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Summary of the Technical Workshop on Wastewater Treatment and Related Modeling

April 18, 2013

Disclaimer

This report was prepared by EPA with assistance from Eastern Research Group, Inc., an EPA contractor, as a general record of discussions during the April 18, 2013, technical workshop on wastewater treatment and related modeling. The workshop was held to inform EPA's *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. The report summarizes the presentations and facilitated discussions on the workshop topics and is not intended to reflect a complete record of all discussions. All statements and opinions expressed represent individual views of the invited participants; there was no attempt to reach consensus on any of the technical issues being discussed. Except as noted, none of the statements in the report represent analyses or positions of EPA.

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Meeting Agenda

Technical Workshop on Wastewater Treatment and Related Modeling

April 18, 2013

U.S. EPA Research Triangle Park Campus
"C" Building Auditorium
Research Triangle Park, NC

8:00 am **Registration/Check-in**

8:30 am **Welcome and Introductions** .... *Ramona Trovato, US EPA*

8:40 am **Opening Remarks** .... *Glenn Paulson, Science Advisor, US EPA*

8:45 am **Purpose of Workshop** .... *Workshop Co-Chairs:*
Cynthia Sonich-Mullin, US EPA
Thomas Starosta, PA DEP

Session 1: Hydraulic Fracturing Wastewater Treatment

8:55 am ***Panel Presentations:***

1. **Overview of Hydraulic Fracturing Wastewater Research** .... *Cynthia Sonich-Mullin and Christopher Impellitteri, US EPA*
2. **Zero Water Discharge: Management for Hydrofracturing Activities** .... *Carl Adams, ENVIRON International Corporation*
3. **From Pilot Study to Daily Processing: Warren, Ohio's Documentary to Hydraulic Fracturing Water Treatment** .... *Thomas Angelo, City of Warren, Ohio, Water Pollution Control Department*
4. **Reducing Fresh Water Use in Upstream Oil & Gas Hydraulic Fracturing** .... *Michael Dunkel, Pioneer Natural Resources*
5. **Treatment for Beneficial Use of Produced Water and Hydraulic Fracturing Flowback Water** .... *David Stewart, Energy Water Solutions, LLC*
6. **Marcellus Wastewater Treatment – Case Study** .... *Daniel Ertel, Eureka Resources, LLC*

Questions of Clarification

Break (10 minutes)

Facilitated discussion among workshop participants focusing on key questions:

- *What are some modern and potential future trends in reuse, recycling, zero-liquid discharge and commercial transport?*
- *How to manage, dispose and characterize residuals of hydraulic fracturing?*
- *What are the consequences of disposal via landfills or beneficial reuse?*

11:45 am **Summary of Session 1** .... *Workshop Co-Chairs:*
Cynthia Sonich-Mullin, US EPA
Thomas Starosta, PA DEP

12:00 pm **Lunch (on your own) and Poster Session**

Session 2: Current and Future Trends in Hydraulic Fracturing Wastewater Management

1:30 pm ***Panel Presentations***

1. **Successful Oilfield Water Management: Five Unique Case Studies** .... *Brent Halldorson, Fountain Quail Water Management*
2. **Produced Water Management in the Marcellus** .... *Meagan Mauter, Carnegie Mellon University*
3. **Mid-Continent Water Management for Stimulation Operations** .... *D. Steven Tipton, Newfield Exploration Company*
4. **Utilizing Models Developed for Water Management and Risk during Carbon Storage to Improve Water Management during Unconventional Gas Exploration and Production** .... *Enid J. (Jeri) Sullivan, Los Alamos National Laboratory*

Questions of Clarification

Facilitated discussion among workshop participants focusing on key questions:

- *What are the contributions of selected contaminants from hydraulic fracturing relative to other potential sources of contamination?*
- *What are some applications of surface and subsurface modeling?*
- *How much flowback or produced water is created, and what happens to it?*
- *How do we currently monitor wastewater disposition?*
- *How do the projected volumes of wastewater compare to wastewater management capacity, including underground injection wells and treatment systems?*
- *What are the regional differences in wastewater quantity and quality and potential impacts on drinking water sources?*

3:45 pm **Summary of Session 2** .... *Workshop Co-Chairs:*
Cynthia Sonich-Mullin, US EPA
Thomas Starosta, PA DEP

3:55 pm **Closing Remarks** .... *Ramona Trovato, US EPA*

4:00 pm **Adjourn**

Poster Session

Sustainable Water Treatment, Recycling and Disposal Practices in the Marcellus Shale Basin
Matthew Bruff, Altela, Inc.

Feasibility of In Situ Sequestration of Toxic Metals in Flowback Water from Hydraulic Fracturing
Andrew Stack, Oak Ridge National Laboratory

Use of Switchable Solvents as Forward Osmosis Draw Solutes
Aaron Wilson, Idaho National Laboratory

Wastewater Made Clear with Green Technology
Patricia Werner-Els, Advanced Waste & Water Technology

List of Meeting Participants

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Introduction

At the request of Congress, the U.S. Environmental Protection Agency (EPA) is conducting a study to better understand the potential impacts of hydraulic fracturing on drinking water resources. The scope of the research includes the full cycle of water associated with hydraulic fracturing activities. In the study, each stage of the water cycle is associated with a primary research question:

- **Water acquisition:** What are the possible impacts of large volume water withdrawals from ground and surface waters on drinking water resources?
- **Chemical mixing:** What are the possible impacts of hydraulic fracturing fluid surface spills on or near well pads on drinking water resources?
- **Well injection:** What are the possible impacts of the injection and fracturing process on drinking water resources?
- **Flowback and produced water:** What are the possible impacts of surface spills on or near well pads of flowback and produced water on drinking water resources?
- **Wastewater treatment and waste disposal:** What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?

In 2013, EPA hosted a series of five technical workshops related to its *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. The workshops included Analytical Chemical Methods (February 25, 2013), Well Construction/Operation and Subsurface Modeling (April 16–17, 2013), Wastewater Treatment and Related Modeling (April 18, 2013), Water Acquisition Modeling (June 4, 2013) and Hydraulic Fracturing Case Studies (July 30, 2013). The workshops were intended to inform EPA on subjects integral to enhancing the overall hydraulic fracturing study, increasing collaborative opportunities and identifying additional possible future research areas. Each workshop addressed subject matter directly related to the primary research questions.

For each workshop, EPA invited experts with significant relevant and current technical experience. Each workshop consisted of invited presentations followed by facilitated discussion among all invited experts. Participants were chosen with the goal of maintaining balanced viewpoints from a diverse set of stakeholder groups, including industry; nongovernmental organizations; other federal, state and local governments; tribes; and the academic community.

The Wastewater Treatment and Related Modeling workshop was co-chaired by Cynthia Sonich-Mullin (EPA) and Thomas Starosta (Pennsylvania Department of Environmental Protection [PADEP]). A morning session addressed *Hydraulic Fracturing Wastewater Treatment*, while the afternoon session focused on *Current and Future Trends in Hydraulic Fracturing Wastewater Management*. In addition, several experts shared technical knowledge during a poster session (Appendix C).

Summary of Presentations for Session 1: Hydraulic Fracturing Wastewater Treatment

Susan Hazen, Hazen Consulting and Support Services, opened the workshop. She noted that EPA was looking for individual participants' frank input and opinion and was not trying to reach consensus on the topics; the workshop was not held under the rules of the Federal Advisory Committee Act (FACA). **Dr. Glenn Paulson,** Science Advisor to the EPA Administrator, and **Ramona Trovato,** Associate Assistant Administrator of EPA's Office of Research and Development, welcomed the participants and thanked them for contributing their knowledge and experience to help answer the wastewater management research questions in EPA's drinking water study. Workshop Co-Chairs **Cynthia Sonich-Mullin**, Director, EPA's National Risk Management Research Laboratory (NRMRL), and **Thomas Starosta** (PADEP) explained that the purpose of the workshop was to obtain input from experts and understand the current state of technology in a rapidly changing industry. They added that the workshops are designed to foster collaboration, and that EPA intends for the published drinking water study to reflect the input from all the technical workshops.

Ms. Sonich-Mullin and **Dr. Christopher Impellitteri,** EPA, presented an overview of the hydraulic fracturing wastewater research in EPA's drinking water study. Ms. Sonich-Mullin noted that the overall goals for EPA's study are to assess whether hydraulic fracturing may impact drinking water resources, and to identify any driving factors that may influence the severity and frequency of any potential impacts. For the water treatment and waste disposal stage of the hydraulic fracturing water cycle, EPA's secondary research questions are:

- What are the common treatment and disposal methods for hydraulic fracturing wastewater and where are these methods practiced?
- How effective are conventional publicly owned treatment works (POTWs) and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater?
- What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater in drinking water treatment facilities?

Dr. Impellitteri described the research projects associated with these research questions. These projects include literature review, well file review, FracFocus analysis, wastewater treatability studies, surface water modeling, source apportionment studies and brominated disinfection byproduct precursor studies. He noted that water quality issues vary greatly from state to state, play to play and even well to well. He also said that the most challenging aspects of this research are the rapid changes in how hydraulic fracturing wastewaters are managed and treated.

Dr. Carl Adams, ENVIRON International Corporation, discussed achieving zero discharge of water from unconventional oil and gas hydraulic fracturing activities by recycling 100 percent of the combined flowback and produced waters for subsequent hydraulic fracturing activities. He described a project in which wastewater is managed using traditional industrial wastewater management protocols. He stated that, in his opinion, high concentrations of total dissolved solids (TDS) are not a treatment problem if biological treatment was considered as an option, citing the example of wastewater with 18 percent salt being treated in the North Sea and in several Middle Eastern industrial situations. He said that the recycling issue could be managed with chemistry and conventional technology solutions, such as filtration. More expensive and complex technologies, such as membranes, chemical oxidation and evaporation, are not warranted. He stated his view that the economics of recycling hydraulic fracturing wastewaters depend on the possible complications from the residual chemical content of the recycled wastewaters.

Dr. Adams stated that, based on data characterization for both flow and quality, a cost-effective water management approach has been developed to recycle flowback and produced water—blended with fresh water in appropriate quantities for TDS control—for use in subsequent hydraulic fracturing well activity. Dr. Adams said that zero discharge might be obtained by operating a staged and/or parallel pretreatment to remove constituents from separate or combined wastewaters and making chemical adjustments to maintain constituents, such as naturally occurring radioactive material (NORM) and heavy metals in solution. Also, pretreatment would be designed to remove only selected compounds that may interfere with subsequent recycling, while avoiding precipitation of large quantities of excess sludge for disposal.

