

Hydraulic Fracturing Wastewater: Treatment Methods for Flowback and Produced Water

Claire Cummins

Advisor: Professor Jewell

Senior Project: Fall 2012

Table of Contents

Objectives	3
Background	3
I: History.....	3
II: Review of Today’s Hydraulic Fracturing Process.....	8
Hydraulic Fracturing Fluids	10
I: Hydraulic Fracturing Chemical Overview.....	10
II: Breakdown of Chemicals Used for Hydrofracking.....	12
III: Green Hydraulic Fracturing Fluid Initiatives.....	14
Treatment of Flowback and Produced Water From Wells	14
I: Introduction to Treatment of Flowback Water.....	14
II: Deep Well Injections.....	16
III: Bioremediation.....	17
IV: Surface Impoundments.....	20
V: Thermal Remediation.....	22
VI: Treatment and Reuse.....	24
VII: Company Initiatives.....	26
Suggested Wastewater Solution	31
I: Overview.....	31
II: Environmental Protection Agency Guidelines and Standards.....	31
III: Recommendation.....	39
Conclusion	42

Objectives

One of the most important processes of natural gas extraction is treating the wastewater that is produced as a result of using hydrofracking technology. This paper will first discuss the chemicals that are used in creating hydrofracking fluids and the purpose of each additive. In addition to hydrofracking fluid, produced water, which is naturally created below the surface of the earth, is another type of wastewater that is a result of the hydraulic fracturing process and requires treatment. The current technologies that are available to companies to treat hydrofracking water and produced water will also be reviewed. Lastly, the methods of how to establish regulations for natural gas drilling using hydrofracking technology and the best treatment methods in order to meet these standards will be explained and discussed.

Background

I: History

The United States Committee on Energy and Commerce defines the hydrofracking process as “a method by which oil and gas service companies provide access to domestic energy trapped in hard-to-reach geologic formations” (Chemicals Used In Hydraulic Fracturing 2012). When companies use hydraulic fracturing to release the natural gas trapped below the earth’s surface, it creates both flowback wastewater and produced wastewater. Although these two types of wastewaters originate from different sources, their compositions are very similar and therefore difficult to differentiate between without conducting a conclusive chemical analysis (Schramm 2011).

Flowback wastewater is the water-based solution that is injected into the ground and contains the chemical additives necessary to fracture the shale basin and release

natural gas. Hydrofracking flowback contains a mixture of chemical additives, dissolved metal ions, and total dissolved solids (Schramm 2011). Each site uses a different amount of these additives that vary with the conditions of where the drilling is taking place. The hydrofracking fluid is ultimately returned to the surface as flowback water and will require treatment (Schramm 2011). One of the ways flowback water is characterized is by the rate at which it returns to the earth's surface. For a typical drilled well, most of the flowback water returns to the surface within the first seven to ten days of drilling. The rest of the flowback water can be returned as much as three to four weeks after drilling has begun (Schramm 2011).

Produced water is different from flowback water because produced water is naturally occurring water that has already formed in the shale (Schramm 2011). According to the United States Department of Interior, produced water is “mainly salty water trapped in reservoir rock and brought up along with oil and gas during production” (Produced Water Facts). The Department of Interior also recognizes that chemicals are added to produced water as a result of the hydraulic fracturing process (Produced Water Facts). While under the earth's surface, the produced water leaches minerals such as barium, calcium, iron, magnesium, and dissolved hydrocarbons from the shale, which then become part of the water's composition (Schramm 2011). Produced water can also contain a mixture of dissolved inorganic salts, dispersed oil droplets, bacteria, and other living organisms (Produced Water Facts).

When produced water is below the surface of the earth, it is in a chemical equilibrium (Produced Water Facts). This equilibrium can be shifted if there is a change in temperature, pressure, or both. If this change occurs, then it can cause a chemical

reaction. These reactions result in mineral scales being formed, solid hydrocarbon deposition, and changes in the pH of the water (Produced Water Facts). Furthermore, because produced water does not usually contain oxygen, if the water comes in contact with air as a result of the hydrofracking process, then it will react with the air and can result in deposition of iron compounds and elemental sulfur (Produced Water Facts).

When flowback and produced water are brought to the surface, there becomes a point when the water being returned switches from being flowback water to being produced water (Schramm 2011). The way in which the transition point can be identified is by measuring the rate of return in barrels per day (Schramm 2011). On average, flowback water comes back at fifty barrels per day, whereas produced water comes back between two to forty barrels per day. Another difference is that flowback water returns to the surface over a much shorter period of time than it takes all of the produced water to reach the surface. As mentioned before, a chemical analysis is usually required in order to truly differentiate between flowback and produced water. (Schramm 2011).

The hydraulic fracturing process first began in the 1860s when oil companies were using liquid nitroglycerin injected into shallow hard rock wells in Pennsylvania, New York, Kentucky, and West Virginia (Montgomery 2012). Later, solidified nitroglycerin was also used to stimulate these wells (Montgomery 2012). The problem with using the nitroglycerin for this process was that companies were detonating it to fracture the shale (Montgomery 2012). Nitroglycerin has explosive properties and therefore was illegal to use for hydraulic fracturing because it very dangerous to use and could lead to injury and even death of workers (Montgomery 2012). However, many times companies would continue to use it because it was very successful for oil well

“shooting” (Montgomery 2012). The purpose of “shooting” was to increase the flow of oil from a well by breaking up the formation that the oil was contained in so that more oil could ultimately be recovered during the extraction process (Montgomery 2012). These basic principles were later used as the foundation for hydraulic fracturing.

By the 1930s, oil and gas companies began to inject acids into the ground to stimulate the wells they were drilling (Montgomery 2012). The reason for using acid was because unlike the nitroglycerin, it is nonexplosive and therefore less dangerous for workers to use. Furthermore, injecting the acid into the ground was advantageous because the fractures that were created from the process would not close completely due to acid etching (Montgomery 2012).

The Stanolind Oil Company was the first company to introduce the modern process of hydraulic fracturing. In 1947, Stanolind Oil ran an experimental hydraulic fracturing treatment on one of their wells to see if stimulating the well in this way would increase the well’s productivity. The experiment was conducted in Grant County, Kansas, and it used naphthenic-acid-and-palm-oil-(napalm-) thickened gasoline and a gel breaker (Montgomery 2012). However, it did not appear to increase the flow of oil (Montgomery 2012). Despite these unsatisfying results, Stanolind Oil continued to develop this method of oil extraction. Also during this time, a Stanolind Oil employee published a paper that more widely introduced the process of hydraulic fracturing to the oil and natural gas industry (Montgomery 2012). Additionally, Floyd Farris began to study the relationship between observed well performance and treatment pressures. Farris specifically looked at “formation breakdown” during acidizing and water injection (Montgomery 2012). Farris also studied squeeze cementing, which is a process that uses

“pump pressure to inject or squeeze cement into a problematic void space at a desired location in the well (Squeeze Cementing). He saw that fracturing the area below the earth where oil and gas were trapped would increase the flow of oil and gas to the surface and therefore increase production (Montgomery 2012).

In 1949, Halliburton Oil Well Cementing Company received a patent for their new hydraulic fracturing process (Montgomery 2012). Within the same year of receiving the patent, Halliburton Oil Well carried out its first two commercial fracturing treatments, followed by the treatment of another 332 wells in that same year (Montgomery 2012). Despite the results of the original experiments that were done, hydraulic fracturing technology on average was now increasing well production by 75%, which significantly increased the United States’ oil supply to amounts that were far greater than people had imagined (Montgomery 2012).

Once the hydraulic fracturing process had been introduced and proven to be an effective way of increasing oil and natural gas extraction, the technology began to spread to wells all around the country. By the 1950s, hydraulic fracturing was being used at over 3,000 well sites. These numbers continued to climb and by 2008, there were more than 50,000 reported uses of hydrofracking technology throughout the world (Montgomery 2012). In addition to this, it was not uncommon to have anywhere between 8-40 “frac stages” for just one well, meaning that companies were now repeating the hydrofracking process multiple times on the same well (Montgomery 2012).

The more widespread use of hydraulic fracturing has driven the demand to continue researching and developing this technology. For example, treatments today involve high-temperature wells, which requires drilling deeper into the earth’s surface

where temperature and pressure are higher (Montgomery 2012). Although this process is more difficult than drilling near the surface, these conditions create wells with more natural gas (Encyclopedia Entry 2012). There have also been a lot of new additives included in the hydraulic fracturing fluids. At first, 5% methanol was being used and gel stabilizers were developed (Montgomery 2012). Now, the chemical stabilizers that are being added to the fluid can either be used alone or they could be used with the methanol (so companies could continue to use this along with other chemical additives) (Montgomery 2012). Today, companies are still working to improve cross-linkers, which keep the hydrofracking fluid viscous as it is injected deeper into the earth where the temperatures are higher, and other additives (What Chemicals Are Used). This is beneficial for companies because they are able to reach natural gas trapped at greater depths without damaging the drilling equipment (Montgomery 2012).

