The Hydrologic Issues Associated with Shale Gas Extraction by Hydraulic Fracturing in the Marcellus Shale

By Natalee C. Pei

Advised by Professor Brian J. Skinner
Reviewed by Professor Michael L. Oristaglio

Fall 2012

A Senior Essay presented to the faculty of the Department of Geology and Geophysics, Yale University, in partial fulfillment of the Bachelor's Degree.

Abstract

The shale gas boom in the Marcellus region has given rise to substantial academic inquiry into the hydrologic issues associated with the water-intensive extraction process, hydraulic fracturing. During extraction, well operators encounter water-related challenges in five major capacities—water acquisition, chemical mixing, well injection, flowback, and wastewater treatment/disposal. On the acquisition end, hydraulic fracturing poses a risk to vulnerable watersheds, though this is relatively minor in the water-rich Marcellus area. The largest water-related challenges arise during the latter four phases wherein water contamination complicates efforts to contain, reuse, treat, and/or dispose of the water. During chemical mixing, toxic additives make the water a contamination hazard due to potential fluid leakage and migration. After well injection and flowback, further contamination by the downhole Marcellus environment makes the water difficult to reuse as fracturing fluid. The inability to reuse flowback water forces operators to dispose of wastewater, typically at deep water injection sites in Ohio. However, with rising disposal costs and environmental risks like injection-induced seismicity, drilling companies are looking for innovative solutions to the wastewater problem. In all of these phases, the risks and potential solutions are incompletely characterized, and research is ongoing. This paper attempts to synthesize the literature to date and to highlight areas in need of further research.

Introduction

With the meteoric rise of shale gas extraction in the United States, hydraulic fracturing is set to substantially alter the nation's energy landscape. The largest producing domestic shale gas formation, the Marcellus shale, contains an estimated ultimate recovery of 50 trillion cubic feet of natural gas (Engelder & Lash 2008), the energy equivalent of roughly 8.6 billion barrels of oil. Other estimates of total recoverable reserves range from 30-270 trillion cubic feet (Lee et al. 2011), between 5.2 and 46 barrels of oil equivalent. This enormous resource, though long known as a vast reservoir of natural gas, has only recently become economically feasible to extract. But already, to many informed observers, there is no question that shale gas will soon supplant oil as the dominant fuel in U.S. primary energy consumption.

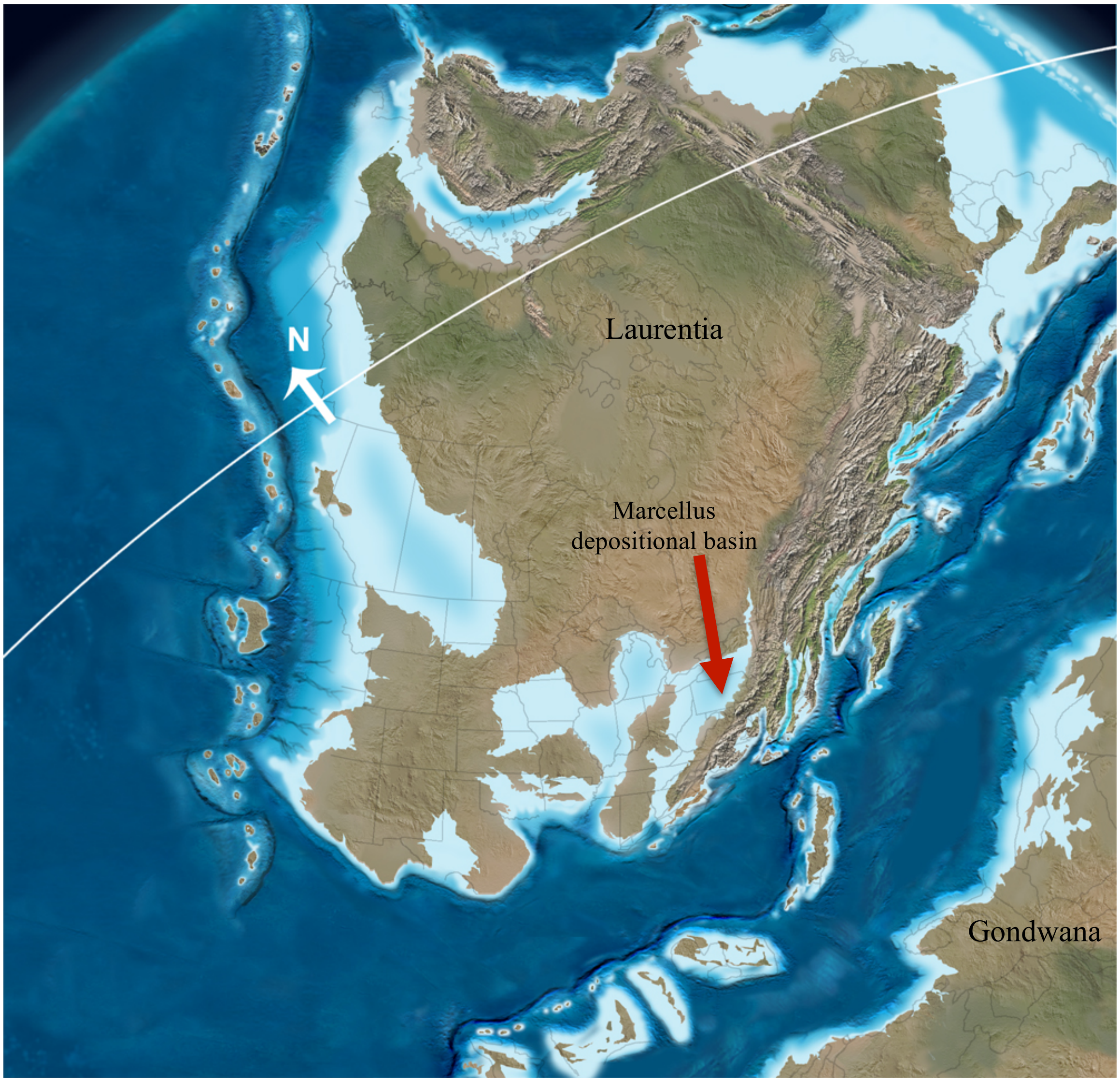
Because of the shear size of the resource and the technological advantages of North American drillers, the United States and Canada so far dominate the world in shale gas production, although China is making significant moves to ramp up production (Zhu 2012). This has profound implications for American energy independence. As independence from Middle Eastern oil becomes increasingly critical for national security, natural gas has already transformed the geopolitical landscape (Medlock et al. 2011). Politics aside, natural gas may also substantially influence our greenhouse gas emissions. Though it remains a contested issue, the prevailing scientific opinion credits natural gas as having a carbon to energy ratio of half that of coal. With the alleged potential to ameliorate two of the largest energy issues facing the United States today—climate change and energy independence—understanding the hydrologic issues associated with this water-intensive technology is paramount.