Dr. Adams' company performed comprehensive technology evaluations and undertook a selection process to develop a reliable process train. The company also developed an economic model to compare costs with traditional approaches. Dr. Adams stated that 100-percent recycling of hydraulic fracturing wastewater may be achievable if the process train is confirmed in bench-scale and field-scale trials. Potential benefits include lower operating costs; reduced presence of sulfide; reduced trucking; an operator-friendly process; and a more reliable, predictable and environmentally sensitive program.

Thomas Angelo, City of Warren, Ohio, Water Pollution Control Department, described a pilot study involving treatment of hydraulic fracturing wastewater in Warren, Ohio. In 2009, Warren began a pilot study to identify the amount of brine that its wastewater treatment plant (WWTP) could receive without causing WWTP or water quality issues. The pilot study determined that if a consistent amount of brine water were discharged over an extended period of time, there would be no adverse effects on the WWTP or adverse changes to the quality of the discharges of treated water based on limits in the existing discharge permit. Mr. Angelo described the model for daily processing of flowback brine water, including requirements for pretreatment, limits on the volume of brine water treated daily, limits on TDS discharged into the WWTP and testing for pollutants of concern (e.g., heavy metals, radiation, volatile organic compounds). Mr. Angelo stated his view that 2½ years of operational data using this model have shown that it is a safe and viable option that complements other disposal options.

Michael Dunkel, Pioneer Natural Resources, described an initiative to reduce fresh-water use in upstream oil and gas hydraulic fracturing. He described a study of three shale plays in Texas aimed at determining the water quality needed for hydraulic fracturing. Recommendations varied in the three cases but included removing total suspended solids (TSS) and blending with 50 to 80 percent fresh water to reduce the impact of specific minerals on hydraulic fracturing design. Mr. Dunkel presented some information about water treatment technologies and pilot tests, indicating that different processes give different results. He described the logistics, economics and environmental aspects of produced water transportation and storage. Using brackish water, he stated, can be more expensive than using ground water but is less costly than recycling. Additionally, brackish water is more plentiful in some areas of Texas than fresh ground water.

Mr. Dunkel also discussed preventing evaporation from storage using pond covers that float on the surface, and indicated that in hot, dry climates, this can be more economical than recycling and could be one component in the effort to conserve fresh water.

Dr. David Stewart, Energy Water Solutions, LLC, discussed treatment of produced and flowback water for beneficial reuse. Water reuse and recycling, he stated, will become an increasingly significant issue for developing oil and gas shale plays in the United States, and this country could potentially become a world leader in technologies for recycling and reuse. Dr. Stewart stated that, while water use for hydraulic fracturing is a small percentage of overall water use, it represents a large amount of water consumed and is especially significant in areas dealing with drought conditions. He discussed constituents of concern for water reuse and the need to develop criteria for reuse. He stated that chemical control of the brine stream, which can contain 50,000 to 300,000 mg/L TDS, is the most difficult issue in recycling/reuse. According to Dr. Stewart, if the scale-forming chemicals can be removed, this type of water potentially could be used for drilling operations or for manufacturing hydrochloric acid or bleach solution and sodium hydroxide. He also indicated that treatment technologies that fit the final reuse and recycling criteria (different for each field) will need to be deployed economically, and that byproduct capture (e.g., lithium) can be a cost-effective aspect of recycling and reuse.

Dan Ertel, Eureka Resources, LLC, presented a case study on centralized treatment of Marcellus wastewater to maximize recycling and protect water quality. He described an approach for centralized treatment of hydraulic fracturing wastewaters that has the flexibility to provide the level of the treatment needed to promote reuse of treated water. He indicated that this method can provide the following for potential reuse: pretreated water, distilled water, concentrated brine purge, salt, calcium chloride brine and treated water meeting Pennsylvania dewasting standards (i.e., water that is no longer considered an industrial waste product and may be stored in less stringently regulated impoundments). Mr. Ertel described the unit processes in pretreatment, secondary treatment (distillation and crystallization) and tertiary treatment (biological/reverse osmosis), saying that co-product reuse studies are underway, focusing on beneficial reuse of dry sodium chloride and liquid calcium chloride.

Summary of Discussions Following Session 1: Hydraulic Fracturing Wastewater Treatment

Following some clarifying questions, participants were asked to consider the following questions during the discussion:

- What are some modern and potential future trends in reuse, recycling, zero-liquid discharge and commercial transport?
- How can the residuals of hydraulic fracturing be managed, disposed of and characterized?
- What are the consequences of disposal via landfills or beneficial reuse?

Key themes from Session 1 discussion:

Potential drinking water impacts. A participant asked about the relationship between the wastewater treatment issue and potential drinking water impacts, stating his view that the brackish water being discussed is not a drinking water resource and never has been. An EPA participant noted that water used initially is sometimes from drinking water sources, that discharge of wastewater to surface waters could potentially impact drinking water sources, and that increased reuse and recycling will probably lessen the impacts on drinking water and drinking water sources because it will likely result in less discharge.

Reuse and Recycling. Several participants stated that there is a clear industry trend toward reuse and recycling of produced and flowback water. One participant noted that five years ago, industry believed that only fresh water could be used for hydraulic fracturing fluid, but the quality of water that industry is using is changing rapidly due to developments in fracturing water formulation, improvements in wastewater treatment/reuse technologies and an increased need for low-cost water. Several participants noted issues that affect the need or ability to reuse or recycle, including wastewater storage, transport and economics (e.g., gas prices). A participant also noted that water availability is a huge issue in the West, necessitating water reuse. While one participant described close to 100-percent reuse in some locations, others stated that economic and technology barriers still exist, and it will take several years to determine which technologies are viable. A participant suggested consulting with well owners/operators about their experience to understand the varying perspectives on limits to reuse. Several participants noted that there is no single solution to water management; it needs to be considered on a site-specific basis. A participant said that in some areas, hydraulic fracturing may have amplified water management issues, but it did not create them. A participant suggested an industrial process approach to increasing reuse and decreasing use of fresh water.

Chemical issues for water reuse. Several participants discussed the need to look at solubility and scale-forming criteria. One participant said that a Texas A&M study and U.S. Geological Survey (USGS) program on scale formation could be useful. Another participant noted that boron can be a problem because it crosslinks the gel fractures; he added that industry is investigating boron removal, which currently is expensive. One participant recommended future research and development to look at the buildup (accumulation) of boron, calcium and magnesium. A participant also stated that an industry consortium is looking at which chemicals are toxic and at what concentrations, and whether there are "green" alternatives.

Transport and mobile treatment. Some participants discussed transport costs associated with recycling, which they said can be 25 to 75 percent of the total cost of handling water. Onsite treatment, it was noted, may be a solution for reducing these costs, depending on the location. A participant stated that multiple pads in a concentrated area facilitate centralized treatment, while in areas where drilling operations are more sparse, mobile and/or onsite treatment may be preferable.

Sharing water. A participant asked whether operators could collaborate and share water to help solve storage and downtime issues. Someone stated that there might be an opportunity to work with a wastewater treatment plant as a "brokerage" (e.g., there have been legal and liability questions, with operators prohibited from transporting to other operators or sites in some areas). A participant noted that Texas has changed its rules to allow operators to share water, and that produced water is starting to be viewed as an asset. Another participant stated that, in the future, there will be networked systems with shared pipelines and storage.

Beneficial reuse of residuals. Some participants noted an industry trend toward more beneficial use of produced and flowback water and treatment residuals (e.g., sodium chloride, calcium chloride, recovered metals). Several participants said that the potential health and environmental impacts of beneficial use must be carefully considered, and that meeting the regulations may not be sufficient. One participant stated that waste streams from hydraulic fracturing are not yet fully characterized. Another participant stated that selective removal of constituents is problematic because of the hazardous sludge it might create. He stated that it might be better to keep chemicals in solution and put them back down the hole than to create more hazardous wastewaters and residual solids.

Several participants raised issues regarding reuse of calcium brine (e.g., levels of bromide, volatile organic chemicals, barium and radioactive materials). A participant noted that the trade secret aspect of hydraulic fracturing fluids can make beneficial use difficult from the regulator's perspective. A participant recommended that more research and development be focused on ways to turn wastes into assets.

Disposal via landfills. Several participants discussed issues with residuals going to municipal solid waste facilities. One participant described a practice of adding sawdust to mud for landfill disposal, which does not prevent leaching. It was noted that there may be a trend toward using landfills that take industrial wastes, which are different from subclass C ("hazardous waste") landfills. One participant described a wastewater treatment plant that has set up a partnership to reuse methane and drill cuttings, and cautioned about sending residuals to power generation facilities because of the potential impacts of inorganics on waste-to-energy processes. A participant noted a need to develop best practices for treating and managing the waste streams.

Summary of Presentations for Session 2: Current and Future Trends in Hydraulic Fracturing Wastewater Management

Brent Halldorson, Fountain Quail Water Management, presented five case studies highlighting five different scenarios for successful oilfield water management. Two of the examples involved using fresh water, two involved reusing saltwater and one involved using brackish water. Selecting salt water or fresh water is the initial, fundamental choice that must be made for water management. Using fresh water costs more but involves lower risks during storage and transport; using salt water is less expensive but is logistically more difficult. After the initial water selection is made, the next step involves setting simple, achievable goals and selecting a treatment partner or technology with a proven track record. New trends include using pit covers to prevent evaporation, combining recycling and disposal, using more brackish and salt water, having commonsense discussions among parties involved in water management and offering incentives for recycling. Mr. Halldorson emphasized the importance of sharing both positive and negative results and experiences to improve water management.

Dr. Meagan Mauter, Carnegie Mellon University, discussed research to quantify the impacts of produced water management in the Marcellus. She said that water transport generates significant regional impacts, some highly visible. Initial results from analysis of PADEP data show significant variations in waste management practices among companies, with much of the variation due to the waste disposal methods selected, the level of company experience in the Marcellus and the drilling practices implemented. Dr. Mauter stated that a key intervention affecting produced water management is "clustering." Companies that drill their wells in clusters reuse a larger percentage of waste and reduce waste transport distances.

Steven Tipton, Newfield Exploration Company, discussed water use and reclamation for the stimulation of the Granite Wash tight reservoirs and the shale oil reservoirs of the Cana Woodford Shale, both in the Anadarko Basin. These areas have evolved as drilling activity has increased and changed, and an infrastructure has been created to support completion operations and the need for water. Mr. Tipton presented an overview of the water sources, transport, storage, treatment and reuse, and disposal, and identified challenges to recycling. He indicated that in Granite Wash, more than 80 percent of water used is recycled and that the flowback and produced water has low chloride content. Water is transported to recycling pits through poly lines. Mr. Tipton said that there are plans to recycle produced water from Cana Woodford, transporting water to a recycling facility by truck. He noted that reusing produced water saves fresh water, is environmentally responsible and improves a company's "social license."

