERMINATION OF DAILY WASTEWATER LOADING

Consider highest flow stated by Lutz et al.: 1000 m³/day/well

Number of wells in Marcellus Shale in 2016 [26]: 153,696 wells

Total area of Marcellus Shale [6]: 95,000 mi²

$$\frac{153,696 \text{ wells}}{95,000 \text{ mi}^2} = 1.618 \approx 1 \frac{\text{well}}{\text{mi}^2}$$

Assuming 10 mi² per treatment unit, resulting in 10 wells per treatment unit, and a total flow of 10,000 m³/day for each unit.

$$10,000 \frac{\text{m}^3}{\text{day}} \times 264.172 \frac{\text{gal}}{\text{m}^3} = 2,641,720 \frac{\text{gal}}{\text{day}}$$
$$2,641,720 \frac{\text{gal}}{\text{day}} \times \frac{1 \text{ day}}{24 \text{ hr}} \times \frac{1 \text{ hr}}{60 \text{ min}} = 1,834.528 \frac{\text{gal}}{\text{min}}$$

Appendix B

COST CALCULATIONS

Two books were used for cost information for the processes discussed in this work: *Cost Estimating Manual for Water Treatment Facilities* by McGivney and Kawamura from 2008, and the EPA's *Estimating Water Treatment Costs, Vol. 2* from 1979 [16], [27]. Costs from the 1979 source were converted to 2008 USD using the Engineering News Record Construction Cost Index (ENR CCI) from 2008 given in the 2008 source. Also, costs in the 1979 source were calculated with the assumption that energy was \$0.03/kWh and wages were \$10/hr [27]. Unless stated otherwise, all costs marked with "\$" are in 2008 USD.

Note that costs calculated with data from the 1979 source are likely to be overestimations, since construction costs have been reduced over the years due to technology development and better practices.

B.1 Coagulation and Flocculation

Costs for this system, as stated in the source, were from construction costs of the feed system. Since alum is the most common coagulant, it was selected for the sample cost of the system. To calculate this cost, the total feed requirement, or total coagulant requirement was needed.

Recommended dosage [14]: 500 mg/L alum

$$2.64172 \text{ MGD} \times 1000 = 2641.72 \frac{\text{L}}{\text{day}}$$
$$2641.72 \frac{\text{L}}{\text{day}} \times 500 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ lb}}{453.592 \text{ g}} \times \frac{1 \text{ day}}{24 \text{ hr}} = 0.1213 \frac{\text{lb}}{\text{hr}}$$

The 2008 source provides an equation for a cost curve of the construction of the feed system:

$$\begin{aligned} \text{Cost in \$} &= 212.32 \times \text{alum dosage} + 73225 = 212.32 \times 0.1213 \frac{\text{lb}}{\text{day}} + 73225 \\ &= \$73,250.76 \end{aligned}$$

B.2 Granular Media Filtration

This calculation utilizes the same parameters that were used in the design of the mixed-media rapid sand filter discussed in Section 5.1 for Stage 1. The calculations for filter area are shown in Appendix C. Construction costs and operation and maintenance costs were considered for the gravity filter and backwash system, and filter media was included in the construction cost. Cost curves from the 2008 source were used for these calculations, as follows.

$$\begin{aligned} \text{Cost of gravity sand filter construction} &= -0.0034 \times (\text{filter area})^2 + 575.85 \times \text{filter area} + 665305 \\ &= -0.0034 \times (306\text{ft}^2)^2 + 575.85(306\text{ft}^2) + 665305 \\ &= \$841,055.95 \end{aligned}$$

$$\begin{aligned} \text{Cost of backwash system construction} &= 292.44 \times \text{filter area} + 92497 \\ &= 292.44 \times 306\text{ft}^2 + 92497 = \$181,911.88 \end{aligned}$$

$$\begin{aligned} \text{Cost of media for multi - media design} &= 62.844 \times \text{filter area} + 21838 \\ &= 62.844 \times 306\text{ft}^2 + 21838 = \$41,052.84 \end{aligned}$$

Operation and maintenance cost curves for this filtration system were not applicable to flows below 10 MGD, so the 1979 source was used for this calculation, and then converted to 2008 USD. For this, linear interpolation had to be used. All further interpolations utilize the same process, and so this will only be exemplified in detail here.