The Marcellus Formation

The Marcellus shale was deposited during the Middle Devonian period roughly 380 million years ago. The shale-forming sediments settled in the foreland basin of the Acadian Mountains (see Figure 1) where the anoxic shallow sea environment trapped organic material—mostly marine plankton—in the formation. Around 300 million years ago, due to burial and rise in temperature, the formation reached the oil window. As oil and gas formed, pressure in the pores increased causing natural fractures to open. The intense stress field caused by the concomitant collision of Laurentia and Gondwana caused these fractures, called J_1 joints, to propagate along what was then the west/northwest to east/southeast axis. Because of North America's counter-clockwise rotation from its Devonian position to its present-day position, these fractures now run east/northeast to west/southwest (Engelder & Lash 2008). Today's hydraulic fracturing operations take advantage of these J_1 joints as the natural axis along which stimulated fractures will propagate. This allows drillers to align their wellbore perpendicular to the stress field, thereby maximizing the total surface area of the fracture network.

The Marcellus shale is an impermeable formation meaning that oil and gas cannot readily migrate through the limited permeability and up to the surface. However, this also means that unlike conventional gas reservoirs that result from the geologic accident of an anticline or similar trapping structure, most of the original gas remains trapped in the Marcellus formation. This helps explain the enormous size and geographic footprint of the resource. We are no longer harvesting just the pockets of gas that leak out of source rock and into permeable rock traps above, rather, we are now accessing the source rock itself.

Figure 1: North America ca. 380mya (Blakey 2006)



Hydraulic Fracturing

The advent of shale gas extraction in the Marcellus shale required the novel combination of two old technologies—horizontal drilling and hydraulic fracturing (fracking). Employed since the 1960s, hydraulic fracturing uses fluid injected at high pressures to fracture otherwise impermeable rock. This allows natural gas to flow freely through the newly formed fractures from the high pressure downhole environment to the surface. Proppants (usually sand) are used to hold open the fractures after the incompressible fluid (usually water) is removed. However, fracking requires the addition of gels to keep the proppant suspended in the frack fluid, and until the early 2000s, these gels prevented drillers from achieving the flow rates necessary in order to fracture the shale along a horizontal wellbore. The breakthrough came when the addition of chemical friction reducers allowed the frack fluid to reach the necessary flow rates of 80-100 barrels/min (URS 2011). This drag-reduced frack fluid, also known as slickwater, was pioneered in the Barnett formation of North Texas. In 2003, Range Resources drilled the first shale gas well in the Marcellus and began producing natural gas in 2005 (Harper 2008). Since then, shale gas extraction in the Marcellus region has taken off.

This dramatic uptick in fracking operations has triggered a flurry of literature discussing the environmental footprint of hydraulic fracturing for shale gas, particularly in the Marcellus where extraction has reached a fever pitch. However, because of the newness of shale gas extraction, the literature I draw on in my depiction of the hydrologic issues behind fracking relies heavily on recently published journal articles as well as industry sources. For this reason, many of the issues, though they are now becoming clearer with increasing research, are still poorly resolved. Because of the politicization and polarization of fracking, it is more important than ever to sift through the evidence and attempt to reach tentative conclusions.

The most controversial aspect of shale gas extraction is its environmental impact. Environmental concerns fall into two general categories—greenhouse gas emissions and water issues. This paper focuses on the hydrologic aspect of shale gas extraction. The influence of fracking on local water sources gained national notoriety as a result of the

2010 documentary, *Gasland*, which showcases instances of methane contamination of drinking water supplies. Whether or not these contamination events were caused by faulty well casings or by the natural migration of methane is a fervently contested issue (Osborn et al. 2011, Saba & Orzechowski 2011). Some argue that the risk is particularly high in Pennsylvania and other areas that have been heavily drilled in the past because old wells may provide conduits for methane released by the frack (Hagstrom 2012). What we know for sure is that hydraulic fracturing, as the name implies, is an extremely water-intensive process that leaves behind substantial quantities of heavily polluted wastewater. Many question marks remain as to how we can and should deal with this wastewater, but the geology and hydrology of the Marcellus region can help us start to unravel these questions.