Dr. Enid Sullivan, Los Alamos National Laboratory, discussed using models developed for water management and risk during carbon storage to improve water management during unconventional gas exploration and production. Dr. Sullivan presented some results from applying the CO_2PENS (Predicting Engineered Natural Systems) model to produced water (with the addition of transport costs and organic pretreatment capability). The results indicate that thermal treatment methods may be more cost effective than membrane methods in many cases. She also described using large-scale computational models to predict carbon storage contaminant fate and transport to evaluate hydraulic fracturing impacts on drinking water quality over large scales and timeframes. In addition, she discussed using large-scale computational models

(ASCEM and AMANZI) to predict environmental contaminant fate and the impacts of climate on water resources, as well as potentially using these models to evaluate hydraulic fracturing impacts on drinking water quality over large scales and timeframes. Dr. Sullivan indicated that industry data and feedback are needed to build these models properly.

Summary of Discussions Following Session 2: Current and Future Trends in Hydraulic Fracturing Wastewater Management

Following clarifying questions, participants were asked to consider the following questions during the discussion:

- What are the contributions of selected contaminants from hydraulic fracturing relative to other potential sources of contamination?
- What are some applications of surface and subsurface modeling?
- How much flowback or produced water is created, and what happens to it?
- How do we currently monitor wastewater disposition?
- How do the projected volumes of wastewater compare to wastewater management capacity, including underground injection wells and treatment systems?
- What are the regional differences in wastewater quantity and quality and the potential impacts on drinking water sources?

Key themes from Session 2 discussion:

Relative contributions of hydraulic fracturing contaminants versus other contaminants. A participant noted that determining relative source contributions can be difficult. One participant recommended looking at load allocations. Another suggested reviewing watershed studies for sources such as runoff, mining, TDS and bromides from pharmaceuticals. A participant noted that an important source of bromides is scrubber discharge from coal-fired power plants. A participant discussed using potential markers of hydraulic fracturing impacts, such as radioisotopes (tritium), which are not found in produced water before reuse. A participant stated that chloride may be a useful marker for ground water but may be useless for surface waters, where there are many other sources. A participant noted that for risk management, the total daily maximum load (TDML) is useful, but for forensics, there are many sources of the contaminants assessed at very low concentrations. One participant recommended a tiered approach (i.e., first measuring simple parameters such as conductivity and turbidity, then following up with methane, barium, etc. if needed). Looking at a suite of chemicals (as opposed to looking at chemicals singly) was also suggested.

Modeling applications. One participant emphasized the importance of establishing the science basis when applying models (i.e., characterizing different sources of contaminants in the watershed). Applications for modeling discussed by participants included the impact of using brackish water on nearby freshwater aquifers, impacts from unlined construction and demolition debris (C&D) landfills and impacts from landfill leachate going to POTWs. Also mentioned was the potential application of agent-based economic models combined with system-based dynamic models to look at social and economic issues surrounding reuse decisions.

Water volumes and disposition. A participant noted that the amount of flowback water varies across plays and geographic areas and also changes over the life of the well. Several participants asked about the desirability of having more flowback water; one participant stated that the productivity of the well is the driver for the amount of flowback water. A participant stated that industry has an efficient system, building additional disposal wells or treatment capacity when needed.

Several participants discussed the issue of reporting and tracking the disposition of hydraulic fracturing wastewater, noting that reporting standards and the accessibility of data are very different among the states. A participant noted that in some states, operators are required to have the data but not necessarily to report them. Several participants recommended more consistent reporting; according to one participant, reporting on a regular basis could help prevent unsafe disposal practices. The practical aspects of tracking in a large, complex system were noted.

One participant stated that operators are very skilled at gathering data on wastewater volume and disposition, and that they track carefully because of costs. Another participant said that it would be better for industry and the environment if new operators could learn from other operators in a formation rather than only from their own experience. The importance of long-term water resource management plans and collaboration between industry and government to obtain needed data were discussed by several participants.

Disposal via underground injection. A participant stated that disposal through treatment facilities is still at a fairly low volume in the Marcellus, and that the dominant pathway for final disposal of wastewaters produced (after reuse and recycle options are exhausted) is underground injection in Ohio. A participant expressed concern about the capacity of Ohio injection wells to meet the ongoing demand for final disposal, should Ohio have cause to restrict this pathway, or if it reaches saturation for any reason.

Regional differences. A participant stated that the Utica and Marcellus formations are using much more water than in the West, and that the volumes per well and overall are increasing substantially. One participant also noted that slick water fracturing uses more water than gel fracturing by a factor of two or three. In formations like the Bakken, less water is used and less water is returned. A participant also stated that the northeast Marcellus wastewater has high TDS but low volume; Oklahoma has a wide variation in water quality across plays.

Concluding Remarks

Ms. Trovato and Dr. Glenn Paulson, EPA, thanked the participants for attending and sharing their knowledge and experience, noting that the workshop discussions highlighted the rapid changes in the industry, which are essential for EPA's study to address. They reminded the participants that once the technical workshops are completed, the technical roundtables will be reconvened to further inform the drinking water study. They noted that this ongoing stakeholder engagement will help ensure that human health and the environment are protected while the nation receives the economic and energy security benefits that unconventional oil and gas extraction can provide.

Appendix A.

Extended Abstracts from Session 1: Hydraulic Fracturing Wastewater Treatment

Overview of EPA's Hydraulic Fracturing Wastewater Research

Cynthia Sonich-Mullin and Christopher Impellitteri
US EPA

Information presented in this abstract is part of the U.S. Environmental Protection Agency's ongoing study and cannot be used to draw conclusions about potential impacts to drinking water resources from hydraulic fracturing. Any mention of trade names or commercial products does not constitute endorsement for use.

Introduction

Natural gas plays a key role in our nation's clean energy future. The United States has vast reserves of natural gas that are commercially viable as a result of advances in horizontal drilling and hydraulic fracturing technologies, which enable greater access to gas in rock formations deep underground. These advances have spurred a significant increase in the production of both natural gas and oil across the country. Responsible development of America's oil and gas resources offers important economic, environmental, and energy security benefits. However, as the use of hydraulic fracturing has increased, so have concerns about its potential human health and environmental impacts; especially for drinking water.

In response to public concern, the U.S. House of Representatives requested that the U.S. Environmental Protection Agency (EPA) conduct scientific research to examine the relationship between hydraulic fracturing and drinking water resources (USHR, 2009). In 2011, EPA began research under its "Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources." (US EPA, 2011). The purpose of the overarching study is to assess the potential impacts of hydraulic fracturing on drinking water resources, if any, and to identify the driving factors that may affect the severity and frequency of such impacts. Scientists are focusing primarily on hydraulic fracturing of shale formations to extract natural gas, with some study of other oil- and gas-producing formations, including tight sands, and coalbeds. EPA has designed the scope of the research around five stages of the hydraulic fracturing water cycle, each associated with a primary research question:

- Water Acquisition: *What are the possible impacts of large volume water withdrawals from ground and surface waters on drinking water resources?*
- Chemical Mixing: *What are the possible impacts of hydraulic fracturing fluid surface spills on or near well pads on drinking water resources?*
- Well Injection: *What are the possible impacts of the injection and fracturing process on drinking water resources?*
- Flowback and Produced Water: *What are the possible impacts of flowback and produced water (collectively referred to as "hydraulic fracturing wastewater") surface spills on or near well pads on drinking water resources?*
- Wastewater Treatment and Waste Disposal: *What are the possible impacts of inadequate treatment of hydraulic fracturing wastewater on drinking water resources?*

The purpose of this presentation is to summarize ongoing research on hydraulic fracturing wastewater and related modeling within this study.

Background

Flowback and produced water, collectively referred to as "hydraulic fracturing wastewater[1]," is generally stored onsite before being transported for treatment, recycling or disposal. Most hydraulic fracturing wastewater is disposed in underground injection control wells (UIC) wells. In Pennsylvania, however, wastewater has been treated in wastewater treatment facilities (WWTFs), which subsequently discharge treated wastewater to surface water bodies. The extent to which common treatment technologies used in WWTFs effectively remove chemicals found in hydraulic fracturing wastewater is currently unclear. Depending in part on the concentration of chemicals in the effluent, drinking water quality and the treatment processes at public water systems (PWSs) that are downstream from WWTFs might be negatively affected. For example, bromide in source waters can cause elevated concentrations of brominated disinfection byproducts (BR-DBPs) in treated drinking water (Brown et al., 2011; Plewa et al., 2008), which are regulated by the National Primary Drinking Water Regulations[2].

To learn more about impacts to downstream PWSs, the Pennsylvania Department of the Environment asked 25 WWTFs that accept Marcellus wastewater to monitor effluent in March 2011, for parameters such as radionuclides, total dissolved solids (TDS), alkalinity, chloride, sulfate, bromide, gross alpha, radium-226 and -228, and uranium (PA DEP, 2011). The department also asked 14 PWSs with surface water intakes downstream from WWTFs that accept Marcellus wastewater to test for radionuclides, TDS, pH, alkalinity, chloride, sulfate, and bromide (PA DEP, 2011). Bromide and radionuclides are of particular concern in discharges because of their carcinogenicity and reproductive and developmental affects.

Wastewater treatability research activities summarized here include an assessment of efficacy of common wastewater treatment processes on removing selected chemicals found in hydraulic fracturing wastewater and the potential for brominated compounds present in the wastewater to form brominated disinfection byproducts (Br-DBPs) during drinking water treatment processes. Surface water modeling is considering bromides and radium at public water supplies downstream from wastewater treatment facilities that discharge treated hydraulic fracturing wastewater to surface waters. Finally, source apportionment modeling studies are considering the identification and quantification of the source(s) of high bromide and chloride concentrations at public water supply intakes downstream from wastewater treatment plans discharging treated hydraulic fracturing wastewater to surface waters. As ongoing research activities, results and conclusions will not be presented here, but the approach and current status will be summarized.

Wastewater Treatability Studies

The EPA is conducting laboratory experiments to assess the efficacy of conventional wastewater treatment processes on selected chemicals found in hydraulic fracturing wastewater. This is being dome to provide data to inform the research question: *How effective are conventional*

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[1] Produced water is produced from many oil and gas wells and not unique to hydraulic fracturing.

[2] Authorized by the Safe Drinking Water Act.

POTWs and commercial treatment systems in removing organic and inorganic contaminants of concern in hydraulic fracturing wastewater?

This project focuses on the efficacy of treatment processes at publicly owned treatment works (POTWs) and centralized waste treatment facilities (CWTs), since discharge of treated wastewater to surface waters provides an opportunity for chemicals found in the effluent to be transported to downstream PWS intakes. The fate and transport of chemicals will be examined through conventional POTW treatment processes and commercial chemical coagulation/settling processes. The objective of this work is to identify the partitioning of selected chemicals between solid and aqueous phases and to assess the biodegradation of organic constituents. In addition, microbial community health will be monitored in the reactors to identify the point where biological processes begin to fail. Contaminants that can pass through treatment processes and impact downstream PWS intakes will be identified.