Table B.1: Operation & Maintenance Cost for Gravity Sand Filter

Total Filter Area (ft ²)	Energy (kWh/yr)	Maintenance (\$/yr)	Labor (hr/yr)	Total Cost (1979 USD)	
140 (x ₁)	44,120	800	900	11,120	(y ₁)
700 (x ₂)	151,850	2,510	1,500	22,070	(y ₂)
306 (x)	76,007	1,306	1,078	14,361	(y)

The equation for linear interpolation is as follows:

$$y = y_1 + (x - x_1) \times \frac{(y_2 - y_1)}{(x_2 - x_1)} \quad (1)$$

The numbers, as labeled in Table B.1, can be entered into this equation to obtain the results shown in the last row. The following example shows the calculation for energy use.

$$\begin{aligned} y &= y_1 + (x - x_1) \times \frac{(y_2 - y_1)}{(x_2 - x_1)} = 44,120 + (306 - 140) \times \frac{(151,850 - 44,120)}{(700 - 140)} \\ &= 76,007 \frac{kWh}{yr} \end{aligned}$$

Table B.2: Operation & Maintenance Cost for Backwashing System

Total Filter Area (ft ²)	Energy (kWh/yr)	Maintenance (\$/yr)	Labor (hr/yr)	Total Cost (1979 USD)	
140 (x ₁)	3,340	700	190	2,700	(y ₁)
700 (x ₂)	16,720	1,100	210	3,700	(y ₂)
306 (x)	7,300	818	196	2,996	(y)

The conversion to 2008 USD from 1979 USD is done as follows [27], using total operation and maintenance costs as an example (all further conversions follow the same process).

$$\begin{aligned} \text{Cost in 2008 USD} &= \text{Total Calculated 1979 Cost} \times \left(\frac{ENR CCI}{265.38} \right) \\ &= 17,357.09 \times \left(\frac{8889}{265.38} \right) = \$581,381 \end{aligned}$$

The total costs are:

Construction - \$1,064,021

Operation & Maintenance - \$581,381 per year

B.3 Micro/Ultra-Filtration

The MF process discussed in Section 4.3 had costs provided in a study by Q. Jiang et al. done in 2008. The information provided included both the capital cost (presented as annualized, over five years), and the operational cost. Since these values were reported for 2008, they required no adjustment.

B.4 Reverse Osmosis

Reverse osmosis cost curves in the 2008 source were not applicable to flow rates lower than 10 MGD, so the 1979 source was used for this calculation. The construction costs and operation and maintenance costs were both calculated using linear interpolation and then converted to 2008 USD using the same method shown previously.

Table B.3: Construction Cost for Reverse Osmosis

Loading (MGD)	Cost (1979 USD)
1 (x ₁)	775,820 (y ₁)
10 (x ₂)	5,467,390 (y ₂)
2.64172 (x)	1,631,625 (y)
In 2008 USD	54,651,873

Table B.4: Operation & Maintenance Cost for Reverse Osmosis

Loading (MGD)	Energy (kWh/yr)	Maintenance (\$/yr)	Labor (hr/yr)	Total Cost (1979 USD)	
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1 (x ₁)	2,514,400	97,280	1,840	191,100	(y ₁)
10 (x ₂)	22,922,500	748,340	2,840	1,464,420	(y ₂)
2.64172 (x)	6,237,110	216,042	2,022	423,371	(y)
In 2008 USD				14,180,951	

The total costs are:

Construction - \$54,651,873

Operation & Maintenance - \$14,180,951 per year

B.5 Forward Osmosis

Construction costs for forward osmosis were considered the same as reverse osmosis, since the processes use very similar principles. However, the process energy cost was removed from the energy cost determination for the operation and maintenance cost calculation to account for the lack of pumping in this process. This change is reflected in Table B.5 below.