II: Review of Today's Hydraulic Fracturing Process

The hydraulic fracturing process is used today as a way of increasing output from oil and natural gas wells. Recently hydraulic fracturing technology has also been paired with horizontal drilling methods, which has significantly increased well productivity (Ehrenberg 2012). Horizontal drilling involves drilling down vertically into the earth, then drilling into the bedrock at an angle. By drilling horizontally, cracks are sent through the rock and increase the area where natural gas can travel into a well (Ehrenberg 2012). This process has been able to unlock a lot of the natural gas that before was believed to be inaccessible.

Companies begin the process of horizontal drilling by first constructing a drill pad and a drill well (Ehrenberg 2012). The drill well is positioned so that it is facing straight

down towards the bedrock. Then, once the drill begins to bore into the bedrock, the bit is turned so that it is now boring into the bedrock horizontally (Ehrenberg 2012). The drill bit cuts through the bedrock by using a “rotating apparatus that usually consists of two or three cones made up of the hardest materials (usually steel, tungsten carbide, and/or synthetic or natural diamonds) and sharp teeth that cut into the rock and sediment below” (How Does a Drill Bit Work 2012). As the bit moves through the well, small holes and cracks form at the far end. Once the drilling is finished, a mixture of hydrofracking fluid, which is made up of water, sand, and chemicals, is injected into the ground (Ehrenberg 2012). Usually, hydrofracking fluid is injected into the ground at pressures that are close to 15,000 psi, which is about the same amount of pressure felt six miles under water (Northrup 2009). The rock then fractures and opens up, allowing the methane that is trapped inside to be released and move into the well where it can then be extracted. During the process of extracting the methane from the well, flowback water is also brought to the surface. This flowback water is a combination of the hydrofracking fluid that was used, as well as the produced water, which had already naturally formed below the surface (Ehrenberg 2012).

The hydraulic fracturing method uses 2-8 million gallons of water per well. Although each company has their own specific mixture of chemicals they use to create their hydraulic fracturing fluid, in general all solutions are 90% water, 9% proppants (ie sand or glass beads used to keep the cracks open), and then the last 1% is the added chemicals (Ehrenberg 2012). As the gas is extracted from the well, this chemical wastewater, plus the produced water, must be treated by the drilling company.

Although hydraulic fracturing has been extensively used in the past, the federal government is now calling the practice into question because of environmental concerns. In order to determine the effects of hydraulic fracturing, the government has requested that the Environmental Protection Agency (EPA) conduct an extensive study due to the large amount of concern the public has expressed (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011). The purpose of the study is to “examine the relationship between hydraulic fracturing and drinking water resources” (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011). More specifically, the study will look at how the hydraulic fracturing process may affect the drinking water supply while paying close attention to which factors of the process tend to increase the frequency and severity of an impact that could occur (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011). Because this research is extensive and ongoing, the two questions from the study that this paper will focus on are what are the possible impacts of surface spills on or near well pads of flowback and produced water on drinking water resources (will be used as a way of examining the “worst case scenario” should hydraulic fracturing fluid infiltrate the ground water), and what are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011).

Hydraulic Fracturing Fluids

I: Hydraulic Fracturing Chemical Overview

Every hydraulic fracturing mixture is different and contains the chemicals that will be the most effective at the well site where they are being used. However, there are broader categories of chemicals that in general are used in almost all hydraulic fracturing

fluid mixtures. Typically, between 3-12 chemicals are added to the fracture treatments and all are used at very low concentrations. Each chemical that is used performs a specific function in the overall process (Chemicals Used In Hydraulic Fracturing). According to the Chemical Disclosure Registry, on average 99.2% of fracking fluid is water, and the last 0.8% is the chemicals that are added (Appendix 1).

Although most people see adding chemicals to fracking fluid as a negative thing, there are some negative consequences as a result of choosing not to add these chemicals. For example, biocides are used to control bacterial growth in the well because without them, there is an increased risk of “souring the formation and increasing corrosion” (Why Chemicals Are Used 2012). Another chemical that could be seen as a positive additive is a gelling agent, which reduces the amount of water needed to frack a well. Additionally, leaving out gelling agents can decrease natural gas recovery by 30 to 50% (Why Chemicals Are Used 2012). Other chemicals that most companies deem necessary to use are acids, corrosion inhibitors, friction reducers, and oxygen scavengers (Appendix 2).

The Chemical Disclosure Registry also provides a more specific table of chemicals that have been used in some hydraulic fracturing fluids, their CAS number, chemical purpose, and product function. For example, glutaraldehyde, quaternary ammonium chloride, and tetrakis hydroxymethyl-phosphonium sulfate are all listed as biocide products whose purpose is to eliminate bacteria in the water that produces corrosive by-products (What Chemicals Are Used 2012). There are over ten other chemical product functions listed, such as acids, breakers, clay stabilizers, corrosion inhibitors, and cross-linkers. The other uses described are to help dissolve minerals and initiate cracks in the rock, maintain fluid viscosity as temperature increases, and slick

water to minimize friction (What Chemicals Are Used 2012). There are thousands of chemicals that could be used in hydraulic fracturing fluids and therefore must be disclosed to the public.

II: Breakdown of Chemical Use for Hydrofracking:

In April of 2011, the Committee on Energy and Commerce met to discuss the chemicals used in hydraulic fracturing. The Committee looked specifically at 2005-2009 and found that 780 million gallons of hydraulic fracturing products alone were used during this time frame (Chemicals Used in Hydraulic Fracturing 2011). The report from this meeting also includes a list of over 750 chemicals that have been used to make hydraulic fracturing products during this same time period (Appendix 3).

Of all the chemicals used, the Committee found that methanol was the chemical used the most because it was found in the greatest number of compounds in the hydrofracking fluid (Chemicals Used in Hydraulic Fracturing 2011). Methanol is a dangerous air pollutant that reacts with other chemicals to form compounds that can become dissolved in hydrofracking wastewater. Therefore, methanol is being considered for regulation under the Safe Drinking Water Act (Chemicals Used in Hydraulic Fracturing 2011). In addition to methanol, there are a number of other harmful chemicals being used that are regulated by federal law. For example, 652 hydrofracking fluids used a total of 29 chemicals that were known or possible human carcinogens. These 29 chemicals were also either regulated under the Safe Drinking Water Act due to the risk they pose to human health or listed as hazardous under the Clean Air Act (Appendix 4) (Chemicals Used in Hydraulic Fracturing 2011). Companies also used a total of 67 products that had at least one out of the eight Safe Drinking Water Act regulated

chemicals, adding up to a total of 11.7 million gallons of hydrofracking fluids that contained at least one, if not more, of these chemicals (Chemicals Used in Hydraulic Fracturing 2011).

The Committee identified a number of chemicals being used that are recognized as harmful to human health. Between 2005-2009, hydrofracking companies used a total of 95 different products each containing 13 different carcinogens (Chemicals Used in Hydraulic Fracturing 2011). There are also a number of potentially harmful chemicals that these companies were using that do not have to be disclosed. The reason for this is because many of these companies list the chemical components they use as “proprietary” or “trade secrets” (Chemicals Used in Hydraulic Fracturing 2011). The knowledge of these chemicals belongs to the companies that supply the chemicals, not the companies that buy and use them. Therefore the companies who purchase these chemicals cannot provide the government with the disclosure information about them. In total, 93.6 million gallons of 279 products contained one or more of these “proprietary” or “trade secret” chemicals. (Chemicals Used in Hydraulic Fracturing 2011). For example, Universal Well Services was asked by the Committee on Energy and Commerce to disclose what chemicals they were using in their hydraulic fracturing process. Universal Well Services responded to this request by explaining that their company “obtains hydraulic fracturing products from third-party manufacturers, and to the extent not publically disclosed, product composition is proprietary to the respective vendor and not to the company.” Because of the law protecting the companies that make these chemicals and the right to own the knowledge of how to make them, the government was unable to get full

disclosure on all the chemicals used by Universal Well Services (Chemicals Used in Hydraulic Fracturing 2011).