The US EPA will initially analyze the fate and transport of selected hydraulic fracturing–related contaminants in wastewater treatment processes, including conventional processes (primary clarifier, aeration basin, secondary clarifier), commercial processes (chemical precipitation/ filtration and evaporation/distillation), and water reuse processes (pretreatment and filtration). The initial phase of this work will involve bench-scale fate and transport studies in a primary clarifier followed by 10 liter chemostat reactors seeded with microbial organisms from POTW aeration basins. In bench- scale work relevant to CWTs, similar fate and transport studies will be performed in chemical coagulation, settling, and filtration processes. In addition to analyzing water samples before and after treatment, concentrations and chemical speciation of inorganic contaminants in treatment residuals will be examined.

Initial bench-scale studies will focus on establishing thresholds of TDS tolerance in chemostat bioreactors. Once the basic salt thresholds have been established, selected chemicals from the 26R Forms (Chemical Analysis of Residual Waste Annual Reports) will be added to the salt stock solutions. Salt concentrations will be kept below the thresholds where effects on the biological processes were observed. Potentially biodegradable pollutants (e.g., organics) will be measured, and the EPA will attempt to identify breakdown products.

Constituents that are not biodegradable (e.g., elements and anions) will be tracked through the treatment process by analyzing system effluent using the appropriate EPA Methods, and by analyzing residuals from the primary clarifier and the bioreactors. The results of these bench-scale studies will be applied to a pilot-scale system that would target compounds identified in bench- scale studies as being the most problematic due to their lack of degradation or removal in the treatment process.

For studies on commercial treatment systems using chemical addition/settling, the EPA plans to conduct jar tests that employ coagulants/flocculants at appropriate contact and settling times. The jar tests will be conducted at the bench-scale using actual hydraulic fracturing wastewater samples. EPA will also attempt to mimic evaporative/distillation processes by using thermal treatment on actual hydraulic fracturing wastewater samples. Elements in the residuals will also be characterized via X-ray diffraction and X-ray absorption microscopy.

Brominated Disinfection Byproduct Precursor Studies

The EPA is assessing the ability of hydraulic fracturing wastewater to contribute to DBP formation in drinking water treatment facilities, with a particular focus on the formation of brominated DBPs. This work will inform the research question: *What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?*

Wastewaters from hydraulic fracturing processes typically contain high concentrations of TDS, including significant concentrations of chloride and bromide. These halogens are difficult to remove from wastewater; if discharged from treatment works, they can elevate chloride and bromide concentrations in drinking water sources. Upon chlorination at a drinking water treatment facility, chloride and bromide can react with naturally occurring organic matter (NOM) in the water and lead to the formation of DBPs. Because of their carcinogenicity and reproductive and developmental affects, the maximum contaminant levels (MCLs) of the DBPs bromate, chlorite, haloacetic acids, and total trihalomethanes (THMs) in finished drinking water are regulated by the National Primary Drinking Water Regulations[2].

Increased bromide concentrations in drinking water resources can lead to greater total THM concentrations on a mass basis and may make it difficult for some PWSs to meet the regulatory limits of total THM listing in Table 44 in finished drinking water. As a first step, this project is examining the formation of brominated THMs during drinking water treatment processes, including bromoform (CHBr3), dibromochloromethane (CHClBr2), and bromodichloromethane (CHCl2Br). The formation of haloacetic acids (HAAs) and nitrosamines during drinking water treatment processes is also being investigated.[3]

Reactions of brominated biocides, used in hydraulic fracturing operations with typical drinking water disinfectants associated with chlorination or chloramination, are also being explored. Brominated biocides are often used in fracturing fluids to minimize biofilm growth. The objective of this work is to assess the contribution, if any, to brominated DBP formation and identify degradation pathways for brominated biocides.

Three treatments will be applied to high-TDS wastewater samples: (1) in order to account for dilution effects, samples will be blended with deionized water at rates that mimic discharge into varying flow rates of receiving water; (2) samples will be blended with deionized water with NOM additions at concentration ranges typically found in surface waters; and (3) samples will be blended with actual surface water samples from rivers that receive treated hydraulic fracturing wastewater discharges. All samples will be subjected to formation potential experiments in the presence of typical drinking water disinfectants associated with chlorination or chloramination. Formation potential measures will be obtained separately for THMs, HAAs, and nitrosamines. DBP formation in surface water samples will be compared with DBP formation in deionized water. In addition, they will be compared to deionized water fortified with several NOM isolates

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[3] Nitrosamines are byproducts of drinking water disinfection, typically chloramination, and currently unregulated by the EPA. Data collected from the second Unregulated Contaminant Monitoring Rule indicate that nitrosamines are frequently being found in PWSs. Nitrosamines are potentially carcinogenic.

from different water sources in order to examine the effects of different NOM on DBP formation.

The brominated biocides 2,2-dibromo-3-nitropropionamide and 2-bromo-2-nitrol-1,3-propanediol, employed in hydraulic fracturing processes, are being subjected to chlorination conditions encountered during drinking water treatment. These experiments should provide insight on the potential formation of brominated THMs from brominated biocides.

Surface Water Modeling

EPA is using established surface water transport theory and models to identify concentrations of selected hydraulic fracturing-relevant chemicals at public water supply intakes located downstream from wastewater treatment facilities that discharge treated hydraulic fracturing wastewater to rivers. This work is expected to provide data that will be used to answer the research question: *What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?*
Mass balance, empirical, and numerical computer models will be used to estimate generic impacts of bromide and radium in wastewater discharges. The models will be based on the presence of these chemicals in discharge data from WWTFs in Pennsylvania, impacts to downstream PWSs' ability to meet National Primary Drinking Water Regulations for DBPs and radionuclides, and the potential human health impacts from the chemicals.[4] Uranium, also a radionuclide, was frequently not detected by analytical methods for the discharges, and therefore not considered for simulations.

The results of the mass balance model simulate possible impacts during a large volume, high concentration discharge without natural attenuation of contaminants. The empirical model and a hybrid empirical-numerical model estimate impacts in a more realistic setting with variable chemical concentrations, discharge volumes, and flow rates of the receiving surface water. The numerical model confirms the results of the empirical and hybrid models. The numerical modeling is based on an approach developed for this study from existing methods (Hairer et al., 1991; Leonard, 2002; Schiesser, 1991; Wallis, 2007). Application of these three types of models provides a panoramic view of possible impacts and enhances confidence in the study results. The generic model results are designed to illustrate the general conditions under which discharges might cause impacts on downstream public water supplies. The analysis will include the effect of distance to the PWS, discharge concentration, and flow rate in the stream or river, among others. The uncertainties in these quantities will be addressed through Monte Carlo analysis. A steady-state mass balance model provides an upper-bound impact assessment of the transport simulation, and a partially transient approach simulates the temporal variation of effluent concentration and discharge. Key data collected to model the transport of potential contaminants include actual effluent data from WWTF discharges and receiving water body flow rates. Effluent data can be obtained from National Pollutant Discharge Elimination System (NPDES) monitoring data reported to states by the dischargers.[5] NPDES information also documents the design of the industrial treatment plants, which can give insights into the

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[4] Discharge data for four WWTFs in Pennsylvania that accepted oil and gas wastewater during 2011 are available on the EPA's website at http://www.epa.gov/region3/marcellus_shale/.

[5] Information on WWTF discharges in Pennsylvania can be found at https://www.paoilandgasreporting.state.pa.us/.

capabilities of these and similarly designed treatment plants. The U.S. Geological Survey (USGS) provides limited water quality and flow rate data from monitoring stations within the watersheds of the receiving water bodies. The surface water modeling results will directly address the applicable research question by evaluating the possible impacts from a permitted release of treated effluent on both a downstream drinking water intake, and in a watershed where there may be multiple sources and receptors.[6]

Currently, sufficient data have been identified to perform generic simulations for the steady-state mass balance simulations and hybrid empirical-numerical models with variable effluent concentration and plant discharge. For two WWTFs in Pennsylvania, USGS flow data have been compiled for segments of the rivers that reach downstream to drinking water intakes (50 to 100 miles downstream) for the two locations. These data will be used to generate realistic model inputs to assess, in a generic sense, the potential impacts of discharges from realistic treatment plants.

The EPA-developed hybrid empirical-numerical model has been favorably compared against a tracer experiment used by Jobson (1996) in developing the original empirical formulas. Calibration or other parameter adjustment was unnecessary for the hybrid model to produce accurate results. EPA plans to compare the hybrid model to five more of the tracer experiments to cover the range of flow conditions used by Jobson (1996). Additionally, data from the more recent Yellowstone River experiment (McCarthy, 2009) are being prepared for testing the hybrid model. Similar comparisons of empirical to tracer experiments were performed by Reed and Stuckey (2002) for streams in the Susquehanna River Basin. EPA's Water Quality Simulation Package numerical model was set up to simulate the same tracer experiment performed for the hybrid model. Additional calibration is planned to refine the results from the Water Quality Simulation Package. After completing the evaluation of the hybrid model, the WWTF simulations will be completed.

A description of the EPA-developed empirical-numerical model and application of the empirical, numerical, and mass balance models to tracer experiments is being developed by EPA scientists, and are expected to be submitted for publication in a peer-reviewed journal. The results from testing of the models and the analysis of the WWTF effluent data will be included in another peer-reviewed journal article.

Source Apportionment Modeling

US EPA is combining data collected from samples of wastewater treatment facility discharges, as well as receiving waters with existing modeling programs, to identify the proportion of hydraulic fracturing wastewater that may be contributing to contamination at downstream public water system intakes. This work has been designed to help inform the research question: *What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?*

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[6] Impacted watersheds may also have other sources of compounds of interest, possibly acid mine drainage and coal-fired utility boilers.

This project's overall goal is to establish an approach whereby surface water samples may be evaluated to determine the extent to which hydraulic fracturing wastewaters (treated or untreated) may be present, and to distinguish whether any elevated bromide and chloride in those samples may be due to hydraulic fracturing or other activities. To accomplish this goal, US EPA is (1) quantifying the inorganic chemical composition of discharges in two Pennsylvania river systems from WWTFs that accept and treat flowback and produced water, coal-fired utility boilers, acid mine drainage, stormwater runoff of roadway deicing material, and other industrial sources; (2) investigating the impacts of the discharges by simultaneously collecting multiple upstream and downstream samples to evaluate transport and dispersion of inorganic species; and (3) estimating the impact of these discharges on downstream bromide and chloride levels at PWS intakes using mathematical models.