Table B.5: Operation & Maintenance for Forward Osmosis

Loading (MGD)	Energy (kWh/yr)	Maintenance (\$/yr)	Labor (hr/yr)	Total Cost (1979 USD)	
1 (x ₁)	105,400	97,280	1,840	118,842	(y ₁)
10 (x ₂)	840,000	748,340	2,840	801,940	(y ₂)
2.64172 (x)	239,401	216,042	2,022	243,448	(y)
In 2008 USD				8,154,386	

The total costs are:

Construction - \$54,651,873

Operation & Maintenance - \$8,154,386 per year

B.6 Ion-Exchange

The ion-exchange process discussed in Section 4.6 had costs provided in a study by Q. Jiang et al. done in 2008. The information provided included both the

capital cost (presented as annualized, over five years), and the operational cost. Since these values were reported for 2008, they required no adjustments.

B.7 Activated Carbon Adsorption

Costs for activated carbon adsorption were not available for design loadings below 10 MGD, so the minimum loading of 10 MGD was used for cost comparison purposes from the 1979 source. Interpolation was not needed for these values, but they were converted to 2008 USD using the method shown previously.

The total costs are:

Construction of steel gravity contactor and fluid bed system – 1,122,600 1979 USD, or 37,601,897 2008 USD

Operation and maintenance with regeneration – 108,080 1979 USD, or 3,620,179 2008 USD

B.8 Distillation

The costs for a distillation process were found as cost curves in the 2008 source. The equations for each curve for construction, and operation and maintenance were given as shown below in Equations 2 and 3, respectively [16].

$$\text{Cost of construction} = 15.275(\text{loading in MGD})^{0.907} \quad (2)$$

$$= 15.275(2.642 \text{ MGD})^{0.907} = \$36,866,553$$

$$\text{Cost of operation and maintenance} = 3.121(\text{loading in MGD})^{0.9384} \quad (3)$$

$$3.121(2.642 \text{ MGD})^{0.9384} = \$7,765,910$$

The total costs are as calculated above.

B.9 Advanced Oxidation Processes

As mentioned in Section 4.9, there are several different advanced oxidation processes with varying requirements. Due to these differences, a sample cost to reflect the entire method is not feasible. However, each method makes use of a contact chamber in which the reactions occur, so the cost of the contact chamber used in Stage 3 of the proposed system was presented as a sample construction cost. The cost of an ozone or hydrogen peroxide feed system could not be found. The cost of the ozone contact chamber was calculated using a cost curve from the 2008 sources. Since advanced oxidation was proposed to be done after forward osmosis, the forward osmosis process was designed to yield 80% recovery of water volume so the flow rate of 2.11 MGD was used as the design flow for this chamber.

$$\begin{aligned} \text{Cost of ozone contact chamber} &= 89.217 \times \left(\text{flow in } \frac{\text{gal}}{\text{day}} \right)^{0.6442} \\ &= 89.217 \times \left(2,113,376 \frac{\text{gal}}{\text{day}} \right)^{0.6442} = \$1,059,000 \end{aligned}$$

Appendix C

STAGE 1 CALCULATIONS

Filter area is typically calculated below:

$$FA = \frac{L}{F} \quad (4)$$

Where FA is the filter area, F is the wastewater flow, and L is the loading that the filter will take. The loading was selected as 6 gpm/ft², and the wastewater flow is 1834.528 gpm.

$$FA = \frac{L}{F} = \frac{1834.528 \text{ gpm}}{6 \frac{\text{gpm}}{\text{ft}^2}} = 305.754 \text{ ft}^2 \approx 306 \text{ ft}^2$$

If 2 filters are used, each has an area of $\frac{306 \text{ ft}^2}{2} = 153 \text{ ft}^2$ with length $l = \sqrt{153 \text{ ft}^2} = 12.364 \approx 13 \text{ ft}$.