III: Green Hydraulic Fracturing Fluid Initiatives

Although it may seem that all companies are using chemicals whenever it is convenient and will allow them to cut costs, there are some companies that are looking at alternative solutions to pumping their hydrofracking fluids full of chemicals. One company in specific, Chesapeake Energy, began a Green Frac program in 2009. The purpose of this program is to examine the chemicals that are currently being used in the hydraulic fracturing process and to see how environmentally friendly these products are (Hydraulic Fracturing Facts). The results of these evaluations are then used to determine which chemicals are actually necessary to the process and which ones can be removed or replaced with something else that is less harmful to the environment. So far, Chesapeake has successfully been able to remove 25% of the additives that are used at most sites without compromising the production of natural gas wells. (Hydraulic Fracturing Facts).

Treatment of Flowback and Produced Water From Wells

I: Introduction to the Treatment of Flowback and Produced Water

The hydraulic fracturing process results in two types of wastewater, flowback water and produced water, which companies are responsible for. As mentioned earlier, these two types of wastewater usually come to the surface together and often times it is very difficult to distinguish between the two. In general, there is more information on treating produced water that is brought to the surface during natural gas extraction because more is known about the different methods for how to treat this type of wastewater. Companies have been producing produced water since basic hydrofracking

principles were first being applied to oil extraction in the 1860s (Montgomery 2012). However, flowback water was not being produced until hydrofracking fluids were being used to extract more of the natural gas trapped below the surface of the earth.

Because flowback and produced water are usually mixed together by the time they both reach the surface, this section includes treatment methods for both of these types of water. There is currently no single technology that is able to completely treat hydrofracking wastewater back to the way it was before it was taken from the environment. Therefore, any technologies or solutions that have been included and are specific to the treatment of one type of wastewater will be considered as only a part of a treatment plan for treating the entire mix of flowback and produced water.

While discussing the different methods of hydrofracking wastewater treatment, there are three potential wastewater treatment and disposal issues that the Environmental Protection Agency (EPA) has identified. First, the EPA is concerned with the hydrofracking fluid chemicals being discharged onto or below the earth's surface and potentially reaching the groundwater supply (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011). The EPA is also concerned with the possible consequences of wastewater not being fully treated. The reason for this is because hydrofracking wastewater contains chemicals and solid residuals that are harmful to humans and the environment (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011). Lastly, the EPA is worried about accidents that could occur during the process of transporting the wastewater (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011).

II: Deep Well Injections

Deep well injection is a form of waste management that stores hazardous liquid waste in wells deep below the earth's surface (Definition of Deep Well Injection). This process began in the 1930s by the oil industry as a way of disposing brine back into the shale formation where it came from (McCurdy). Then in the 1940s, oil refineries began to use deep well injection to dispose of their refinery waste. As the use of deep well injection became more popular, states finally began to regulate this process as a way of disposing brine to protect the groundwater drinking supply. However, despite these new regulations, the first case of groundwater contamination as a result of deep well injection was reported in the 1960s. It was not until 1974 that the Safe Drinking Water Act was passed, which gave the EPA the authority to regulate any waste that companies wished to dispose of using underground injection methods (McCurdy). Since the Safe Drinking Water Act was passed, the Federal Underground Injection Control (UIC) was also passed, which regulated five (now six) classes of wells that fall under the program (McCurdy). This program also sets requirements for states to have primary enforcement of their lands. More recently, this has been amended to allow states to enforce even stricter regulations for deep well injections of hazardous wastes (McCurdy).

In 2012, the United States House of Representatives had a hearing to discuss the information on the quantity, quality, and management of water produced during oil and gas production. During the hearing, deep well injection was identified as the most popular method of wastewater disposal because it is the least expensive method and requires little to no treatment beforehand (Energy Water Nexus). This method is so popular that the federal government estimates that about 90% of produced waters are

disposed of using deep well injection (Energy Water Nexus). Although not much treatment is required, this process is still regulated under the Safe Drinking Water Act's Underground Control Program, which "prevents contamination of aquifers that supply public water systems by ensuring the safe operation of injection wells if produced water is being injected into the ground" (Energy Water Nexus).

Although this process is widely used in the oil and natural gas industry, there are still issues that could potentially threaten the drinking water supply. The EPA has identified four of these issues, the first of which is an accidental release into ground or surface water (ie a well malfunction) (Plan to Study the Potential Impacts of Hydraulic Fracturing). The EPA is also concerned the hydraulic fracturing fluids that contain these harmful chemicals will eventually either infiltrate into the drinking water aquifers or that the formation fluid will be misplaced and released into an aquifer (Plan to Study the Potential Impacts of Hydraulic Fracturing). The last thing the EPA is concerned with is the possibility of the hydrofracking fluid moving into an aquifer in the event that there is movement of the shale or other formations surrounding it (Plan to Study the Potential Impacts of Hydraulic Fracturing). Because of these concerns, there are costs involved in deep well injection, such as some treatment of the water before it is injected and making taking the necessary precautions to avoid a preventable mistake. However, due to the fact that it is a relatively inexpensive method of hydrofracking wastewater disposal, it is the method preferred by most companies.

III: Bioremediation

The Environmental Protection Agency recognizes that a substantial amount of wastewater is produced from the hydraulic fracturing process and that there is a great

need for this water to be properly disposed of (Natural Gas Extraction 2012). Because there is currently no standard for the disposal of this wastewater, in many cases the wastewater gets released into the environment and ends up at both the public and private wastewater treatment facilities (Natural Gas Extraction 2012). When hydrofracking wastewater reaches these facilities, it becomes an issue because these types of wastewater treatment plants are not equipped to deal with hydrofracking contaminants (Natural Gas Extraction 2012).

Bioremediation, also known as biological treatment or biotreatment, is a process that “uses microorganisms (bacteria and fungi) to biologically degrade hydrocarbon-contaminated waste into nontoxic residues” (Fact Sheet- Bioremediation 2012). This treatment process is designed to mimic the natural decomposition process. However, by controlling factors such as oxygen, temperature, moisture, and nutrient parameters, the process of decomposition can be accelerated to make the wastewater treatment plant work more quickly and efficiently to release water safely back into the environment (Fact Sheet- Bioremediation 2012).

The process of bioremediation mainly uses bioreactors to treat the water that reaches wastewater facilities. Inside the bioreactors, the chemical process that is going on is very similar to the reactions that are taking place in land treatment and composting by using aerobic biological reactions (Fact Sheet- Bioremediation 2012). However, the main difference between these two processes is that bioremediation takes place in an open or closed containment system or in an impoundment (Fact Sheet- Bioremediation 2012). This allows operators to control the factors that can accelerate decomposition (ie temperature, oxygen, etc.). These containment vessels act as a container that hold the

fresh water and microorganisms that are needed for biological treatment. When a shipment of wastewater is received, it is added to the containment vessel and treatment can begin (Fact Sheet- Bioremediation 2012).

Once the wastewater is received in the containment vessels, nutrients and a source of air are then added to begin the process. The air source mixes everything inside the vessel, which increases the amount of contact between the microorganisms and the waste to accelerate the process, and maintains the dissolved oxygen concentration in the water (Fact Sheet- Bioremediation 2012). Plant operators can further speed up this process by adding microbes that will “eat” what is in the reactor (Fact Sheet- Bioremediation 2012). When the air is turned off, the mixing stops and the microbes are able to settle out along the bottom of the tank. The layer of microbes is referred to as sludge, which can be treated to remove almost all of the water and disposed of as solid toxic waste. In the past, microbes have proven to successfully “eat” waste that is sent to the treatment plant, however there are also some facilities that have not had much success with their microbes eating the waste inside the reactor. Instead, these companies have turned to using agricultural products of plant and animal waste, which in some cases they have found to be more effective (Fact Sheet- Bioremediation 2012).

There are many advantages to using bioremediation as a method for treating wastewater, and overall this process as seen as one that is environmentally friendly. One of the major advantages of this process is that compared to other methods of wastewater treatment, bioremediation generates very few greenhouse gas emissions and requires very little transportation of the waste to get it to the treatment facilities (Fact Sheet- Bioremediation 2012). Another advantage is that it takes liquid waste and removes the

hazardous solid materials suspended in the water, leaving behind a solid material that is easier to landfill that will not generate leachate (Fact Sheet- Bioremediation 2012).

Additionally, the solid waste that is produced is much more stable and therefore makes it safer to dispose of in a landfill (Fact Sheet- Bioremediation 2012). Lastly, bioremediation can easily be incorporated as one of many steps that make up a larger wastewater treatment plan (Fact Sheet- Bioremediation 2012).