In this effort, water samples are being collected at five locations on two river systems; each river has an existing WWTF that is currently accepting hydraulic fracturing wastewater for treatment. Source profiles for significant sources, such as hydraulic fracturing wastewater, WWTF effluent, coal-fired utility boiler discharge, acid mine drainage, and stormwater runoff from roadway deicing, will be developed from samples collected from these sources during the study. Computer models will then be used to compare data from these river systems to chemical and isotopic composition profiles obtained from potential sources.

US EPA will analyze the river samples and effluent samples according to existing US EPA methods. Inorganic ions (anions and cations) are being determined by ion chromatography. Inorganic elements are being determined using a combination of inductively coupled plasma optical emission spectroscopy for high-concentration elements, and high-resolution magnetic sector field inductively coupled plasma mass spectrometry for low concentration elements. Additionally, the characteristic strontium (Sr) ratios (87Sr/86Sr; 0.7101– 0.7121) in Marcellus Shale brines are extremely sensitive tracers, and elevated concentrations of readily water soluble strontium are present in the hydraulic fracturing wastewaters (Chapman et al., 2012). Isotope analyses for 87Sr/86Sr are being conducted on a subset (~20%) of samples by thermal ionization mass spectrometry to corroborate source apportionment modeling results.
US EPA is using the data gathered through the analyses described above to support source apportionment modeling. This effort will use peer-reviewed receptor models to identify and quantify the relative contribution of different contaminant source types to environmental samples.[7] EPA-implemented models and commercial off-the-shelf software are being used to analyze the data from this particular study (e.g., Unmix, Positive Matrix Factorization, chemical mass balance). These models have previously been used to evaluate a wide range of environmental data for air, soil, and sediments (Cao et al., 2011; Pancras et al., 2011; Soonthornnonda and Christensen, 2008), and are now being used for emerging issues, such as this application.

River samples collected near PWS intakes are being evaluated to discern the contributing sources (e.g., hydraulic fracturing wastewater or acid mine drainage) of bromide and chloride to those stream waters. Receptor models require a comprehensive analysis of environmental samples to provide a sufficient number of constituents to identify and separate the impacts of different

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[7] The receptor model, Positive Matrix Factorization, was peer-reviewed in 2007 (version 1.1) and 2011 (version 4.2), and Unmix (version 5.0) underwent peer review in 2007.

source types. Contaminant sources may be distinguished by unique ranges of chemical species and their concentrations; the models provide quantitative estimates of the source type contributions along with robust uncertainty estimates.

Summary

The ongoing wastewater treatment and related modeling activities that are part of US EPA's "Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources," have been summarized here. Using a variety of laboratory and bench-scale experiments, as well as modeling tools, these research activities focus on key factors of concern related to hydraulic fracturing wastewater, such as bromides and radionuclides. More information about each of these study activities can be found in "EPA's Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report." (US EPA, 2012). Results from these research projects will be included in the final report of the EPA study, which is expected to be released for public comment and peer review in 2014.

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Achieving Zero Discharge of Water from Non-Conventional Oil & Gas Hydrofracturing Activities

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Introduction/Background

The rapid expansion of non-conventional oil and gas hydraulic fracturing activities has created anxiety in inexperienced or local citizens in the vicinity of the activities. Foremost among these concerns are potential water sustainability issues, especially surface contamination from stormwater and spills and insufficient management of the water from the fractured well itself. In June 2012, the concept presented herein was initiated to enhance sustainability and minimize all environmental impacts, particularly water-related issues.

Emerging policy on hydraulic fracturing activity is being debated between the various agencies (US EPA, states, local municipalities). The major debate will focus on pretreatment for municipal and commercial treatment vs. injection back into new and expired hydraulic fracturing wells. The process described herein is flexible to adapt to emerging and more stringent criteria.

The major objectives of this project were to:

- Reduce trucking and acquisition costs of freshwater supplement
- Reduce off-site trucking and disposal costs of associated wastewaters (Flowback & Produced Waters)
- Reduce quantity of chemical additives into the fracturing fluids
- Organize and implement the project along Industrial Wastewater Management methodology protocols

Approach

ENVIRON'S approach to this complex project was to organize and manage it as a traditional Industrial Wastewater Management project. This brought a perspective that other practitioners had not incorporated into their project organization.

The basic agenda was to meet with on-site operators, hydraulic fracturing water managers, global chemical suppliers and technology providers, especially various filtration manufacturers. The team collected, assimilated and correlated available data, consistent with industrial wastewater management protocols.

The inlet characteristics and outlet criteria (for both recycle and discharge disposal) were evaluated and comprehensive data correlations assembled to allow evaluation of chemistry techniques and application of appropriate, cost-effective technologies. A comprehensive technology evaluation and selection process was then conducted to develop a technically reliable and operationally predictable process train. An economic model was then developed to compare capital and operational costs of current and predicted management approaches. Over 90 wells were surveyed and utilized for the data processing

Results and Discussion

The most significant parameters for a process design are: 1) water flow rate; 2) water volume accumulation during a fracture; and, 3) water constituent quality. The significance of these design elements is:

- Flow Rate
    - Influences sizing and capital cost of surge/handling/pretreatment facilities
- Accumulative Flow Volume
    - Influences required equalization/storage requirements
    - Influence on blending management of TDS concentrations in recycled Flowback and Produced Water
- Water Constituent Concentration
    - Influences supplemental chemical additives
    - Defines technology required for discharge or recycle
    - Influences selected pretreatment technology used for reinjection/recycle of wastewaters
    - Major influence on on-going operational costs

Water Flow Rate and Volume Accumulation: Flowback and Produced Waters

From the beginning, the project was treated as a traditional industrial wastewater management activity. Over 90 wells in the Marcellus shale formations were evaluated based on available data. A database was developed on controlled and uncontrolled water sources and outlets (Water Lifecycle) as shown below:

- Controlled Sources in the Water Lifecycle
    - Surface water (river, lake, POTW treated effluent, mining wastewater)
    - Subsurface (groundwater: potable, non-potable)
- Uncontrolled Sources
    - Rain/Storm water (collected and utilized)
- Controlled Outlets in the Water Lifecycle
    - Trucked/Piped to disposal
        - Injection well
        - POTW
        - Commercial Disposal
        - On-site treatment and direct discharge to receiving surface water
    - Reused on site
    - Reused at another site
    - Sanitary & utilities
- Uncontrolled Outlets
    - Loss to formation
    - Leaks & spills
    - Evaporation

Figures 1, 2 and 3 present the flow data for Flowback Water and statistical analysis to develop surge and forward flows required for process design. The same approach was used for Produced Water. The correlated flow results are given in Table 1.

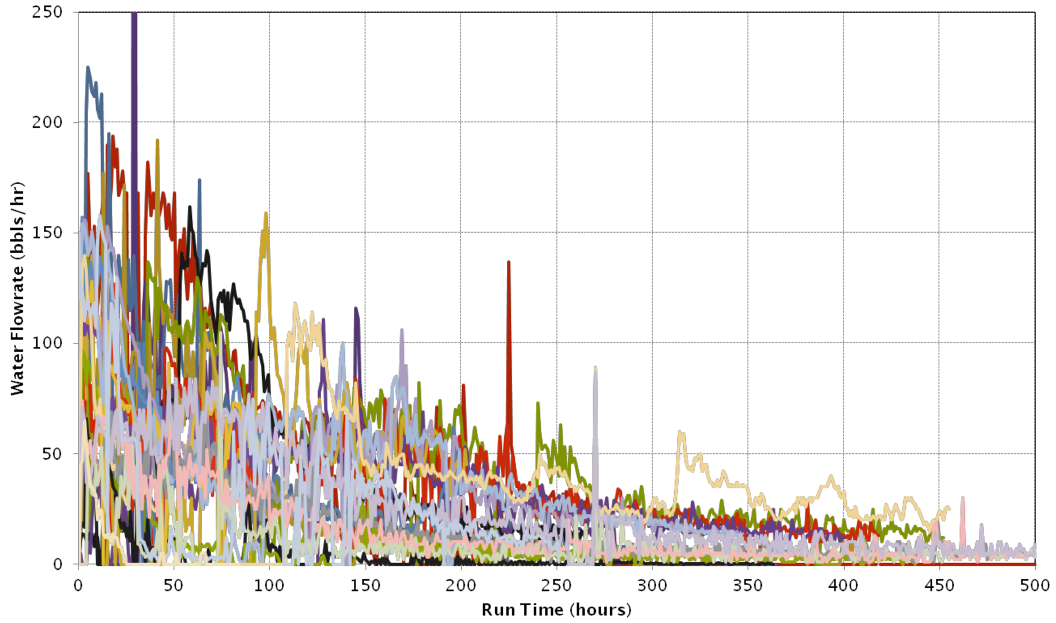
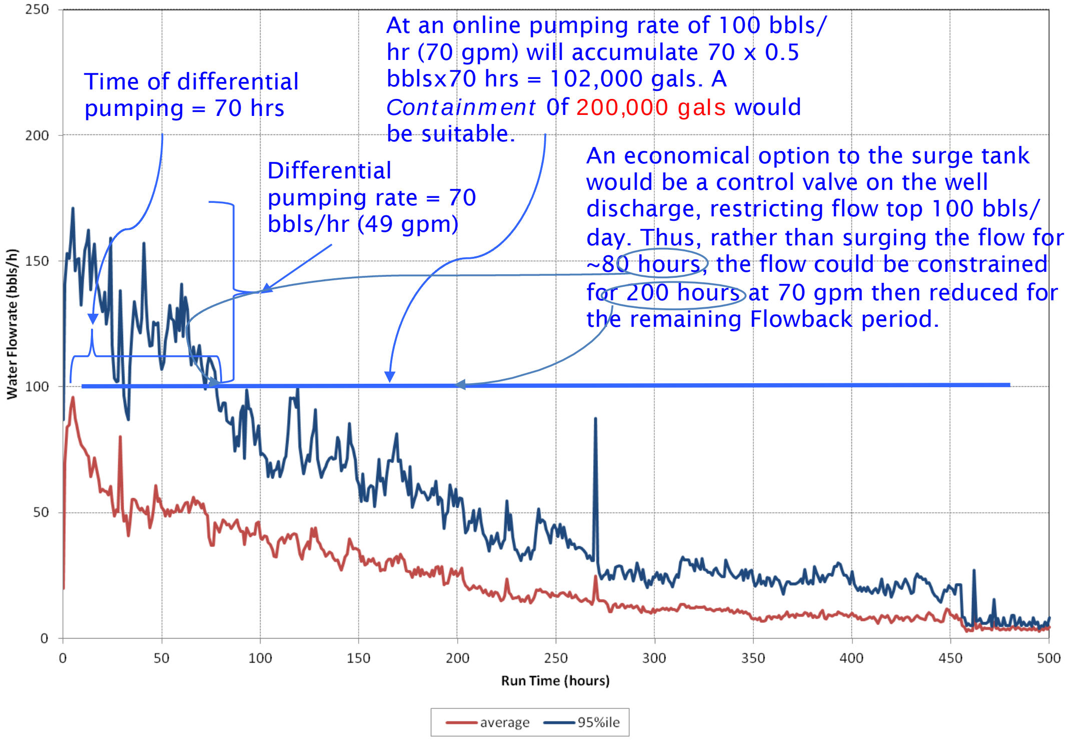


Figure 1. Water Flow Rates During Flowback Period (2-3 Weeks)



Time of differential pumping = 70 hrs

At an online pumping rate of 100 bbls/hr (70 gpm) will accumulate 70 x 0.5 bblsx70 hrs = 102,000 gals. A *Containment* Of 200,000 gals would be suitable.