The calculation of the cost of the mixed-media sand filter discussed is shown in Appendix B. The coagulation dosage is typically determined by a jar test, so as a sample dosage, the recommended 300 mg/L of polyaluminum chloride from a study by Daud et al. (2015) was used. Calculation of the cost of the feed system is

$$13662 \times \left(\text{dose in } \frac{\text{lb}}{\text{day}} \right) + 20861 = 13662 \times \left(1.747 \frac{\text{lb}}{\text{day}} \right) + 20861 = \$44,731.25$$

Appendix D

STAGE 2 CALCULATIONS

First, the osmotic pressure of the wastewater was estimated using van't Hoff's equation, shown below.

$$\pi = CRT \quad (5)$$

Where π is the osmotic pressure in bar; C is the molarity of the solute in the wastewater; R is the gas constant, 0.083245 L-bar/mol-k; and T is the temperature in Kelvin, which was assumed to be 296 K.

To use this, the molarity of each specified solute in the wastewater was found by dividing their mass concentrations by their molar masses, as in Equation 5 below.

$$C = \frac{C_m}{mm} \quad (6)$$

Where C_m is the mass concentration of the solute, and mm is the molar mass of the solute.

Each of the above equations were applied to the average concentration of solutes listed in Table 4 previously. The results are shown in Table D.1 below. Since the total mass concentration of the solutes adds up to only 90% of the TDS of the wastewater (theoretically, the entire TDS content should contribute to the osmotic pressure), the osmotic pressure calculated in this way would be an underestimation. Also, high concentrations are often given an osmotic pressure correction factor ϕ [13], however this coefficient could not be found for the solutes calculated here. 10% was added to the total to account for this.

Table D.1: Estimating Osmotic Pressure of Fracking Wastewater

Solute (mg/L)	C _m (mg/L)	mm (g/mol)	C (mol/L)	π (bar)
SO ₄	71	96.06	0.001	0.018
Cl	57447	35.453	1.620	39.879
Br	511	79.904	0.006	0.157
Na	24123	22.9898	1.049	25.824
Ca	7220	40.078	0.180	4.434
Mg	632	24.305	0.026	0.640
Ba	2224	137.327	0.016	0.399
Sr	1695	87.62	0.019	0.476
Fe (dissolved)	40.8	55.845	0.001	0.018
Total π (bar)				71.845
With 10% adjustment (bar)				79.0

Next, the flux of the feed water through the membrane needed to be calculated. This was done with Equation 6 below. The selected draw solute, the volatile gas NH₄HCO₃, has an osmotic pressure of 4.80 MPa as a 1.1 M solution. Since osmotic pressure varies directly with the concentration (when all other variables are held constant), simply doubling the solution will double the osmotic pressure, and so on. In this way, it was determined that a 10 M solution with osmotic pressure of 436 bar is enough to produce a sufficient flow rate.

$$J_w = A_w(P - \pi) \quad (7)$$

Where J_w is the water flux across the membrane; A_w is the water permeability coefficient of the membrane; P is the osmotic pressure of the draw solution; and π is the osmotic pressure of the feed solution, or wastewater.

Since the permeability coefficient, A_w, was given as 0.79 L/m²-h-bar, it could be used directly with the osmotic pressures in bar. For this study's purposes, the membrane size is unknown so the 1 m² area was kept the same (as given by the coefficient).

$$\begin{aligned}
 J_w = A_w(P - \pi) &= 0.79 \frac{L}{m^2 - h - bar} (436.36 \text{ bar} - 79.03 \text{ bar}) = 0.078 \frac{kg}{s} \\
 &= 4.705 \frac{L}{min} = 6775 \frac{L}{day}
 \end{aligned}$$

The cost of the draw solute is calculated using its molar mass 79.07 g/mol. The cost of the solute was given as \$8.75/kg [22].

$$\begin{aligned}
 \text{Total cost of solute} &= C \times mm \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \text{cost} \\
 &= 10.0M \times 79.07 \frac{g}{mol} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{\$8.75}{kg} \\
 &= \$6.92 \text{ per liter draw solution}
 \end{aligned}$$

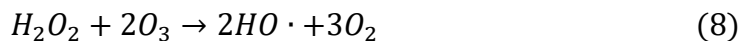
This also yields an intermediate value of the mass of draw solute needed, 0.791 kg per liter of draw solution. Regeneration of this draw solute is important since it is a volatile compound that is easily removed through heating, however the exact energy requirements are unknown. Since the cost of this process is assumed to be similar to reverse osmosis, the cost of pumping is assumed to instead be the cost of regeneration of the draw solute.