Despite the advantages of bioremediation, there are some disadvantages that make it an unattractive solution to the problem of dealing with hydrofracking wastewater. One of the biggest problems is the high initial cost of building the facility, which includes both the technology that will be used to treat the wastewater and the land where the bioremediation facility will be built (Fact Sheet- Bioremediation 2012). Another drawback to using bioremediation is that according to the Drilling Waste Management Information System database, it can take months, and sometimes even years, to treat hydrofracking wastewater enough so that it can be released back into the environment (Fact Sheet- Bioremediation 2012). The amount of time it takes for the process to be completed depends on the hydrocarbons that are in the wastewater (Fact Sheet- Bioremediation 2012). Because hydraulic fracturing produces million of gallons of wastewater from only hydrofracking job, bioremediation can be an undesirable solution because it will not be able to produce clean water at a fast enough rate to keep up with the demand for treatment (Fact Sheet- Bioremediation 2012).

IV: Surface Impoundments

A temporary solution to dealing with hydraulic fracturing wastewater is to store it in a surface impoundment until actual treatment can be pursued. According to the

Citizen's Campaign organization, "centralized impoundments are hydro-fracking liquid waste lagoons that store freshwater and flowback fluid for dilution and reuse to service gas wells in a four mile radius" (What's the Hydro-fracking Rush). Surface impoundments can be helpful for initially dealing with the wastewater as it flows back to the surface. However, leaving it in an impoundment is not a treatment option and the water will not naturally reach the point where it would pass regulations to be released back into the environment.

In addition to only being a temporary solution to the wastewater problem, surface impoundments have other disadvantages as well. One disadvantage to using surface impoundments is that they take up a lot of space at the drilling site. A typical lagoon can be as large as five acres, which does not include the additional access roads that need to be built around the lagoon so that trucks and other vehicles can get to and from the site (What's the Hydro-fracking Rush). Another potential disadvantage is that the lagoon may attract wildlife (What's the Hydro-fracking Rush). Because surface impoundments are usually so large, it can be very difficult to cover them or restrict animals from reaching them. If animals are able to come in contact with this water, it can be very harmful and even fatal due to the chemicals that these surface impoundments contain. In addition to animals being able to reach this water, it could also be released into the environment if there was a storm in the area or if the liner on the inside of the impoundment were to break (What's the Hydro-fracking Rush). In this case, it is much more difficult to prevent animals and other wildlife from coming into contact with this harmful wastewater once it has been released into the environment. The last disadvantage to holding hydrofracking

fluid in surface impoundments is that it has the potential to be a significant source of air pollution (What's the Hydro-fracking Rush).

V: Thermal Remediation

Thermal remediation is a process that can be applied in a number of different ways, one of which is in the treatment of hydrofracking wastewater. The Environmental Protection Agency explains the process as “the injection of energy into the subsurface to mobilize and recover volatile and semi-volatile organic contaminants” (Thermal Remediation). Additionally, thermal remediation can be used at the surface either alone or as part of a group of wastewater treatment methods. The ways in which this process is commonly done are steam-enhanced extraction, electrical-resistance heating, and thermal conductive heating. All of these methods are used today as ways to remediate contaminants from source zones (Thermal Remediation).

One place where thermal remediation has been used to treat produced water and hydrofracking flowback water is near Decatur, Texas, at a sight controlled by Devon Energy (Thermal Distillation Technology 2008). Devon Energy uses a technology called Aqua-Pure, a type of thermal distillation technology, as a method of treating the hydraulic fracturing water enough so that it can be reused in the future for other hydrofracking jobs (Thermal Distillation Technology 2008). First, Devon collects the produced water and hydrofracking fluid that comes back to the surface (Thermal Distillation Technology 2008). When the water first begins treatment at the facility, it contains a lot of total dissolved solids (ie salt), organic materials (mainly the bacteria from the earth found in the rock formation as well as from the chemicals added to the hydrofracking fluid), polymers (friction reducers and cross-linked gels), residual

hydrocarbons, and suspended solids (Thermal Distillation Technology 2008). Depending on the level of treatment, the water can either be sent for further treatment and be released back into the environment, or reused in the hydraulic fracturing process.

The process begins with pretreatment, which involves mixing the wastewater with flocculant chemicals to coagulate and flocculate any solids (Thermal Distillation Technology 2008). Then, the newly formed solids are removed by passing the wastewater through an inclined plate separator. The solids are then collected and taken to filter press to remove all the water that may still be contained within the solids. Once the water is removed, the solids can be held in a dumpster until it can be properly disposed of offsite (Thermal Distillation Technology 2008). Next, the total dissolved solids (TDS) are removed by pumping the remaining fluid into the Aqua-Pure MVR evaporator. Once this water moves through the evaporator, it can be stored in a tank on-site to be re-used for future hydrofracking jobs (Thermal Distillation Technology 2008).

Although Aqua-Pure is an effective system that treats produced water and hydrofracking flowback water so that it can be re-used, it is still less expensive for companies to dispose of this water off-site and buy new water for every new hydrofracking job (Thermal Distillation Technology 2008). Despite this, Aqua-Pure continues to develop their technology so that their system works more efficiently and can be sold at a lower cost (Thermal Distillation Technology 2008). Although right now Aqua-Pure is too expensive to be a competitive solution for produced and flowback water, the company hopes that in the future this might change if hydraulic fracturing begins to threaten the amount of available clean drinking water and stricter regulations are imposed on the industry (Thermal Distillation Technology 2008).

VI: Treatment and Reuse

Another way to deal with hydraulic fracturing wastewater is to recycle the water that comes back to the surface (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011). Hydraulic fracturing water can be reused if it treated, however the level of treatment can be lower than the level required by companies that choose to dispose of their wastewater or release it back into the environment (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011). By reusing hydraulic fracturing water, the demand for clean drinking water can be reduced. Although water that is being reused will eventually have to be treated and properly disposed of, by reusing the water on site it reduces the immediate need for proper treatment and disposal (Plan to Study the Potential Impacts of Hydraulic Fracturing 2011).

According to the New York State Department of Environmental Conservation (DEC), “reuse involves either straight dilution of the flowback water with fresh water or the introduction on-site of more sophisticated treatment options prior to flowback reuse” (Natural Gas Development Activities). The DEC also reports that as hydraulic fracturing continues to be used in the Marcellus Shale, more water is being reused for multiple fracking jobs (Natural Gas Development Activities). After the water is reused for a fracking job, it can be properly treated and reused again by other industries. In general, there are more uses for produced water than flowback water, which can be used to reduce the demand for water (Guerra 2011). This is mainly due to the fact that produced water can be easily treated to and reused in the agricultural industry, which is currently the largest consumer of fresh water in the United States (Guerra 2011). However, in order to

decrease the amount of clean water this process demands, it is important to reuse as much of the wastewater possible that hydrofracking produces.

The most obvious application of reusing hydrofracking wastewater is to reuse it for the hydrofracking process itself (Natural Gas Extraction 2012). Some of the water that returns to the surface can replace the fresh water needed to fracture a new well or to re-fracture an existing well (Natural Gas Extraction 2012). Reusing the wastewater depends on which pollutants are in the wastewater and if they would effect the next hydrofracking job. Reuse also depends on how far the wastewater is from the next site where it would be used (Natural Gas Extraction 2012). If the site is too far away, it may not be economical for companies to transport the wastewater from the site where it was produced. However, when water can be reused it can reduce discharges to treatment facilities or surface waters, minimize underground injection of wastewater, and conserve water resources (Natural Gas Extraction 2012).

One way produced water can be reused after it has been treated is for livestock watering. In the United States, livestock require an estimated 1,760 million gallons of water every day, which puts a lot of pressure on the clean drinking water supply in many parts of the country (Guerra 2011). Unlike humans, livestock do not need high quality drinking water to survive. However, there are certain contaminants (such as particular ions or high salinity levels) they cannot tolerate, which is why the water still must receive treatment before livestock can consume it (Guerra 2011). This is mainly done using a number of desalination technologies that can easily be transported to the drilling site, such as reverse osmosis, forward osmosis, or using a thermal process (Guerra 2011). Drilling mainly takes place on property that is leased by farmers and ranchers. Therefore,

the produced water can remain locally available and reduce the need to transport this water from a drilling site to the livestock (Guerra 2011). If the demand for clean drinking water becomes too high, then in the future it may become economical for some companies to treat the water and reuse for livestock watering.

In addition to reusing produced water for livestock watering, produced water can also be reused for irrigating farmland. In most states, irrigation is the largest consumer of fresh water (Guerra 2011). However, in order for this water to be reused for irrigation, it first must be treated. One problem with using untreated produced water is the sodium absorption ratio, which says that if the salinity of the water is too high, it can kill the crops (Guerra 2011). Produced water also has to be treated for calcium and magnesium, which can also be found in produced water as it reaches the surface.