Water Use

A typical hydraulic fracturing operation in the Marcellus uses 7,000 to 18,000 cubic meters of fluid, or roughly 2 to 5 million gallons, to complete the well (Gregory et al. 2011). Combined with the water required to maintain downhole pressures, cool the drillbit, and remove drill cuttings, most wells require at least 3 million gallons of water. This scale of water consumption is a huge hurdle in more arid places like Texas's Barnett shale where fracking accounts for 9% of Dallas's total annual water use (Nicot & Scanlon 2012). By contrast, shale gas occupies a minor share of total water use in the water-rich Marcellus area. Assuming 5 million gallons of water per well and peak drilling activity, Arthur (2010) estimated water use in the neighborhood of 650 million barrels per year, which is less than 0.8% of the total annual water use in the Marcellus region. Similarly, Gaudlip & Paugh (2008) estimated that the total daily water use of fracking in the Susquehanna River Basin will reach only 8.4 million gallons, less than 0.06% of the daily water consumption of the power generation industry within the same area.

Because of water's relative abundance in the Marcellus region, the lion's share of frack fluid water—roughly 60-70%—is drawn directly from surface waters (Gaudlip & Paugh 2008). Though fracking as a whole does not put a significant dent in regional water usage, it can prove to be a problem in specific locations at specific times. At times of low flow, local restrictions may be placed on daily withdrawal rates. As a result, some companies pump water into large, on-site impoundments in advance of the frack (see Figure 2). Others have proposed more radical solutions; some raise the possibility of using acid mine drainage as a source of water (Kargbo et al. 2010, Rassenfoss 2011). However, much more research is necessary to determine how pure water must be in order to generate a good frack.

Figure 2: Surface Water Extraction in Pennsylvania (taken by author on 10-25-12)

Further, fracking is a young technology, so it remains to be seen how often wells will need to be "refracked" in order to remain productive (Lee et al. 2011). If it turns out that fractures close up faster than we previously expected, it could substantially increase industry water use projections. There is also some question about the physical footprint of fracking operations in the delicate watersheds that overlay the Marcellus. Some worry that the increase in heavy truck traffic and well pad construction may cause damaging erosion in small watersheds (Soeder & Kappel 2009, Drohan 2011).

Chemical Mixing

Once the necessary water is acquired, it is mixed with a series of frack fluid additives. First, slickwater mixtures use a series of chemical additives in order to keep the wellbore clear of obstructions. Acids, usually hydrochloric or muriatic acid, are used to clear the well of drilling mud so that the frack fluid has clear access to the formation (URS 2011). Biocides are also added in order to prevent the growth of microbial mats and to kill sulfate-reducing bacteria that could produce gaseous contaminants (Ibid.). Because of their toxicity to humans, biocides, even in small concentrations, make frack fluid containment particularly important. Corrosion inhibitors like ammonium bisulfate and methanol are also added to keep the wellbore clear by inhibiting rust formation on the steel well casings and steel tubes (Ibid.). In addition, potassium chloride is used as a clay stabilizer to prevent in situ clays from blocking the well. Other obstruction-preventing additives include an iron control agent, like citric acid, which inhibits the precipitation of iron oxides. Finally, scale inhibitors, such as ethylene glycol and ammonium chloride, prevent the development of $CaCO_3$/$CaSO_4$/$BaSO_4$ scales (Ibid.).

Aside from blockage prevention, chemical additives are also used to increase the fluid's viscosity allowing higher proppant carriage and to increase flow rates in spite of relatively high viscosities. A guar gum or petroleum distillate is usually used as a gelling agent and potassium hydroxide or a borate salt may be used as a crosslinker (Ibid.) Both of these components increase the fluid's viscosity, and thus, its ability to carry the proppant. However, well operators must raise flow rates in order to achieve high enough pressures and to augment water recovery rates. To this end, peroxydisulfates, friction reducers, and surfactants are added (Ibid.). These chemical additives comprise less than half a percent of the total frack fluid volume, but even at these low concentrations, many components are toxic.

Produced Water

After the frack fluid is injected and the rock fractured, between 10 and 50 percent of the water returns to the surface (Gregory et al. 2011, NRC 2012). The mechanisms by which the formation sequesters the remaining 50 to 90% of injected fluid remains poorly characterized, although drilling companies and geologists are working to tackle this question. The process by which frack fluid returns to the surface is known as “flowback” and the water is commonly referred to as “produced water.” Flowback occurs during the first 2 to 3 weeks after the frack, and 60% of total flowback tends to occur within the first four days (URS 2011). From the well operator’s perspective, the goal during flowback is to minimize proppant return to the surface while maximizing fluid return.

Produced water contains more than just the chemical additives sent down with the original frack fluid; it also contains dissolved solids from the shale environment that are carried back to the surface. The total dissolved solids (TDS) in flowback water typically consist of 1) soluble salts; 2) radionuclides like radium, 3) metal ions such as iron, barium, calcium, strontium, and arsenic; 4) microbes that produce scales and gas; and 5) anions such as carbonate, bicarbonate, sulfate, and chloride (Blauch 2010, Balaba 2012). Produced water TDS can reach levels five times higher than seawater (Gregory et al. 2011, Haluszczak 2012) with concentrations ranging from 1,470 to 402,000 mg/L (Gaudlip & Paugh 2008, Rowan 2011). Though these levels are characteristically high, TDS concentrations vary from well to well and over time. Early in the flowback process, TDS levels are so low that some of the produced waters can be directly reused as frack fluid (Gaudlip & Paugh 2008, Rowan 2011).