Appendix E

STAGE 3 CALCULATIONS

The selected advanced oxidation process is a reaction with ozone (O_3) and hydrogen peroxide (H_2O_2). While ozonation itself is a common process, the addition of H_2O_2 increases hydroxyl radical ($HO\cdot$) production through its dissociation as a weak acid into HO_2^- . This reacts with O_3 to produce hydroxyl radicals [28].

The overall reaction for $HO\cdot$ production with O_3 and H_2O_2 is given in *Principles of Water Treatment* [13] as



Equation 7 gives the stoichiometric ratio of 1:2 for H_2O_2 to O_3 . The full mechanism of reactions occurring in the addition of these chemicals to water involves several intermediate steps and up to four other radicals ($HO_3\cdot$, O_3^- , $HO_2\cdot$, and O_2^-). However, around a neutral pH, these radicals react so quickly that a net zero rate of formation can be assumed, resulting in a pseudo-steady-state approximation [13]. This assumption allows a system of equations from the full reaction mechanism to be condensed to solve for the initial pseudo-steady-state $HO\cdot$ concentration, $[HO\cdot]_{ss,0}$. The initial pseudo-steady-state $HO\cdot$ concentration is

$$[HO\cdot]_{ss,0} = \frac{2k_1[HO_2^-][O_3]}{k_2[HCO_3^-] + k_3[R]} \quad (9)$$

The constants in Equation 8 are the rate constants of certain reactions at 25 °C in L/mol-s. Constants k_1 and k_2 are, respectively, rate constants for $HO\cdot$ production from HO_2^- and O_3 , and $HO\cdot$ destruction by HCO_3^- . The values are: $k_1 = 2.8 \times 10^6$ and $k_2 = 8.5 \times 10^6$. The third constant, k_3 , is typically the rate constant for the target compound R with $HO\cdot$. Since the identities of organic compounds are unknown, it was assumed

that the compounds can be cumulatively categorized as naturally occurring organic matter. Therefore, k_3 has a value of 1.4×10^8 L/mol-s as carbon. Equation 8 requires that the concentrations used be initial concentrations.

Chemical dosage for this process varies greatly with wastewater conditions such as alkalinity, pH, and target organic concentration, and is typically determined through laboratory testing. However, a rule of thumb is that 1-2 mg/L of O_3 be added per mg/L of dissolved organic carbon (DOC) [28]. DOC is determined by first finding the TOC, and then finding the fraction that passes through a $0.45 \mu\text{m}$ filter [29]. Since this exact value is unknown for the Marcellus wastewater used for analysis, the TOC was used in its place as it is typically numerically similar. In the case of higher alkalinity water (greater than 100 mg/L as CaCO_3), higher dosages are used [28]. Since this wastewater has an alkalinity of 165 mg/L, a dosage of 2 mg/L O_3 per mg/L of TOC was used. The TOC of this wastewater is 160 mg/L from Table 4, yielding

$$160 \frac{\text{mg}}{\text{L}} \text{TOC} \times \frac{2 \frac{\text{mg}}{\text{L}} O_3}{\frac{\text{mg}}{\text{L}} \text{TOC}} = 320 \frac{\text{mg}}{\text{L}} O_3$$

Dividing by the molar mass of O_3 , 48 g/mol, yields a concentration of 0.00667 mol/L O_3 (a fraction of 1/150). As mentioned earlier, the stoichiometric ratio of H_2O_2 to O_3 is 1:2, so that the concentration of H_2O_2 that should be added is 0.00333 mol/L (a fraction of 1/300).