There are two ways produced water can be treated before it can be used for irrigation purposes. The first is to treat the water using conventional methods (ie distillation, bioremediation, ect) to remove the salts and other minerals. The second method is to dilute the water with clean drinking water so that the salinity levels are low enough that they will not kill the crops (Guerra 2011). The drawback to this method is that it still uses freshwater for irrigation. However, it can still be seen as a positive solution because the overall demand for clean drinking water is still being reduced.

VII: Company Initiatives

There are a number of companies that have developed unique technologies to help treat the wastewater from hydrofracking. Many of these technologies are not used on a large scale because they are not an efficient economic solution to treating wastewater. However, companies continue to use and improve these systems to make them more

efficient. Furthermore, as the demand for fresh drinking water increases, these technologies will become more economical and therefore more widely used.

Halliburton is one of the larger companies that uses hydrofracking technology for natural gas drilling. One of the environmentally responsible ways they treat their wastewater is by using CleanWave technology. The idea behind this technology is to destabilize and coagulate the microscopic suspended particles distributed throughout the wastewater (CleanWave 2012). To do this, the wastewater is passed through electrocoagulation cells, which releases positively charged ions. The suspended particles in the wastewater have a negative charge and therefore bond with the positive ions, which creates the coagulation (CleanWave 2012). While this is occurring, a cathode is producing gas bubbles that bring the coagulated material to the surface. Once at the surface, it can be skimmed off (CleanWave 2012). Some of the coagulates are too heavy to float and instead sink to the bottom and leave behind water that is now clean enough to be reused in the hydrofracking process (CleanWave 2012). CleanWave technology is considered to be environmentally benign because it cleans wastewater to a level where it can be reused to make new fracturing fluids and therefore decrease the demand for fresh drinking water. Additionally, it reduces Halliburton's cost of disposing the wastewater that otherwise could not be used without the CleanWave technology (CleanWave 2012).

There are some companies that are being created specifically to deal with hydrofracking wastewater, such as the Clarion Altela Environmental Services, LLC (CAES), which is a new hydrofracking wastewater recycling facility (Sas 2012). The facility was scheduled to open in the summer of 2012, however it has yet to go online. Because this project required high initial investment, building the water treatment facility

was done together by ACI Energy, which is an investment holding company, and Altela, which is a water desalination company (Sas 2012). The treatment facility will use AltelaRain technology, which is designed to treat produced water to a quality level higher than state and federal standards. The process creates water that is of the same quality as distilled water by using condensation and evaporation (Technology: AltelaRain 750 2012). Furthermore, the technology is made more efficient by using the “low-grade energy given off from the condensation (the second step) to evaporate the water (the first step) and start the process all over again” (Technology: AltelaRain 750 2012). The treated water can then be reused for future fracking jobs (Sas 2012). The benefits of this system are that it requires very little capital (after the initial investment), has a very low operating cost, produces a very high quality of water, and is convenient for customers because it can easily be transported and used at the drilling site (Technology: AltelaRain 750 2012).

Siemens Water Technologies is another company that is also in the process of building a wastewater treatment facility. The technology Siemens plans to use is a Hydro Recovery LP system (Siemens to treat wastewater). This system is designed specifically for the treatment of natural gas hydraulic fracturing flowback water by using “continuous precipitation and sludge dewatering” (Siemens to treat wastewater). More specifically, the plant markets themselves as a company that would be able to treat wastewaters to a level where they could be reused again in the hydraulic fracturing process and reduce the overall demand for fresh water in the hydraulic fracturing market (Siemens to treat wastewater). Originally, the Siemens Water plant was going to be completed and go

online by April 2011, however Siemens was unable to meet this deadline and the plant has yet to go online (Siemens to treat wastewater).

In addition to building facilities to treat wastewater, on-site wastewater systems are another solution that companies are investing in. One treatment plan for natural gas companies is to use the MIOX system, which can be used and stored on-site and is a more cost-effective way to treat wastewater. This process uses salt and electricity, which reduces both costs and chemical volume, to generate a solution that is chlorine-based that has more powerful oxidants in it (Oil & Gas Flowback and Produced Water Treatment). By using salt and electrolysis instead of harmful chemicals that are traditionally used in treating wastewater, companies see a decrease in carbon emissions. Furthermore, by reducing the number of harmful chemicals needed for treatment, MIOX is a safer process than traditional treatment methods (Oil & Gas Flowback and Produced Water Treatment). These generated oxidants have a higher ability to kill any algae in the wastewater and can be made even more efficient by increasing the pH of the water where the reaction is occurring (Oil & Gas Flowback and Produced Water Treatment).

The MIOX system is safe to handle and store on-site because the only chemical it requires is food grade salt (Oil & Gas Flowback and Produced Water Treatment). The reason the oxidant solution is not toxic is because it is stored and injected into the wastewater at concentrations that are less than 1 percent, which is not a high enough level to be considered toxic (Oil & Gas Flowback and Produced Water Treatment). MIOX technology is also very easy to transport because it is a relatively small system (Oil & Gas Flowback and Produced Water Treatment). Companies that wish to use this treatment method can choose to either use it alone, or integrate it with another water

treatment system (Oil & Gas Flowback and Produced Water Treatment). The one disadvantage the company states is that the initial investment in this system is very high. However, companies see a fast return (about 18 to 36 months) on their investment (Oil & Gas Flowback and Produced Water Treatment).

Another treatment method that doesn't use harmful chemicals was created by Ecosphere Energy Services, which uses Ozonix technology (Innovative Solution). This technology was designed, manufactured, and patented by Ecosphere Technologies and uses an "advanced oxidation process that combines ozone, hydrodynamic cavitation, acoustic cavitation, and electro-oxidation in a piece of equipment used to destroy bacteria, biofilms, organics, and contaminants" (Innovative Solution). Ozonix has been tested at independent laboratories that have been able to recycle millions of gallons of wastewater into water that could be reused by natural gas companies (Innovative Solution). Unlike the drawbacks of many other systems, Ozonix is cost effective because it reduces the need for expensive things such as liquid chemicals scale inhibitors and friction reducers (Innovative Solution).

The Ozonix Technology is capable of treating up to 3,300 gallons per minute per Ozonix unit (Innovative Solution). Because it is very easy to transport these systems, companies can purchase multiple units depending on their water treatment demand and have them transported to the site. Water that is treated using Ozonix Technology can be completely reused to re-frack a well or to frack a new well without producing a secondary stream of waste (Innovative Solution).

Suggested Wastewater Solution

I: Overview

Since the discovery of natural gas trapped in the Marcellus Shale, extracting natural gas by using hydraulic fracturing technology has recently become more popular. However, as discussed earlier, the hydraulic fracturing process is not a new technology and has been used for decades on oil wells. In general, the oil industry is much more developed and, unlike the natural gas industry, has much stricter guidelines that have already been established to regulate how much pollution is discharged into ground and surface water. In order to regulate natural gas drilling companies as efficiently as possible, federal agencies should focus on creating a similar set of strict guidelines for the natural gas industry that are based on the oil industry standards. Due to the increasing demand for energy independence in the United States, many companies would like to begin drilling for natural gas in the Marcellus Shale as quickly as possible. In order to keep up with the amount of wastewater that will inevitably be generated by this demand, standards should be put in place as quickly as possible before large amounts of hydrofracking wastewater are discharged into ground and surface waters and contaminate clean drinking water supplies.

II: Environmental Protection Agency Guidelines and Standards

The Environmental Protection Agency has created effluent limitations, guidelines, and pretreatment standards for wastewater discharges created by the petroleum refining industry. This would be a good industry for the federal government to model natural gas regulations after because the standards are well developed and designed, both industries produce a similar amount of wastewater, and the standards that are used could be applied

to the natural gas industry. It would also be efficient for the EPA to take on the role of creating these standards because they have experience doing it for other industries in the past. They are also currently conducting a study on the impacts of hydraulic fracturing to assess its potential impacts on fresh drinking water, and the results of this study could be used as the starting point for setting the maximum pollution discharge limits.

In 1974, the Environmental Protection Agency set standards for the petroleum refining industry for Best Practicable Control Technology Currently Available (BPT), Best Available Technology Economically Available (BAT), New Source Performance Standards (NSPS), Pretreatment Standards for Existing Sources (PSES), and Pretreatment Standards for Existing Sources (PSNS) (Technical Support Document 2004). These were known as the effluent limitations guidelines (ELFs) (Technical Support Document 2004). Since the original creation of these standards, there have been a few changes made. For example, the Best Available Technology Economically Available standard was remanded in 1976 after it was legally challenged, however it was reinstated in 1982 and set equal to the Best Practicable Control Technology Currently Available. Then in 1985 it underwent further revisions and was revised for phenol and chromium (Technical Support Document 2004).