High TDS levels are typical of Ordovician/Devonian formations drilled for oil and gas. In the case of the Marcellus shale, the formation's chemistry arose from evaporatively concentrated seawater. The sedimentary environment included sulfate-reducing bacteria that produced hydrogen sulfide (Haluszczak 2012). Then, during diagenesis, the formation underwent dolomitization as magnesium replaced calcium due to freshwater mixing. The formation's depositional history gives rise to flowback waters with low pH values and high TDS. However, flowback TDS concentration depends not only on the Marcellus sedimentary environment, but also on the relative solubility of constituent solids.

For example, although thorium and uranium exist in a relatively concentrated state (Adams & Weaver 1958), they are poorly soluble compared to their daughter isotope, radium, so they tend not to flow back to the surface (Rowan 2011). By contrast, Marcellus flowback concentrations of radium are consistently higher than comparable non-Marcellus samples (Rowan 2011). Haluszczak (2012) observed levels of radium up to 6,540 pCi/L, or roughly 1500 times the maximum contaminant level for drinking water. This type of pollution originating from the native formation is known as technologically advanced naturally occurring radioactive material (TENORM). TENORM in produced waters far exceed drinking water standards and can reach levels 267 times the safe disposal limit (Kargbo et al. 2010, URS 2011). Because radioactive waste is particularly difficult to treat, the radioactivity associated with flowback water generates a host of disposal problems.

Other solutes also far exceed drinking water standards. In Haluszczak's (2012) analysis of flowback water from 34 shale gas wells in Pennsylvania, the maximum concentration of chloride ions observed was 151,000 mg/L while normal freshwater concentrations would contain only a few tens of mg/L. Similarly, while standards require only 2 mg/L barium, observed concentrations in flowback water ranged in the thousands of mg/L (Haluszczak 2012). These high concentrations give rise to substantial concern about surface contamination by leaked flowback water. The addition of as little as 0.1% produced water as a percentage of total surface water volume could exceed drinking water standards for several dissolved solids (Kight 2011). So even though fracking operations theoretically have no pollutant effect on local watersheds when all the proper safeguards are in place, the margin for error is low.

Flowback Leakage

Because of the low threshold at which produced water leakages can cause significant damage, the mechanisms by which leaks occur and the methods of testing such leaks are important areas of inquiry. There is not yet a sound consensus among geologists whether or not contamination can occur via fluid migration upward from the fracture site. Evidence on both sides remains incomplete. A recent article published by Warner et al. (2012) matches strontium isotope signatures typical of Marcellus brines with some surface aquifers in order to establish a geologic link between the two. However, as Engelder argues, Warner et al. offer no time scale for this fluid migration making the risk of pollution on anthropogenic time scales a hazy conclusion (personal correspondence with Terry Engelder). And if such migration is occurring on relevant time scales, why would denser brines leak out of the formation while most of the natural gas remained in situ? Similarly, Warner et al. do not explain the contradiction between their data and extensive well log data showing a lack of brines present in the Marcellus formation (Ibid.). Another piece of contradictory evidence lies in the work of Chapman (2012) who uses strontium isotope ratios to establish that flowback water signatures closely track Marcellus signatures indicating that the frack fluid does not come into contact with underlying or overlying units. Clearly, more analysis is needed to explain the apparent upward migration of Marcellus brine into surface aquifers.

Though vertical contamination from the Marcellus to surface aquifers is still subject to heated debate, contamination via other mechanisms is not uncommon. Several contamination incidents have already been documented. The most likely avenues for flowback water to cause local pollution occur at or near the surface. In 2008, a wastewater facility treating acid mine drainage as well as Marcellus flowback water caused a spike in TDS levels, specifically sulfate, chloride, and bromide, in the Monongahela River (PA DEP 2009). This event is likely attributable to produced water TDS levels that exceeded the treatment facility's capacity to remediate. Similar releases were documented in the Susquehanna River Basin (Chapman 2012). In 2010, the Pennsylvania Department of Environmental Protection responded to these contamination incidents by issuing regulations that limit TDS levels in the effluent water of wastewater treatment plants (Abdalla 2011). However, achieving this 500 mg/L TDS cap mandated by the state is not technically feasible at any of Pennsylvania's existing industrial wastewater treatment facilities, so in practice, this regulation precludes the treatment of produced water by traditional wastewater treatment plants (Blauch 2009).

In spite of these new regulations, there are still important avenues for contamination. After a frack, many operations will store flowback water in impoundments or 21,000 gallon semi-truck tanks (URS 2010). Though these containment methods involve significant precautions including state-mandated leak detection, it remains difficult to determine when fracking is the root cause behind local water pollution. Barium, chlorine, and carbon are all bad indicators for leakage because there is too much alternate causality (Chapman 2012). In the Marcellus region, fly ash impoundments, abandoned oil wells, acid mine drainage, road salt, and other industrial sources are all potential culprits for contamination (Ibid.). In the future, resolving the confusion between these sources will require more rigorous monitoring techniques such as: 1) drawing comparisons with pre-frack baselines, and 2) using strontium isotope ratios which are relatively unique to each potential pollution source point (URS 2011, Chapman 2012).

Deep Water Injection

The huge amount of wastewater produced by hydraulic fracturing in the Marcellus poses a serious challenge because of the hazardous solutes found in flowback. As mentioned above, regulations on TDS in the effluent water of treatment facilities are tightening, and this has made treatment at local wastewater plants impractical. Consequently, most well operators in the Marcellus are turning to deep water injection sites for Class II (i.e. non-hazardous) waste where the water is pumped down a reinforced well shaft and into a porous target formation that is sealed off by impermeable layers. There are few such injection sites available in the state of Pennsylvania where the majority of Marcellus fracking occurs, so produced water is often trucked to Ohio where injection sites are relatively abundant (Gregory et al. 2011, Gaudlip & Paugh 2008). Though this has already become the modus operandi in the Marcellus region, the total costs of transportation from drill site to injection site and then for use of the actual injection site are high—roughly $5.50/barrel and rising (Rassenfoss 2011).