To determine the HCO_3^- concentration, the equation for alkalinity was used. The wastewater alkalinity of 165 mg/L was converted to mol/L using the molar mass of CaCO_3 , which is 100.09 g/mol, resulting in a concentration of 0.00165 mol/L.

$$2[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (10)$$

The CO_3^{2-} concentration in Equation 9 can be replaced with an expression from the acid-base equilibrium between CO_3^{2-} and HCO_3^- .

$$[\text{CO}_3^{2-}] = k \frac{[\text{HCO}_3^-]}{[\text{H}^+]} \quad (11)$$

Where k is the dissociation constant in the reaction, given as $k = 10^{-10.33}$ [30]. The H^+ and OH^- concentrations were found using the pH of the wastewater, which is stated in Table 4 as 6.56. After plugging in Equation 10 for $[\text{CO}_3^{2-}]$, the values for alkalinity, $[\text{H}^+]$, and $[\text{OH}^-]$ into Equation 8, the HCO_3^- concentration was calculated as 0.00330 mol/L.

The HO_2^- concentration was found using the acid-base equilibrium between H_2O_2 and HO_2^- , shown below. The pK_A of the reaction in Equation 11 is given as 11.75 [13].



$$10^{11.75} = \frac{[\text{H}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]} \quad (13)$$

By using the initial, final, and change in concentrations of the ions, Equation 12 was re-written as

$$10^{11.75} = \frac{(10^{-6.56} + x)(x)}{(0.00333 - x)}$$

Solving as a quadratic yields x , or the concentration of HO_2^- equal to 2.006×10^{-8} mol/L.

The concentration of organic material was approximated by dividing the TOC content of 160 mg/L as carbon by the molar mass of carbon, 12.01 g/mol. This yielded a concentration of 0.0133 mol/L.

The concentrations calculated above can be used in Equation 8 to calculate $[HO\cdot]_{ss,0}$ as follows.

$$\begin{aligned} [HO\cdot]_{ss,0} &= \frac{2k_1[HO_2^-][O_3]}{k_2[HCO_3^-] + k_3[R]} \\ &= \frac{2\left(2.8 \times 10^6 \frac{L}{mol-s}\right)\left(2.006 \times 10^{-8} \frac{mol}{L}\right)\left(0.00667 \frac{mol}{L}\right)}{\left(8.5 \times 10^6 \frac{L}{mol-s}\right)\left(0.00330 \frac{mol}{L}\right) + \left(1.4 \times 10^8 \frac{L}{mol-s}\right)\left(0.0133 \frac{mol}{L}\right)} \\ &= 3.96 \times 10^{-10} \frac{mol}{L} \end{aligned}$$

The pseudo-steady-state rate constant between $HO\cdot$ and the target compound is given by Equation 13 below [13].

$$k_R = k_3[HO\cdot]_{ss,0} \quad (14)$$

$$k_R = k_3[HO\cdot]_{ss,0} = \left(1.4 \times 10^8 \frac{L}{mol-s}\right)\left(3.96 \times 10^{-10} \frac{mol}{L}\right) = 0.0554 s^{-1}$$

Which can be used to determine r_R , the rate of destruction of the target compounds (organic matter), which is

$$r_R = -k_R[R] \quad (15)$$

$$r_R = -(0.0554 s^{-1})\left(0.0133 \frac{mol}{L}\right) = 7.38 \times 10^{-4} \frac{mol}{s}$$

Once reactions begin in a contactor, the half-life of the target compound can be given by [13]

$$t_{1/2} = \frac{\ln(2)}{k_3 C_{HO\cdot}} \quad (16)$$

Where the product of k_3 and the hydroxyl radical ion concentration $C_{HO\cdot}$ is the pseudo-steady-state rate constant, k_R , resulting in

$$t_{1/2} = \frac{\ln(2)}{0.0554 s^{-1}} = 12.5 s$$

Finally, the total contact time can be found with [13]

$$t = \frac{1}{k_R} \ln \left(\frac{C_0}{C} \right) \quad (17)$$

Which, when solved for 95% removal of organic material ($C_0/C = 100/5$) results in a contact time of

$$t = \frac{1}{0.0554 \text{ s}^{-1}} \ln \left(\frac{100}{5} \right) = 54.1 \text{ s}$$