Differential pumping rate = 70 bbls/hr (49 gpm)

An economical option to the surge tank would be a control valve on the well discharge, restricting flow top 100 bbls/day. Thus, rather than surging the flow for ~80 hours, the flow could be constrained for 200 hours at 70 gpm then reduced for the remaining Flowback period.

Figure 2. Water Rate Statistical Summary

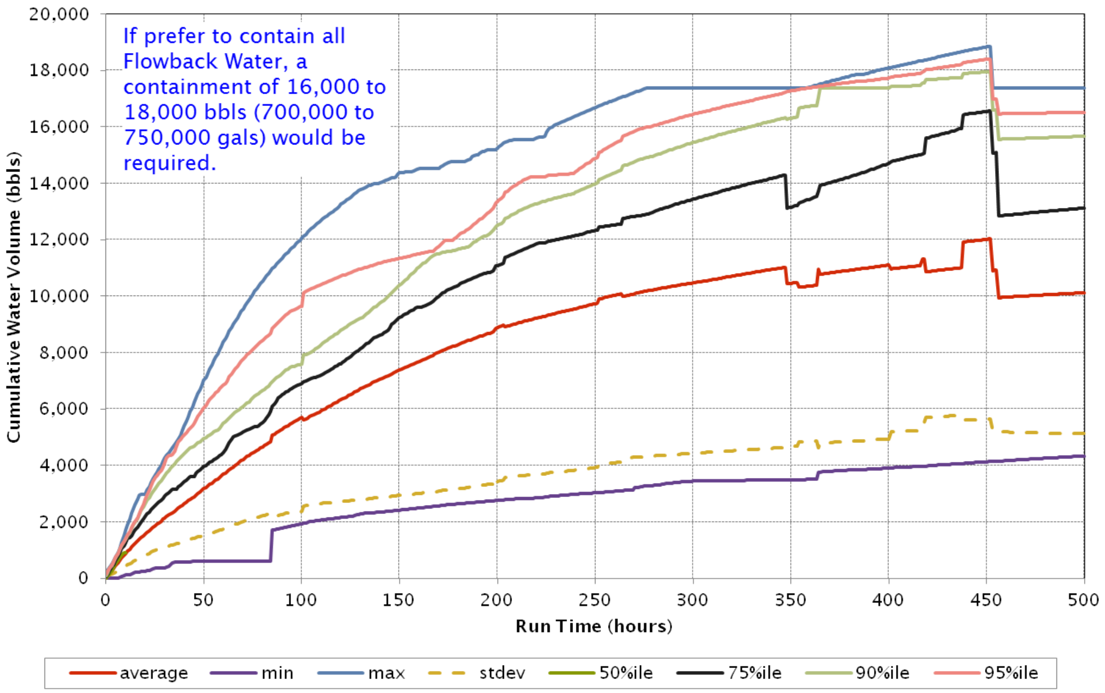


Figure 3. Water Flow Accumulation During Flowback Period (2-3 Weeks)

Table 1. Summary of Water Flow Rates during Flowback and Produced Water Periods

Water Category	**Average**	**Maximum**	**Typical**
Fracturing Injection Water (gallons)[1]	520,0000	9,000,000	6,500,000
Flowback Water in First 1-3 Weeks			
% of Water Injected	8.9%	20.0%	10.0%
Flowback Cumulative	360,000	780,000	650,000
Produced Water (gpd/days to 1 mil gal)[2]			
21 days to 50 days	3652 / 273	12,713	6,300 / 158
50 days to 250 days	1,001 / 1,000	1,990	3,780 / 264
250 days to 1 year	452 / 2,212	1,066	2,630 / 380
1 year to end of well	96 / 10,416	13,158	1,300 / 769

[1] Flowback statistics based on 25 wells
2 Produced Water statistics based on 64 wells

Water Quality Constituents: Flowback and Produced Waters

Many chemicals can be considered in hydraulic fracturing activities, which are naturally occurring or which are added to enhance or protect the integrity of the fracturing process. Basically, the chemicals, which occur in the hydraulic fracturing wastewaters, either originate in the strata from ages of dissolution or are added to enhance the hydraulic fracturing process.

1. Major Water Quality Constituents: Naturally occurring (equilibrium from dissolution, only a little from acid dissolution)
    a. Calcium
    b. Barium

c. Magnesium
d. Iron, ferrous
e. Chlorides
f. Total Dissolved Solids
g. Total Suspended Solids
h. NORM (radium, thorium, strontium, radon, etc.)
i. Heavy Metals e.g., As, Cd, Cr^{+6}, Cu, Hg, Se, Zn

Figure 4 is an example of the inorganic ion concentrations as they accumulate due in the Flowback Water due to equilibrium dissolution. Table 2 summarizes the Flowback and Produced Water ionic concentrations that can be expected in the return water to the surface.

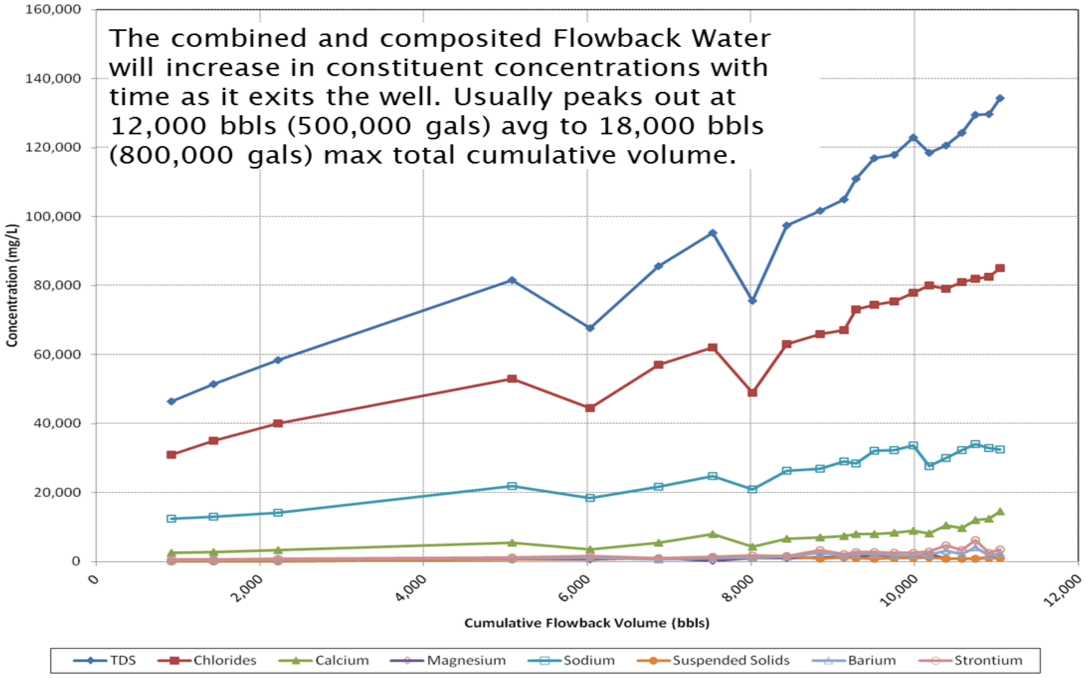

The combined and composited Flowback Water will increase in constituent concentrations with time as it exits the well. Usually peaks out at 12,000 bbls (500,000 gals) avg to 18,000 bbls (800,000 gals) max total cumulative volume.

Figure 4. Flowback Water Chemistry Interactions

2. Chemicals added to injected water to enhance/stabilize hydraulic fracturing activities.

   The major chemical additives and cost comparisons to facilitate gas completion are:

   a. Friction Reducers (decreases water flow head loss): 50-70% of cost
   b. Biocides (prevents odors and sulfide corrosion): 20-30% of cost
   c. Anti-Scalants (minimizes precipitation and scaling, specifically, Calcium, Barium, Magnesium, Iron): 10-15% of cost
   d. Remaining chemicals: 5-10% of cost

   Costs are for additive chemicals only, do not include sand or guar.

Table 2. Summary Flowback & Produced Water Quality Concentrations

Parameter	Units	Flowback Water					Produced Water	
		Average	Minimum	Maximum	50th Percentile	95th Percentile	Average	Maximum
Total Hardness	mg/L	3,077	116.1	104,090	27,624	89,698	15,100	29,000
Total Alkalinity	mg/L	428	16.0	3,301	400	863	--	--
Total Dissolved Solids	mg/L	10,9156	10,013	331,202	102,550	298,289	114,449	177,310
Chlorides	mg/L	69,315	5,999	196,956	65,985	187,158	70,400	104,000
Sulphates	mg/L	8.4	0.0	500	0.0	30	--	--
Calcium	mg/L	9,861	30.5	36,671	8,737	31,461	13,767	26,400
Magnesium	mg/L	1,330	5.8	17,014	1,118	3,160	1,333	2,600
Sodium	mg/L	27,617	1.0	96,975	24,700	83,695	27,500	40,500
Potassium	mg/L	174	1.0	500	200	300	690	1,600
Total Iron	mg/L	145	0.6	4,600	43	688	753	2,200
Barium	mg/L	6,506	95.0	96,000	2,300	55,800	6	10
Suspended Solids	mg/L	896	20.0	4,110	900	1,792	109	150
Ferrous Iron	mg/L	11.0	0.0	108	4.3	44	--	--
Biochemical Oxygen Demand	mg/L	--	--	--	--	--	1,100	1,400

Notes:
1) Statistics based on all samples reported as "Flowback" in EXCO Pa Database.
2) Statistics based on 3 samples representing 2 locations in Pennsylvania from September 1986 as reported by the American Petroleum Institute.
3) Numbers in red are calculated.

Comments on Water Chemistry Friction Reducers: The concern with friction reducers is the biggest issue in reuse of a high salinity (TDS) water from a blend of Flowback and Produced Waters. Generally, a form of anionic polyacrylamide is preferred to control friction during the injection of pressurized water. Divalent cations are considered a major problem, and, if so, cationic polyacrylamides might resolve the issue. These cationic polymers are more expensive, but fewer chemicals are required. Polymers are not a fouling issue due to tight shale; they are a surface fouling phenomenon only. The higher TDS, anticipated in this project, may actually aid in friction reduction. Polymeric and non-polymeric scaling inhibitors have also had value as friction reducers.