Cost is not the only concern with the deep water injection solution. Once injected, wastewater can lubricate existing fault lines by increasing ambient pore pressure. The concomitant drop in shear friction can cause earthquakes, known as injection-induced seismicity (Horton 2012). This phenomenon is by no means new. The first documented case of injection-induced seismicity took place during the 1960s at the Rocky Mountain Arsenal outside of Denver, Colorado. After wastewater had been injected into moderately impermeable basement rock, three earthquakes ensued with magnitudes ranging from 5.0 to 5.5 (Nicholson & Wesson 1990). In this and subsequent cases of injection-induced seismicity, the causality can be difficult to prove, but several pieces of evidence corroborate the link between injection and earthquake. Strong geographic ties exist between earthquake epicenters and fluid injection zones. These correlations are further bolstered by theoretical calculations which confirm that measured injection pressures exceeded the hypothetical limit for frictional sliding given the assumed levels of ambient stress in the region (Nicholson & Wesson, 1990).

This causative relationship, though well-documented in other contexts, has only recently been observed during the injection of shale gas produced waters. On February 27, 2012, an earthquake of magnitude 4.7 hit a flowback injection site near Guy, Arkansas (Zoback 2012). This along with other incidents in Texas and Ohio created cause for concern (National Research Council 2012). As Horton (2012) observed, although induced earthquakes tend to be small, the 2012 earthquake in Arkansas was not far from a nuclear power cooling tower. In light of the 2011 Fukushima disaster, the proximity of these seismic disturbances is alarming. Some argue that the concern is overstated because in the more than fifty year history of high pressure fluid injection in the United States, triggered earthquakes have yet to cause any fatalities or substantial property damage (Zoback 2012). But with the exponential increase in fracking activity, this issue deserves re-examination.

Treatment Alternatives

Against the specter of injection-induced seismicity and the rising costs of transportation and injection at disposal sites, drilling companies are racing to find affordable ways to deal with the briny, radioactive byproduct of fracking. In the nation's second most intensely fracked formation, the Barnett Shale, operators have captured the region's abundant land and solar energy to evaporate produced waters thereby concentrating the solid waste. Unfortunately, this technique does not work in the Marcellus region where it is neither dry nor sunny (Soeder & Kappel 2009). Some raise the possibility of a similar approach more suitable to the Northeast climate, an approach known as freeze-thaw evaporation. Though it has already been deployed with some success, high land use and the unpredictability of weather patterns make freeze-thaw evaporation a less than ideal choice (Gaudlip & Paugh 2008). However, evaporation and injection are not the only ways to deal with waste.

There are a whole slew of different on-site treatment technologies ranging in cost from approximately $3.50-7.50 per barrel of produced water. Each mode of treatment has its own set of advantages and disadvantages (Gaudlip & Paugh 2008, URS 2011, Gregory et al. 2011). The first and most basic option is filtration. Filtration is relatively inexpensive and does not require large amounts of energy. Unfortunately, this method is not particularly effective at removing TDS. The same can be said of ion exchange, which achieves slightly lower levels of TDS but requires slightly higher energy consumption. On the other end of the spectrum, electro dialysis and thermal distillation are extremely energy intensive, but they are highly effective at reducing TDS, and their clean water recovery rates range from 60-85%. To some extent, this helps offset the cost of treatment by reducing the cost of water acquisition. Toward the middle of the spectrum, reverse osmosis is moderately expensive and has clean water recovery rates in the neighborhood of 30-50%, but maintenance costs are high because the chemistry of the flowback water makes the system prone to scaling and micobiological fouling of the osmotic barrier.

An additional understated drawback of on-site treatment, particularly with the more energy-intensive technologies, is the risk of inadvertently concentrating radioactive material in the process of extracting clean water (URS 2011). This raises a new set of problems on the disposal end, since certain levels of radiation carry more rigorous, and therefore expensive, disposal requirements. Typically these classes of waste must be buried or injected into subterranean disposal sites. Although this substantially reduces the volume of waste, the cost of transportation to the disposal location is not eliminated. For these reasons, none of these treatment options have yet been able to displace deep water injection as the preferred method of disposal. But new methods and experimental permutations of existing technologies leave ample room for new developments on this frontier.

<u>Recycling</u>

The last and perhaps most compelling alternative in dealing with flowback water is the prospect of reusing produced water for future fracks. This paradigm has several obvious advantages—reducing disposal costs while simultaneously eliminating many of the water sourcing issues and associated costs. But again, even in the early stages of this experimental approach, significant challenges arise. The primary hurdle lies in the negative and inhibitory interactions between the TDS from the formation and the chemical additives that are integral to the effectiveness of the frack.

The high TDS characteristic of produced waters has been shown to inhibit the efficacy of the friction reducers that are so critical to achieving the flow rates necessary for fractures to propagate (Shah &Vyas 2010). Previously, the only available solution was treating the flowback water prior to reuse which carries all the same downsides as mentioned in the previous section. However, the recent advent and use of a special salt-resistant friction reducer by Cabot Oil & Gas could be a game-changer on this front (Blauch 2010, Papso et al. 2010). The introduction of TOC-tolerant frack additives may also decrease the future dissolution of these ions *in situ* since the recycled frack fluid would already contain relatively high concentrations of these ions.