Between 1992 and 1996, the EPA reviewed the petroleum refining industry to see if these changes that were made to the effluent limitations guidelines were justifiable (Technical Support Document 2004). By 1996 the results of the review were published in the *Preliminary Data Summary for the Petroleum Refining Category*. The review included “a general description of the industry, treatment technologies used, water usage,

analysis of dioxins in catalytic reformer wastewater, estimated pollution discharges, environmental issues, and economic profile” (Technical Support Document 2004).

The natural gas industry will ultimately need to be regulated by at least one, if not many, government agencies to ensure that companies are using hydraulic fracturing technology in a safe and environmentally conscientious way. It would be efficient to have the EPA be one of the main agencies regulating natural gas drilling because they have already set guidelines for the petroleum refinery industry that are similar to the regulations that will be needed for hydrofracking and natural gas extraction. Additionally, the EPA is already conducting a study on natural gas and hydraulic fracturing technology that could also be used as an outline for setting these standards.

The majority of wastewaters that are produced from the oil refinery industry are sour water (which can come from multiple processes), scrubber water from reformer catalyst regeneration, and spent potassium hydroxide streams (Technical Support Document 2004). Appendix 5 includes a complete list of all the different types of wastewaters and their estimated amount of flow. These estimates were reported by the United States Department of Energy in their publication *Water Use in Industries of the Future: Petroleum Industry* (Technical Support Document 2004). The complete publication lists the wastewater treatment processes that are used, a description of the wastewater (ie the possible pollutants), flow rate for individual types of wastewater, and the total percentage of wastewater flow rate (Technical Support Document 2004).

Companies that are using potentially harmful chemicals could also provide the EPA with the information to create this list for the wastewaters produced by natural gas drilling. For example, thermal remediation could be listed as a way to remove the salt that

comes to the surface with produced waters, and bioremediation can be used to remove hydrocarbons added to hydrofracking fluids (Technical Support Document 2004). In order to create a complete list for every pollutant involved in hydrofracking and natural gas extraction, a full report would need to be conducted by the EPA first to determine which pollutants they are going to regulate. Also, there are not a lot of technologies that have been developed yet that are solutions to cleaning hydrofracking wastewaters because most companies are still holding wastewaters in surface impoundments or using deep well injection to dispose of it below the earth. However, once the EPA passes more regulations, it will create a demand for more technologies to treat all the pollutants that are now being regulated.

The effluent guidelines used by the Environmental Protection Agency are divided into five subcategories, which are topping refineries, cracking refineries, petrochemical refineries, lube refineries, and integrated refineries (Technical Support Document 2004). The type of facility that the discharge is coming from determines which subcategory the effluent is placed in (Technical Support Document 2004). It may however be more efficient for the natural gas limitations to be divided up in one of two ways. The first way would be to look at produced vs. flowback water, or to divide it up by the types of chemicals that are used in the hydrofracking fluid (chemicals used in hydrofracking fluid varies from site to site). The second comparison may be better because it is almost impossible to tell the difference between produced water and flowback water without a chemical analysis (Schramm 2011). Therefore, it will be very difficult to set regulations for companies without requiring them to perform a chemical

analysis on all the wastewater they produce, which can become both complicated and expensive.

Another component of the petroleum refinery industry that the EPA regulates is how in-plant controls and end-of-pipe treatments will be regulated from a technical standpoint (Technical Support Document 2004). For example, the basis for Best Practicable Control Technology Currently Available for in-plant control needs sour water strippers that can reduce the sulfide and ammonia that is sent to the wastewater treatment plant (Technical Support Document 2004). As mentioned earlier, it may be difficult for the EPA to fully outline the technical basis of regulation for the natural gas industry before a complete report of all the impacts of hydraulic fracturing fluids on drinking water is conducted. Without this information, it is unclear exactly what technologies will be needed to completely treat hydrofracking wastewater to meet federal standards.

The EPA specifically lists the pollutants used by the petroleum refining industry that they regulate. Some of the pollutants that are regulated include, but are not limited to, ammonia as nitrogen, oil and grease, pH, and phenolic compounds (Technical Support Document 2004). The report sets a maximum level for each of these pollutants. For example, the EPA demands that oil and grease do not exceed 100 milligrams per liter if following daily maximum pretreatment standards for existing sources, and may not exceed 100 mg/L if following the daily maximum pretreatments standards for new sources in all subcategories (Technical Support Document 2004). These regulations are based on the treatment technologies, which are also explained in the report (Technical Support Document 2004).

If the EPA were to be put in charge of setting regulations for the natural gas industry, they will already have a list of the potential harmful pollutants that are produced from the hydrofracking process that is made available through the Chemical Disclosure Registry. There still may be more chemicals companies are using that are not disclosed in the registry, however the list that has been made available includes most of the chemicals that are currently used by hydrofracking companies. Using this list will save the EPA time and money that they would otherwise have to spend trying to identify these chemicals.

The limitations that are set are also listed as “mass limitations and specific refinery limitations” (Technical Support Document 2004). The mass limitation is based on feedstock productions, which is measured in pounds of pollutant per 1,000 barrels of feedstock (Technical Support Document 2004). The specific refinery limitations are based on size factors, process configuration factors, and processes, which are measured in 1,000 barrels of feedstock per stream day (Technical Support Document 2004). To set these same limitations for hydrofracking chemicals, the EPA may want to use smaller limitation standards. This is because hydraulic fracturing only uses a small amount of chemicals relative to the amount of water that is required for the process (hydrofracking mixtures are usually 90 percent water, 9 percent proppants, and 1 percent chemical additives) (Ehrenberg 2012). Despite the fact that there is a relatively small amount of chemicals used in hydrofracking, the chemicals that are being used are still harmful and should not be overlooked. However, it may be more efficient to measure the chemicals using smaller units that are similar to the scale of the volume of chemicals being used.

The petroleum refinery industry is also subjected to other regulations besides the effluent limitations guidelines and standards (Technical Support Document 2004). Due to the processes that this industry uses, the EPA also regulates solid and hazardous waste management activities, air pollutants, and stormwater regulations (Technical Support Document 2004). Similar to petroleum refining, hydrofracking and natural gas extraction also must deal with these additional pollutants and therefore should also be included when regulations are being determined.

The EPA also limits specific wastewater discharge volumes (Technical Support Document 2004). On average, wastewater from the petroleum refinery industry has a flow rate of about 0.4 to 8.1 million gallons per day and averages about 2.3 million gallons per day (Technical Support Document 2004). In total, this can add up to over 3,000 million gallons of wastewater per year (Technical Support Document 2004). Based on what is known about wastewater that is produced by hydrofracking, the same limit could be used to regulate wastewater that is discharged by the natural gas industry because in order to frack a well, 2 to 8 million gallons of water are required (Ehrenberg 2012). However, in order to encourage companies to reuse wastewater or to use water more efficiently, the EPA could set a lower specific discharge volume for hydrofracking wastewater.

The volume of wastewater discharge is always reported, however these reports do not always include the specific type of wastewater that is being disposed. Therefore, the volumes that are reported could also be including stormwater and noncontact cooling water that is used to cool the treat systems but never actually comes in contact with actual wastewater (Technical Support Document 2004). This is a problem because if regulating

agencies only have one number for total volume that is being discharged, then it is unclear how much of each type of wastewater is being disposed. This problem should be addressed if the EPA creates regulations for the natural gas industry by mandating companies to report which type of wastewaters are being disposed of and the exact volumes of each. By requiring this, it will make regulating the disposal of harmful chemicals a lot less difficult.

Although they do not need to report the types of wastewater that makes up the total volume that is discharged, refineries do need to report both the direct discharges, which is the mass of the pollutants released directly into receiving streams, and the indirect discharges that are made before treatment, which is the mass of the pollutant that is transferred to publicly-owned treatment works (Technical Support Document 2004). This is an important distinction that should also be made when specifying the regulations for the natural gas industry to be sure of exactly how much wastewater is being discharged by companies. Furthermore, it will prevent companies from disposing of wastewater in an environmentally irresponsible way to avoid reporting it or paying to have it properly treated and disposed.

When petroleum refineries treat processed wastewater on site, there are a number of different technologies that are used. For example, steam stripping is used to remove hydrogen sulfide, other sulfur compounds, and ammonia for sour water pretreatment (Technical Support Document 2004). Another method used is oil and solid separation by using an “API separator corrugated plate interceptor, or other type of separator followed by DAF or settling ponds to remove emulsified oils” (Technical Support Document 2004). Petroleum refineries even use biological treatment by using activated sludge units,

trickling filters, or rotating biological contactors, followed by an effluent polishing procedure (Appendix 6) (Technical Support Document 2004).