Biocides: Biocides are used to control bioactivity of sulfate reducers (heterotrophic bacteria in an oxygen-depleted environment), and the resulting "souring" and corrosion from hydrogen sulfide (odors) production transforms to sulfuric acid (corrosion) at compatible pH values.

The most common biocide during hydraulic fracturing is Gluteraldehyde + Quaternary Amines. Sometimes THPS is utilized. Oxidizers, such as chlorine, bromine or ozone, have side effects or are prohibitally expensive. These oxidants are very effective biocides, but can be consumed inefficiently in the presence of organics. The presence of dissolved organics will substantially increase the cost of oxidizing biocides, as well as generate dechlorinated and brominated toxic organics.

Peracetic acid is an effective non-oxidizing biocide without the disadvantages of non-selective oxidation. However, there is limited residual inhibition of bioactivity with peracetic acid. It may be cost-effective to use an economical non-oxidant biocide (peracetic acid, etc.), followed with lower dosages of a traditional longer acting biocide.

It may even be feasible to add an electron acceptor, such as nitrate (as sodium nitrate or nitric acid) to eliminate sulfate as a problem. Nitrate is preferred over sulfate by anoxic biomass, containing sulfate and nitrate reducing bacteria (same microbes), and releases harmless nitrogen gas instead of toxic and corrosive sulfide.

Anti-Scalants: Classical scalants in hydraulic fracturing are Calcium, Barium, Magnesium and Iron. Scaling forms from flash precipitation on a surface, and there is software available to reliably predict implications of scalants in varied waters. It is feasible to utilize a scaling model to scan various conditions.

The prevailing thought is that the high concentrations of ionic scalants in Flowback Water are due to equilibrium dissolution and will not increase substantially with recycle. Thus, only a slight amount of Flowback may require pretreatment for scalant precipitation and removal by filtration.

Summary of Discussion

Based on the data characterization (both flow and quality), a cost-effective water management concept was developed. This concept realizes that all of the Flowback and Produced Waters, blended in appropriate quantities, can be recycled into subsequent well activity. It is also promising that some of the chemical additives can be recycled, and the need for other chemical additions may be reduced due to correct blending of high TDS waters (friction reducers) and pretreatment of bioactivity with oxidants (biocides, e.g., peracetic acid).

Technology Evaluation and Selection

Based on the summary observations noted above, complete recycle of all Flowback and Produced Waters is the most appealing option. It is recommended that this option be pursued to develop a reliable performance and cost estimate. This option is referred to herein as the "Achieving Zero Discharge of Water Initiative."

For the Technology Review and Evaluation, every proven technology that has been piloted or implemented full-scale was examined and only those, which were deemed to fit the selection criteria, were chosen for further consideration. The major technology categories evaluated were:

- Adsorption/Exchange
- Chemical/Catalytic Conversion
- Chemical Oxidation
- Concentration/Volume Reduction
- Membrane Processes
- Physical Separation

- Thermal/Catalytic Destruction
- Biological Oxidation/Reduction/Conversion (presented at end)
- Miscellaneous

The constituents to be treated via two optional outlets, i.e., pretreated (recycle) or final treated (discharge to receiving water, POTW or commercial industrial treatment facilities) are given below:

Processes For Treatment & Discharge to Receiving Water, POTW or Commercial Treatment Facilities

- pH adjustment
- Oil removal
- Suspended solids removal
- Metals removal (including NORM radioactivity)
- Evaporation (some cases)
- Solids handling & disposal
- Inorganic salts removal
- Soluble organics removal

Processes For Recycle

- pH adjustment
- Oil removal
- Suspended solids removal
- Scalant removal
- Solids handling & disposal

Technology Evaluation Categories

- Technical Feasibility
- Cost-Effectiveness
- Operational Reliability
- Environmental Issues
- Aesthetic Considerations

Achieving Zero Discharge of Water from Hydrofracturing Activities

The main premise of this concept is to operate a suspended solids removal pretreatment step of all combined wastewaters. The contaminants, such as NORM, heavy metals, mercury, organics and TDS, etc., can be chemically adjusted to remain in solution and, thus, be reinjected into subsequent well activities. It is emphasized that 80 to 90% of the injected fracturing water (on the order of 5.4 mil gallons) will remain in the shale strata, and only 0.4 to 0.8 mil gallons will resurface as Flowback Water. This Flowback Water will be blended with a small percentage (10 to 30%) of Produced Water and, then combined with 4 to 5 mil gallons of Fresh Water for the new "fracture."

Thus, the technology review was oriented towards those technologies and methodologies that are most effective for this option, specifically, filtration alternatives. Oxidation, tight membranes (both micro and nano membrane filtration were considered) and biocide oxidants were evaluated.

All containment will possess floating roofs so that no air is emitted and no rain or wind spillage or overflow can occur. The pad will be "bathtubbed" so that all pad spills (truck loading, etc.) and stormwater will be contained and routed to a sump for recycle. This concept will involve:

- Minimal containment (with no environmental exposure to air or surface/ground water or soils).
- Pumped blending of Flowback and Produced Waters to maintain a predictable TDS blend.
- Chemical addition to preferentially precipitate selected constituents, if required.
- Cost-effective, staged filtration (plate & frame or belt press, followed by polishing filter)
- Ease of residual solids handling, with either on-site or off-site disposal

Final Process Train

1. Surge / Containment Tanks
    a. Bladder & swimming pool
    b. Plastic, covered
    c. Erected within lined earthern basin
2. Various Pumps
    a. Materials designed for high brine concentration
3. In-line pH Control System
4. In-line Chemical Addition System for Pretreatment (not fracturing chemicals)
    a. Coagulant, chelation, polymer, etc.
5. Filter /Dewatering Equipment: one step solids handling
6. Straining Filtration Polishing to Low Levels of Suspended Constituents for Reinjection

The process train is schematically presented in Figure 5.

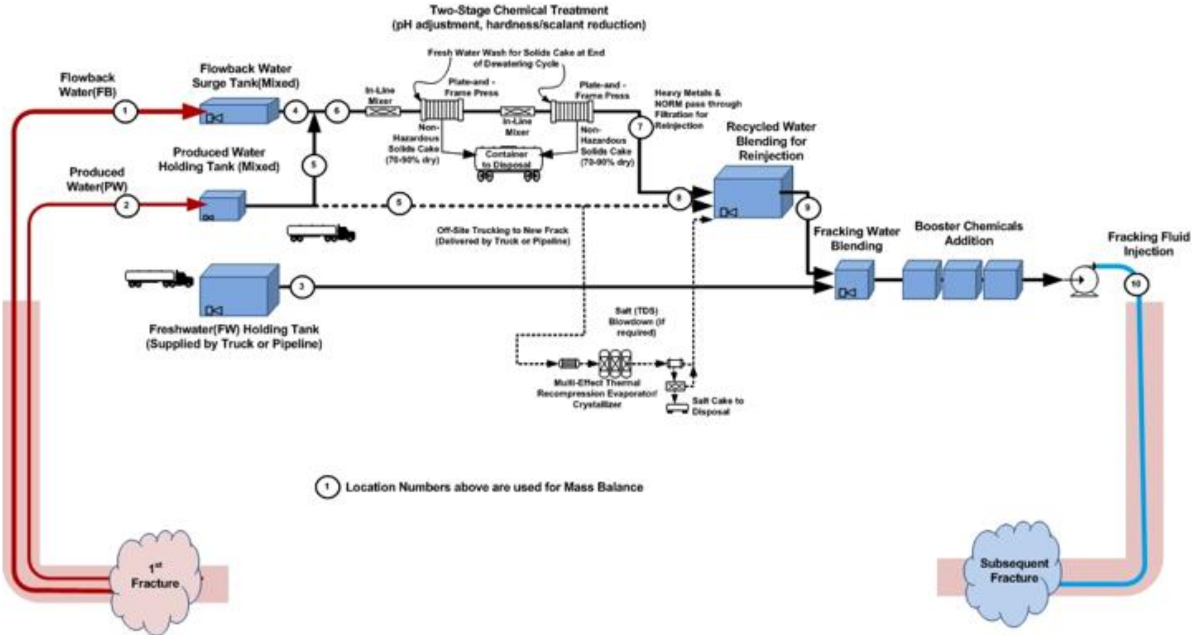


Figure 5. Concept: Achieving Zero Discharge of Water

The implementation goals were all achieved:

1. 100% achievement of performance and operations
2. Environmentally sound with no contact with air, groundwater, surface water and soils
3. Cost-effective
4. Maximum flexibility to apply to any hydraulic fracturing activity globally
5. Modularly expandable to accommodate emerging regulatory criteria

Thus, the achievement of a 100% recycle or Zero Discharge of Water Initiative has been achieved, subject to treatability screening and confirmation. In sum, the final program will result in:

1. A reliable, predictable and environmentally sensitive program,
2. A cost-effective solution
3. De-risking the hydraulic fracturing process
4. Increased and improved gas completion
5. Facilitating environmental permitting while reducing public concerns for future hydraulic fracturing activities.

A reasonable bench-scale screening investigation will be conducted to effectively delineate the performance conformation and cost-effective feasibility of the Achieving Zero Discharge of Water.

From Pilot Study to Daily Processing Warren, Ohio's Documentary to Hydraulic Fracturing Wastewater Treatment

Thomas A. Angelo
City of Warren, Ohio

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Overview

In May of 2009, The City of Warren and Patriot Water Treatment LLC began discussions with the Ohio Environmental Protection Agency (OEPA) to initiate the treatment of brine water from the Marcellus Shale. A series of letters and meetings culminated to a letter issued to Warren by OEPA to perform an eight (8) week pilot study to "clearly identify the amount of brine that Warren can receive without causing WWTP or water quality issues."
Charged with this task, Warren first had a whole effluent toxicity (WET) test accomplished on September 4, 2009 to determine the ceiling of brine water acceptance. This demonstrated that the facility could accept up to 664,000 gallons of brine water at 50,000 mg/l TDS before toxic conditions caused a water flea kill. This was based on an 8 MGD flow. Knowing that typical flow rates are approximately 13.38 MGD allowed for a protective buffer of 5.38 MGD dilution ratio.