Salinity aside, many of the ions transported to the surface by the flowback can also cause scaling and an increase in anaerobic microbial activity (URS 2011). The high concentrations of barium, calcium, carbonate, iron, magnesium, strontium, and sulfate cause scaling within the fractures, perforations, piping, and surface equipment (Kargbo et al. 2010). Augmenting the amount of scale inhibitors is generally an effective means of counteracting most of these scale-forming ions. However, iron scaling is uniquely difficult to control since iron scale inhibitors traditionally lower pH which reduces the effectiveness of friction reducers (Blauch 2010). But again, Cabot Oil & Gas seems to have overcome this issue with the addition of a newly patented neutral pH iron control agent (Papso et al. 2010). These innovations have led to the first frack operation using 100% reused frack fluid. According to preliminary results from Cabot, this frack was highly effective, and in fact, exceeded the performance of ordinary fracks in comparable geological settings. Though exciting, these results are not yet widespread enough to prove that recycled frack water will overtake virgin frack fluid as the primary fracking agent.

One even more radical solution to the water problem is the proposition of replacing water altogether as a fracking agent. There is good reason to think that liquefied carbon dioxide and liquefied petroleum gels could equally serve as replacements for water as a frack fluid (URS 2011, Kargbo et al. 2010). In demonstrations so far, liquefied CO_2 and liquefied petroleum gels have not required as many chemical additives as water in order to achieve an effective frack. CO_2 is particularly attractive since it would simply vaporize, leaving the proppant behind. Liquefied petroleum gel had similar advantages since its high viscosity makes it an excellent proppant carrier. Like CO_2, liquefied petroleum gel is not difficult to separate from the natural gas product (URS 2010). The potential for alternative fracturing agents is an exciting prospect, though nothing has been proven yet on a commercial scale.

Conclusion

Since the advent of shale gas extraction by hydraulic fracturing in the early 2000s, research into the hydrologic issues caused by this water-intensive technique has elucidated many of the risks associated with fracking. First, fracking has a tangible impact on watersheds with water usage rates averaging between 3 and 5 million gallons of water per well. In the Marcellus, this effect is negligible on a regional level, but may be an issue in particularly sensitive local watersheds. Second, shale gas extraction mixes toxic chemical additives with the water in order to increase the efficiency of the frack. Once mixed with chemical enhancers, the frack fluid becomes a contamination hazard. Potential avenues for contamination are well documented at or near the surface, though some disputed evidence exists for fluid migration from the fracture site up to surface aquifers. Third, the flowback water after well injection contains a range of dissolved solids originating from the Marcellus shale. These produced waters characteristically show high TDS and radioactivity because of the chemical environment present in the Marcellus formation. High TDS inhibits several of the chemical additives used in virgin frack fluid thus precluding reuse of flowback water for future fracks. High TDS and radioactivity also limit the available treatment and disposal options. Fourth, wastewater disposal at deep water injection sites, the most common method of flowback disposal, carries the risk of injection-induced seismicity. So far these induced seismic events have been too small to cause substantial property damage or loss of life, but the problem is considerable if injection occurs areas with already weak faults or high-risk structures like nuclear power plants.

In spite of extensive and ongoing research into the hydrologic issues associated with hydraulic fracturing, many questions remain. More research is needed in order to characterize the potential avenues for contamination. In particular, more research will be necessary to determine whether or not geologic pathways exist for frack fluid to migrate up from the horizontal wellbore and into surface aquifers. Similarly, we do not yet have sufficient data or monitoring equipment in place in order to differentiate between various causes of water pollution in the Marcellus region. This makes it difficult to determine when fracking is in fact to blame for contamination events. Further, it remains to be seen whether or not flowback water can be reused on a widespread scale. The addition of TDS tolerant friction reducers and neutral pH iron scale inhibitors has worked in one isolated test frack, but it is far from commercially viable. Lastly, nascent research into alternative fracking agents like LPG and liquefied CO_2 could virtually eliminate the hydrologic issues associated with hydraulic fracturing. The lack of a mature literature base combined with the complexity of the hydrologic issues associated with shale gas extraction leaves a lot of unanswered questions, but the wealth of new research can and should guide the way we approach hydraulic fracturing in the Marcellus shale.

Bibliography

Abdalla, Charles W., J.R. Drohan, K.S. Blunk, J. Edson. (2011). "Marcellus Shale Wastewater Issues in Pennsylvania—Curent and Emerging Treatment and Disposal Technologies." *Pennsylvania State University Extension.*

Adams, John A.S., C.E. Weaver. (1958) "Thorium-to-uranium ratios as indicators of sedimentary processes—example of concept of geochemical facies." *AAPG Bulletin*. 42(2):387–430.

Arthur, J.D., B. Bohm, B.J. Coughlin, M. Layne, D. Cornue. (2009). "Evaluating the environmental implications of hydraulic fracturing in shale gas reservoirs." *SPE Americas E&P Environmental and Safety Conference*, March 2009, 23-25.

Arthur, J.D., M Uretsky, P. Wilson. (2010). "Water Resources and Use for Hydraulic Fracturing in the Marcellus Shale Region." ALL Consulting, LLC.

Balaba, Ronald S., R.B. Smart. (2012) "Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater." *Chemosphere*. 89(11):1437‑1442.

Bernstein, Paula, T.C. Kinnaman, M. Wu. (2012). "Estimating Willingness to Pay for River Amenities and Safety Measures Associated with Shale Gas Extraction." *Eastern Economic Journal,* 1-17.