Because the petroleum refining industry is much more heavily regulated than the natural gas industry, the demand for the technologies that are used in cleaning the wastewater from refineries is much higher and well known as to which of these technologies is the more economical and effective. However, the natural gas industry has not yet had its regulations clearly established for hydrofracking and therefore there is not a lot of demand for specific treatment processes. There are some technologies that are emerging, however the demand for these products is not very high and only a few companies are testing and using them to exclusively. Until regulations are put on the disposal of hydrofracking wastewaters, companies will continue to use the most economical methods of disposal, such as deep well injections or hold the wastewater in lined pits, which are not necessarily the safest and most sustainable way to deal with this problem.

III: Recommendations

Based on all of the information that is known about the different methods of treating wastewater that is produced when companies use hydrofracking technologies on natural gas wells, a decision must be made as to which method or combination of methods would be the most effective yet realistic approach to dealing with this issue. Hydraulic fracturing technology has unlocked a potential source of natural gas in the Marcellus Shale that was once thought to be unattainable. This potential new source of energy is so large that it could be a very important factor in making the United States energy independent, which is something that most people agree should be one of the

nation's top priorities. However, before the natural gas industry grows much larger, the government should invest in the proper infrastructure to make sure that there is a way for companies to properly treat the wastewater that is generated before the United States becomes dependent on natural gas, and then discover it is contaminating drinking water.

The need to build the proper infrastructure to treat hydrofracking wastewater is especially important in places like Pennsylvania, where there have already been reports of groundwater contamination. These reports have mostly come from areas that are near natural gas wells that are being fracked. In his new controversial film *Gasland*, Josh Fox investigates the dangers of hydrofracking that is not properly managed. He has interviewed a number of citizens who describe the changes to their drinking water that they believe to be caused by recent drilling activity in their area. In Dimock, Pennsylvania, Fox interviewed citizens whose water faucets were producing dirty water that they could no longer use for laundry, dishes, drinking, etc. They also reported children and animals are becoming unexplainably sick. Some people even reported being able to light their water on fire, which they demonstrated for the film. However, the EPA tested 61 homes in Dimock, Pennsylvania and found that there were no elevated levels of contaminants that were of concern and therefore did not require further action (Garner 2012). Despite these reports, some people still believe that natural gas drilling and hydrofracking are causing their health issues. Therefore, more extensive and conclusive tests need to be conducted to determine whether or not these allegations are true.

The solution that many companies are using to remedy the contaminated drinking water issue is trucking in water to people whose drinking water has been contaminated. However, this is incredibly expensive and would be unsustainable if a company were to

contaminant a drinking water source that supplies a much larger number of people. Although building the proper wastewater treatment infrastructure would be expensive, it could avoid the billions of dollars being spent on treating and shipping clean drinking water to people whose water has been contaminated.

The first step to creating a sustainable infrastructure for dealing with hydrofracking wastewater should be for the federal government to invest in researching the most efficient way of biologically treating wastewater. The biological treatment method is the most sustainable and environmentally responsible choice because the toxins that are removed from the water can be disposed of as hazardous solid waste. If properly researched and done efficiently, this method can effectively remove a lot of the chemicals in the wastewater. Thermal remediation should also be used as part of the treatment plan because the produced water that comes to the surface has high salinity content. If this salt is not removed before the wastewater is discharged back into the environment, then it will kill any plants in the ecosystem where the water is disposed. Thermal remediation is also a good process to include as a part of an overall solution because it is a relatively easy process that has been used in a number of different industries with technology that is more developed.

The last step in the wastewater treatment cycle should be to reuse the wastewater on site as much as possible, and then reused it in other applications. Doing this will reduce the amount of clean drinking water farmers have to purchase for irrigation and livestock watering, which will decrease the demand for fresh water to be used for purposes other than drinking. This is critical in certain areas in the country where there the fresh drinking water supply is being depleted. Furthermore, if this method were to

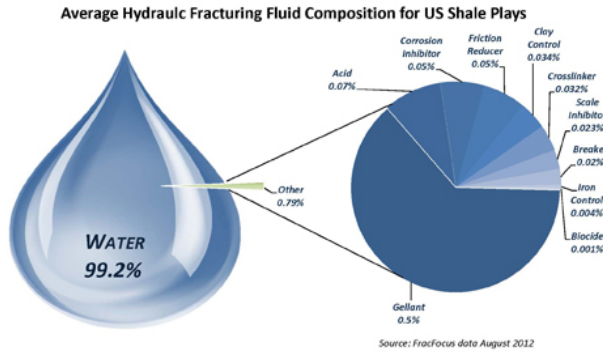
become more efficient, then reused water may actually become less expensive than purchasing new clean drinking water, which would provide farmers with an incentive to purchase reused water because it will reduce their cost of operating the farm.

Conclusion

In conclusion, in order to prevent groundwater contamination that could potentially put millions of human's health at risk, as well as billions of the federal government's money on solving the problem, hydraulic fracturing needs to be heavily regulated. This will ensure that hydrofracking is being done in an environmentally responsible way by every natural gas drilling company and not just those who are willing to pay extra for systems and treatment methods that are more expensive but also more effective. The technology for treating hydrofracking wastewater has not been fully developed and would be used a lot more widely throughout the industry if there were regulations that were put in place that required companies to invest in different treatment options. Hydrofracking technology has the potential to make large amounts of natural gas available that otherwise would remain trapped below the earth. However, in order to maximize the potential benefits of hydraulic fracturing, regulations must first be put in place to encourage companies to handle their wastewater in a safe and responsible way.

Appendix:

Appendix 1



Appendix 2

Chemicals Commonly Used in Shale Fracturing and consequences of not using the chemical

Chemical	Use	Consequences of not using chemical
Acid	Removes near well damage	Higher treating pressure, slightly more engine emissions.
Biocides	Controls bacterial growth	Increased risk of souring the formation (H ₂ S gas from sulfate reducing bacteria growth) and increasing corrosion.
Corrosion Inhibitor	Used in the acid to prevent corrosion of pipe	Sharply increased risk of pipe corrosion from acid. Well integrity compromised.
Friction Reducers	Decreases pumping friction	Significantly increases surface pressure and frac pump engine emissions .
Gelling Agents	Improves proppant placement	Increased water use. Natural gas recovery may decrease in some cases by 30 to 50% where frac fluids must be gelled (conventional fracs).
Oxygen scavenger	Prevents corrosion of well tubulars by oxygen	Corrosion sharply increased and well integrity (containment) compromised.

Appendix 3

Table 1. Chemical Components Appearing Most Often in Hydraulic Fracturing Products Used Between 2005 and 2009

Chemical Component	No. of Products Containing Chemical
Methanol (Methyl alcohol)	342
Isopropanol (Isopropyl alcohol, Propan-2-ol)	274
Crystalline silica - quartz (SiO ₂)	207
Ethylene glycol monobutyl ether (2-butoxyethanol)	126
Ethylene glycol (1,2-ethanediol)	119
Hydrotreated light petroleum distillates	89
Sodium hydroxide (Caustic soda)	80

Appendix 4

Chemical Component	Chemical Category	No. of Products
Methanol (Methyl alcohol)	HAP	342
Ethylene glycol (1,2-ethanediol)	HAP	119
Diesel ¹⁹	Carcinogen, SDWA, HAP	51
Naphthalene	Carcinogen, HAP	44
Xylene	SDWA, HAP	44
Hydrogen chloride (Hydrochloric acid)	HAP	42
Toluene	SDWA, HAP	29
Ethylbenzene	SDWA, HAP	28
Diethanolamine (2,2-iminodiethanol)	HAP	14
Formaldehyde	Carcinogen, HAP	12
Sulfuric acid	Carcinogen	9
Thiourea	Carcinogen	9
Benzyl chloride	Carcinogen, HAP	8
Cumene	HAP	6
Nitrotriacetic acid	Carcinogen	6
Dimethyl formamide	HAP	5
Phenol	HAP	5
Benzene	Carcinogen, SDWA, HAP	3
Di (2-ethylhexyl) phthalate	Carcinogen, SDWA, HAP	3
Acrylamide	Carcinogen, SDWA, HAP	2
Hydrogen fluoride (Hydrofluoric acid)	HAP	2
Phthalic anhydride	HAP	2
Acetaldehyde	Carcinogen, HAP	1
Acetophenone	HAP	1
Copper	SDWA	1
Ethylene oxide	Carcinogen, HAP	1
Lead	Carcinogen, SDWA, HAP	1
Propylene oxide	Carcinogen, HAP	1
p-Xylene	HAP	1
Number of Products Containing a Component of Concern		652

Appendix 5

Table 7-4. Process Wastewater at Petroleum Refineries

Process	Wastewater Description (Possible Pollutants)	Wastewater Flow Rate (gallon/barrel of crude petroleum)	Percentage of Total Wastewater Flow Rate
Distillation	Sour water (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, and phenol)	26.0	44%
Fluid catalytic cracking	Sour water (hydrogen sulfide, ammonia, suspended solids, oil, phenols, and cyanides)	15.0	26%
Catalytic reforming	Sour water (hydrogen sulfide, ammonia, suspended solids, mercaptans, oil)	6.0	10%
Alkylation	Spent potassium hydroxide stream (hydrofluoric acid)	2.6	4%
Crude desalting	Desalting wastewater (salts, metals, solids, hydrogen sulfide, ammonia, and phenol)	2.1	4%
Thermal cracking/Visbreaking	Sour water (hydrogen sulfide, ammonia, suspended solids, dissolved solids, and phenol)	2.0	3%
Catalytic hydrocracking	Sour water (hydrogen sulfide, ammonia, and suspended solids)	2.0	3%
Coking ²	Sour water (hydrogen sulfide, ammonia, and suspended solids)	1.0	2%
Isomerization	Sour water (hydrogen sulfide and ammonia) and caustic wash water (calcium chloride or other chloride salts)	1.0	2%
Additive production: ethers manufacture	Pretreatment wash water (nitrogen contaminants)	<1.0	
Catalytic hydrotreating	Sour water (hydrogen sulfide, ammonia, suspended solids, and phenol)	1.0	2%
Chemical treating: sweetening/Merox process			
Sulfur removal/Claus process	Sour water (hydrogen sulfide and ammonia)	<1.0	
Lubricating oil manufacture	Steam stripping wastewater (oil and solvents) and solvent recovery wastewater (oil and propane)	<1.0	
TOTAL		58.7	100%

Appendix 6

**Table 7-8. Wastewater Treatment Operations Reported By Petroleum Refineries,
TRI Reporting Year 2000**

Wastewater Treatment Technology	Number of Refineries Reporting Use	
	Direct ¹ (93 refineries)	Indirect ¹ (18 refineries)
Steam stripping - in-process treatment that removes ammonia and mercaptans from sour waters.	30	6
API separator - operated for oil recovery. Considered process step. Separator effluent is the influent to the end-of-pipe wastewater treatment (count is for P15 oil skimming).	86	23
Dissolved air flotation - removes oils and particulate material prior to biological treatment. DAF float is a listed hazardous waste.	66	17
Biological treatment - most refineries use aerobic biological treatment (activated sludge or aerated basins) to reduce wastewater organic carbon (BOD and COD) load. Biological treatment can also remove phenolic compounds.	100 ¹	9
Sedimentation - always follows activated sludge basins. Separate clarification might also follow aerated basins (count is for P11 settling/clarification).	78	13
Polishing - sand, dual media, or multimedia filtration removes fine particulate (count is for P12 filtration).	33	6
Activated carbon adsorption - removes soluble organic material and some metals.	14	1

Bibliography

- “Chemical Use in Hydraulic Fracturing.” *FracFocus*. Chemical Disclosure Registry, 2012. Web. 26 Sep. 2012.
- “Chemicals Used in Hydraulic Fracturing.” United States. Congress. House of Representatives. Committee on Energy and Commerce and Minority Staff. April 2011. Print.
- "CleanWave Frac Flowback and Produced Water Treatment." *Halliburton*. 2012. Web. <<http://www.halliburton.com/ps/Default.aspx?navid=2427&pageid=4975>>.
- "Definition of Deep Well Injection ." *Enviro News and Business* . Web. <http://www.enviro-news.com/glossary/deep_well_injection.html>.
- Ehrenberg, Rachel . "The Facts Behind the FRACK." *Science News*. 182.5 (2012): 20-25. Print.
- "Encyclopedic Entry: Natural Gas." *National Geographic*. National Geographic Society, Web. <http://education.nationalgeographic.com/education/encyclopedia/natural-gas/?ar_a=1>.
- “Energy-Water Nexus: Information on the quantity, quality, and management of water produced during oil and gas production.” United States. House of Representatives. Washington: GAO, 2012. Print.
- “Fact Sheet- Bioremediation.” *Drilling Waste Management Information System*. Argonne National Laboratory. Web. 25 Sep. 2012.
- Gardner, Timothy. "Dimock, PA Water Deemed Safe By EPA." *Reuters* [Washington] 11 May 2012. Print. <http://www.huffingtonpost.com/2012/05/11/dimock-pa-water-safe-epa_n_1510035.html>.

"GreenFrac Program." *Hydraulic Fracturing Facts* . Chesapeake Energy. Web.

<<http://www.hydraulicfracturing.com/Green-Frac/Pages/information.aspx>>.

Guerra, Kaite et al. *Oil and Gas Produced Water Management and Beneficial Use in the Western United States*. U.S. Department of the Interior. Sep. 2011. Web. 27 Sep. 2012.

"How Does A Drill Bit Work?" *RigZone*. 2012. Web.

<http://www.rigzone.com/training/insight.asp?insight_id=294&c_id=24>.

"Innovative Solutions." *Ecosphere Technologies*. 2012. Web.

<<http://www.ecospheretech.com/technology>>.

McCurdy, Rick. "Underground Injection Wells For Produced Water Disposal."

Chesapeake Energy . Chesapeake Energy Corporation. Web.

<http://www.epa.gov/hfstudy/21_McCurdy_-_UIC_Disposal_508.pdf>.

Montgomery, Carl T. and Michael B. Smith. "Hydraulic Fracturing: History of and Enduring Technology." *NSI Technologies*. December 2010. Web. 27 Sep. 2012.

"Natural Gas Extraction- Hydraulic Fracturing." *Environmental Protection Agency*. 2 Oct. 2012. Web. <<http://www.epa.gov/hydraulicfracture/#wwrecycling>>.

New York State Department of Environmental Conservation. "Natural Gas Development Activities and High-Volume Hydraulic Fracturing." 2011. Print.

Northup, James. "Hydrofracking is literally a 'dirty bomb', says former insider." *Sierra Club*. 2009. Web. <http://newyork.sierraclub.org/SA/Vol40/Frackspllosion.htm>

"Oil & Gas Flowback and Produced Water Treatment." *MIOX On Demand Chemistry*. Web. <<http://www.miox.com/applications/Oil-and-Gas.aspx>>.

“Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water.” United States. Environmental Protection Agency. Washington, DC: 2011. Print.

"Produced Water Facts." *Produced Water Society* . Web.

<http://producedwatersociety.com/index.php/produced_water_facts/>.

Sas, Andrea. "New Frac Water Recycling Plant to Significantly Reduce Truck Miles on Pennsylvania Roads." *Altela: Treating Water Naturally* . 13 Jun. 2012. Web.

<<http://www.altelainc.com/applications/detail/press-releases/>>.

Schramm, Erich. 2011. *What is flowback, and how does it differ from produced water?* Institute for Energy and Environmental Research of Northeastern Pennsylvania Clearinghouse. < <http://energy.wilkes.edu/pages/205.asp>>.

"Siemens to treat wastewater from hydrofracking." *Greenbang*. Web.

<http://www.greenbang.com/siemens-to-treat-wastewater-from-hydrofracking_16834.html >.

"Squeeze Cementing Overview." *Halliburton*. Web.

<<http://www.halliburton.com/ps/default.aspx?navid=2203&pageid=4690&prodgrid=PRG::L7YY7KKG4>>.

“Technical Support Document for the 2004 Effluent Guidelines Program Plan.” United States. Environmental Protection Agency. Washington, DC: 2004. Print.

"Technology: AltelaRain 750." *Clarion Altela Environmental Services*. 2012. Web.

<<http://caeswater.com/technology/>>.

"Thermal Remediation." *Environmental Protection Agency*. 15 Aug. 2012. Web.

<<http://www.epa.gov/ada/gw/thermal.html> >.

Veil, John A. *Thermal Distillation Technology for Management of Produced Water and*

Frac Flowback Water. Water Technology Brief #2008-1. May 13, 2008.

“What Chemicals Are Used.” *FracFocus*. Chemical Disclosure Registry, 2012.

Web. 26 Sep. 2012.

“What’s the Hydro-Fracking Rush?.” *Citizens Campaign*. Web. 26 Sep. 2012.

“Why Chemicals Are Used.” *FracFocus*. Chemical Disclosure Registry, 2012.

Web. 26 Sep. 2012.