Blauch, Matthew, R.R. Myers, T.R. Moore, B.A. Lipinski. (2009). "Marcellus Shale Post-Frac Flowback Waters – Where is All the Salt Coming From and What are the Implications?" *SPE Unconventional Gas Conference*. SPE 125740.

Blauch, Matthew. (2010). "Geochemical fixes boost shale completion efficiency." *World Oil*. July 2010, D121-D124.

Blakey, R.C. (2006). *Paleogeographic Maps Arranged as Time Slices*. http://www2.nau.edu/rcb7/namD385.jpg.

Cathles, Lawrence M. III, L. Brown, M. Taam, A. Hunter. (2012). "A commentary on 'The greenhouse-gas footprint of natural gas in shale formations' by R.W. Howarth, R. Santoro, and Anthony Ingraffea." *Climatic Change,* 113:525-535.

Chapman, Elizabeth C., R.C. Capo, B.W. Stewart, C.S. Kirby, R.W. Hammack, K.T. Schroeder, H.M. Edenborn. (2012). "Geochemical and Strontium Isotope Characterization of Produced Waters from Marcellus Shale Natural Gas Extraction." *Environmental Science & Technology.* 46:3545-3553.

Davies, Richard J. (2011). “Methane contamination of drinking water caused by hydraulic fracturing remains unproven.” *Proceedings of the National Academy of Sciences,* 108(43):E871.

Dresel, P. Evan, A.W. Rose. (2010). “Chemistry and origin of oil and gas well brines in western Pennsylvania.” *Pennsylvania Geological Survey*. 4th series. Open-File Report OFOG 10–01.0.

Drohan, P.J., M. Brittingham, J. Bishop, K. Yoder. (2012). “Early Trends in Landcover Change and Forest Fragmentation Due to Shale-Gas Development in Pennsylvania: A Potential Outcome for the Northcentral Appalachians.” *Environmental Management,* 49:1061-1075.

Edwards, Pamela J., L.L. Tracy, W.K. Wilson. (2010). “Chloride Concentration Gradients in Tank-Stored Hydraulic Fracturing Fluids Following Flowback.” United States Department of Agriculture, Forest Service. Research Paper NRS-14.

Engelder, Terry, G.G. Lash. (2008). “Marcellus shale play’s vast resource potential creating stir in Appalachia.” *American Oil and Gas Reporter*, 51(6):76-87.

Engelder, Terry. (2012). Personal correspondence in response to Walter et al.’s “Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania.”

Gaudlip, A.W., L.O. Paugh. (2008). “Marcellus shale water management challenges in Pennsylvania.” *2008 SPE Shale Gas Production Conference*, Forth Worth, TX, SPE 119898.

Gregory, Kelvin B., R.D. Vidic, D.A. Dzombak. (2011). “Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing.” *Elements,* 7:181-186.

Hagstrom, Earl L, J.M. Adams. (2012). “Hydraulic Fracturing: Identifying and Managing the Risks.” *Environmental Claims Journal,* 24(2):93-115.

Haluszczak, Arthur W.R., L.R. Kump. (2012). “Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA.” *Applied Geochemistry.* Accepted Manuscript.

Harper, John A. (2008). “The Marcellus Shale—An Old “New” Gas Reservoir in Pennsylvania.” *Pennsylvania Geology.* 38(1):2-13.

Holland, Austin. (2011). “Examination of Possibly Induced Seismicity from Hydraulic Fracturing in the Eola Field, Garvin County, Oklahoma”. *Oklahoma Geological Survey.* OFI.

Horton, S. (2012). “Disposal of hydrofracking waste fluid by injection into subsurface aquifers triggers earthquake swarm in central Arkansas with potential for damaging earthquake.” *Seismological Research Letters,* 83(2):250-260.

Howarth, Robert W., R. Santoro, A. Ingraffea. (2011). “Methane and the greenhouse-gas footprint of natural gas from shale formations.” *Climatic Change,* 106:679-690.

Howarth, Robert W., R. Santoro, A. Ingraffea. (2012). “Venting and leaking of methane from shale gas development: response to Cathles et al.” *Climatic Change,* 113:537-549.

Jackson, Robert B., S.G. Osborn, A. Vengosh, N.R. Warner (2011). “Reply to Davies: Hydraulic fracturing remains a possible mechanism for observed methane contamination of drinking water.” *Proceedings of the National Academy of Sciences,* 108(43):E872.

Jiang, Mohan, W.M. Griffin, C. Hendrickson, P. Jaramillo, J. VanBriesen, A. Venkatesh. (2011). “Life cycle greenhouse gas emissions of Marcellus shale gas.” *Environmental Research Letters,* 6(3):1-9.

Kargbo, David M., R.G. Wilhelm, D.J. Campbell. (2010). “Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities.” *Environmental Science & Technology,* 44:5679-5684.

Kight, Melody D. (2011). “A Protocol To Characterize Flowback Water Contamination To Shallow Waters From Shale Gas Development.” *Marcellus—Production and Disposal of Produced Water.* Session No. 16.

Lee, Dae Sung, J.D. Herman, D. Elsworth, H.T. Kim, H.S. Lee. (2011). “A Critical Evaluation of Unconventional Gas Recovery from the Marcellus Shale, Northeastern United States.” *Journal of Civil Engineering,* 15(4):679-687.

Medlock, Kenneth B., A.M. Jaffe, P.R. Hartley. (2011). “Shale Gas and U.S. National Security.” *James A. Baker III Institute for Public Policy of Rice University.*

National Research Council. (2012). *Induced Seismicity Potential in Energy Technologies*. Washington, DC: The National Academies Press.

Nicholson, Craig, R.L. Wesson. (1990). “Earthquake Hazard Associated With Deep Well Injection: A Report to the U.S. Environmental Protection Agency.” *U.S. Geological Survey Bulletin.*

Nicot, Jean-Philippe, B.R. Scanlon. (2012). “Water Use for Shale-Gas Production in Texas, U.S.” *Environmental Science & Technology,* 46:3580-3586.

Osborn, Stephen G., A. Vengosh, N.R. Warner, R.B. Jackson. (2011). "Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing." *Proceedings of the National Academy of Sciences,* 108(20):8172-8176.

Osborn, Stephen G., A. Vengosh, N.R. Warner, R.B. Jackson. (2011). "Reply to Saba and Orzechowski and Schon: Methane contamination of drinking water accompanying gas- well drilling and hydraulic fracturing." *Proceedings of the National Academy of Sciences,* 108(37):E665-666.

Papso, John, M. Blauch, D. Grottenthaler. (2010) "Cabot Gas Well Treated With 100% Reused Frac Fluid." *Harts E&P*.

Passey, Q.R., K.M. Bohacs, W.L. Esch, R. Klimentidis, S. Sinha. (2010). "From Oil-Prone Source Rock to Gas-Producing Shale Reservoir – Geologic and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs." *Society of Petroleum Engineers,* 131350:1-29.

Pennsylvania Nonpoint Source Management Program FFY2008 Annual Report. (2009) Pennsylvania Department of Environmental Protection, Harrisburg, PA. http://www.epa.gov/reg3wapd/pdf/pdf_nps/nps_annualreports/2008/FY2008_PA-Final-Annual-Report.pdf.

Rassenfoss, Stephen. (2011). "From Flowback to Fracturing: Water Recycling Grows in the Marcellus Shale." *Journal of Petroleum Technology.* July, 2011:48-51.

Ross, Daniel J.K., R. M. Bustin. (2009). "The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs." *Marine and Petroleum Geology,* 26:916-927.

Rowan, E.L., M.A. Engle, C.S. Kirby, T.F. Kraemer. (2011). "Radium Content of Oil- and Gas-Field Produced Waters in the Northern Appalachian Basin (USA): Summary and Discussion of Data." *Scientific Investigations Report 2011–5135.* U.S. Geological Survey.

Saba, Tarek, M. Orzechowski. (2011). "Lack of data to support a relationship between methane contamination of drinking water wells and hydraulic fracturing." *Proceedings of the National Academy of Sciences,* 108(37):E663.

Schon, Samuel C. (2011). "Hydraulic fracturing not responsible for methane migration." *Proceedings of the National Academy of Sciences,* 108(37):E664.

Schrag, Daniel P. (2012). "Is Shale Gas Good for Climate Change?" *Dædalus, the Journal of the American Academy of Arts & Sciences,* 141(2):72-80.

Shah, S.N., A. Vyas. (2011). "Temperature and Salinity Effects on Drag-Reduction Characteristics of Polymers in Coiled Tubing." *Society of Petroleum Engineers*. 26(1):55-66.

Soeder, Daniel J., W.M. Kappel. (2009). "Water Resources and Natural Gas Production from the Marcellus Shale." *U.S. Geological Survey,* Fact Sheet 2009-3032.

Stephenson, Trevor, J.E. Valle, X. Riera-Palou. (2011). "Modeling the Relative GHG Emissions of Conventional and Shale Gas Production." *Environmental Science & Technology,* 45:10757-10764.

Struchtemeyer, Christopher G., M.D. Morrison, M.S. Elshahed. (2012). "A critical assessment of the efficacy of biocides used during the hydraulic fracturing process in shale natural gas wells." *International Biodeterioration & Biodegradation*. 71:15–21.

U.S. Senate. (2011). Committee on Energy and Natural Resources. *First Session To Examine Marcellus Shale Gas Development And Production In West Virginia*. (S. Hrg. 112-223). Washington: Government Printing Office. 74-436 PDF.

U.S. Senate. (2011). Committee on Energy and Natural Resources. Subcommittee on Water and Power. *First Session To Examine Shale Gas Production And Water Resources In The Eastern United States.* (S. Hrg. 112-247). Washington: Government Printing Office. 72-795 PDF.

URS. (2011). Water-Related Issues Associated With Gas Production In The Marcellus Shale. *Water Consulting Services in Support of the Supplemental Generic Environmental Impact Statement for Natural Gas Production.* NYSERDA.

Wang, Jinsheng, D. Ryan, E.J. Anthony. (2011). "Reducing the greenhouse gas footprint of shale gas." *Energy Policy,* 39:8196-8199.

Warner, Nathaniel R., R.B. Jackson, T.H. Darrah, S.G. Osborn, A. Down, K.G. Zhao, A. White, A. Vengosh. (2012). "Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania." *Proceedings of the National Academy of Sciences.* 109(20):11961-11966.

Wrightstone, Gregory. (2009). "Marcellus Shale – Geologic Controls on Production." *Search and Discovery.* Article #10206.

Zhu, J., J. Chen, G. De Blok. (2012). "Drilling and Frac Stimulation Waste Management in Unconventional Gas Projects in Sichuan, China." IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition, 9-11 July 2012, Tianjin, China.

Zhu, Yaping, E. Liu, A. Martinez, M.A. Payne, C.E. Harris. (2011). "Understanding geophysical responses of shale-gas plays." *The Leading Edge,* 30(3): 332-338.

Zoback, Mark D. (2012). "Managing the seismic risk posed by wastewater disposal." *Earth Magazine.* Tuesday, April 17.