An organizational meeting was held January 8, 2010 to review current information and to set guidelines for the pilot study. The guidelines were set as follows:

- Patriot Water Systems would supply ten 20,000 gallon frac tanks.
- The tanks would be connected together to create one 100,000 gallon mixing system.
- Brine water would be re-circulated in the combined tanks to create a homogeneous mix.
- The initial mix will be tested for the parameters as defined by OEPA.
- The City will sample influent, effluent, upstream and downstream prior to the discharge of brine water to develop a baseline concentration of TDS.
- The City would conduct a live, 8 week, phased in trial to monitor and record effects on treatment processes, accumulation loading and receiving stream TDS.
- The maximum amount of TDS in the brine water will not exceed 50,000 mg/l.
- Brine water will be phased in as follows (all flows will be over an 8 hour period):
    - Week 1 – 5 days at 20,000 gallons
    - Week 2 – 5 days at 40,000 gallons
    - Week 3 – 5 days at 60,000 gallons
    - Week 4 – 5 days at 80,000 gallons
    - Week 5 – 5 days at 100,000 gallons
    - Week 6 – 5 days at 100,000 gallons
    - Week 7 – 5 days at 100,000 gallons
    - Week 8 – 5 days at 100,000 gallons
- Testing will be accomplished as defined in Addenda 3 (revised 3/1/10).

The pilot study was initiated on Tuesday, February 9, 2010. This required a deviation from the schedule because the first week did not start on a Monday. As a result, week 1 only had 4 days of discharge. The pilot was postponed mid-way through week 2 because source water wasn't available due to extreme weather conditions making the remote well site locations inaccessible to truck traffic. The pilot study resumed on March 1, 2010 at 40,000 gallons per day and followed the documented schedule throughout the remainder of the study.

Baseline Sampling

Initial baseline testing was accomplished on the river and plant flow to determine TDS levels prior to start-up of the pilot study. The baseline levels are as follows:

Baseline Levels	TDS	Chloride
Raw	584	143
Final	599	157
Up	336	70
Down	332	60
Liquid Sludge		296

Initial radioactivity sampling
Collect date 2/17/10

Parameter	Results	Units
Gamma Scan	All other nuclides <LLD	pCi/L
K-40	2.6E+02 +/- 2.6E+01	pCi/L

Ram Chandrasekar, Ph. D., Manager of Lab Operations for the Bureau of Public Health Laboratories, Ohio Department of Health, provided this explanation on why Thorium tests were not conducted:

Subject: Thorium versus Gross Alpha
ODH Lab methods for radiological testing includes gross alpha screen which includes alpha emitted by Thorium nuclides. Hence if the gross alpha value is below the threshold value, there is no need to perform the Thorium estimation. When the initial gross alpha value is high, separate Thorium determination is required to identify the level.

Pilot Study

The pilot study commenced as scheduled with no other interruptions except for the one noted above. Sampling was accomplished as scheduled. OEPA was on site March 17, and March 31, 2010 and conducted sampling. At the time of this writing, the results of these samples have not been received.

TDS Overview

Sludge

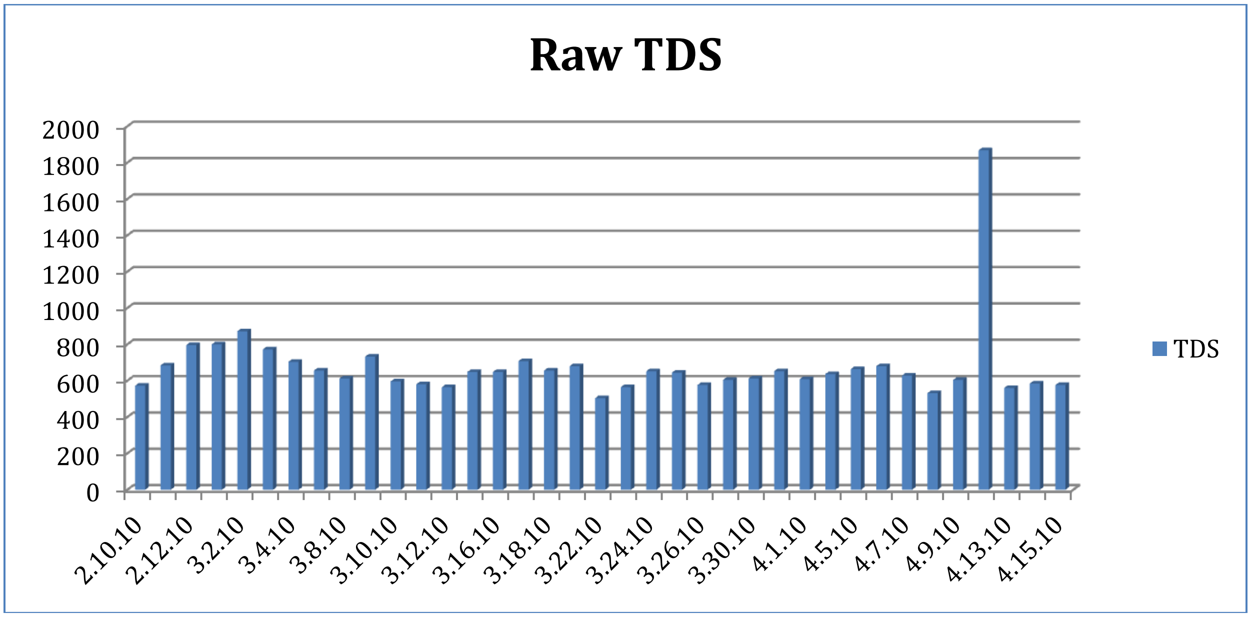
Three (3) sludge samples were tested for Chlorides during the pilot study. The results of these samples are:

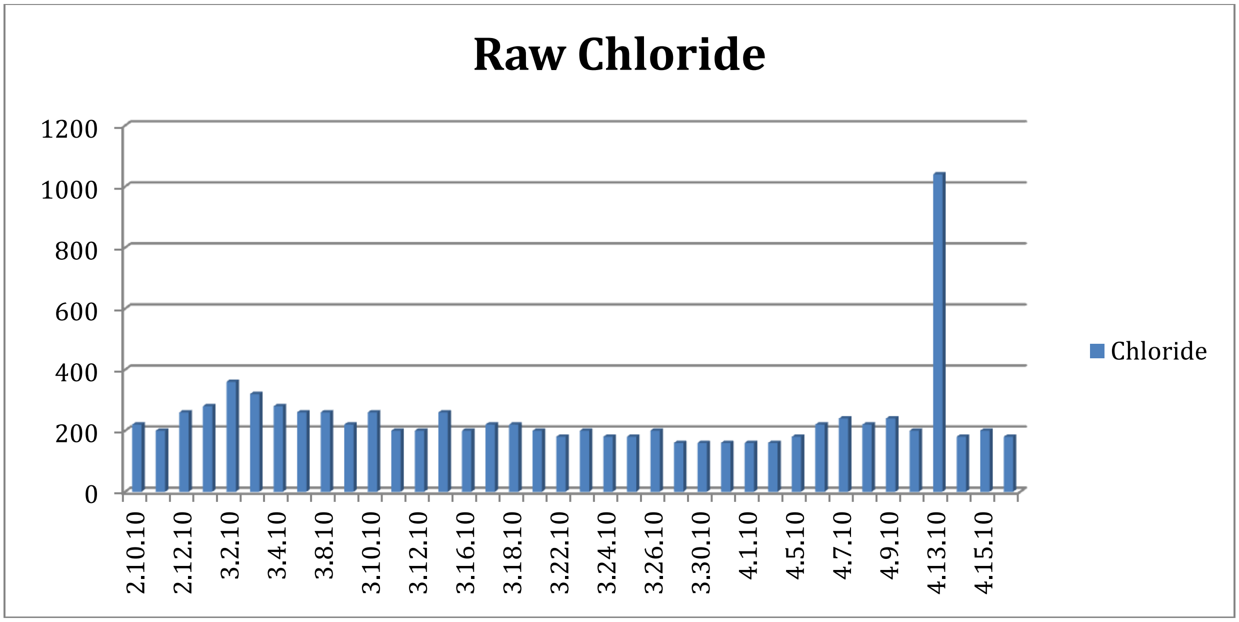
Sample Date	Chloride mg/Kg
2/17/2010	250
4/05/2010	184
4/16/2010	456

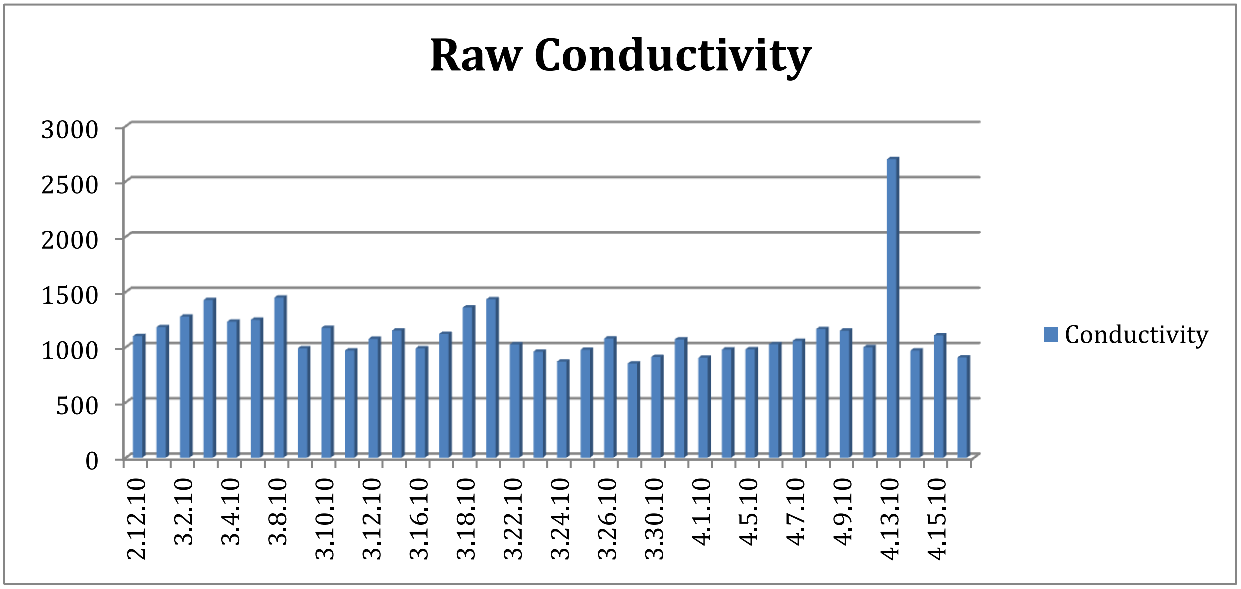
The increase in Chlorides in the sludge potentially can be a result of TDS becoming colloquial solids and settling. However, one data point does not provide sufficient evidence to make a clear determination. Therefore, additional observations will be necessary in order to see if this is actually occurring. If this is a fact, than a percentage of the brine water is actually being treated. Additional observations will allow for a percentage of treatment to be determined if this continues as a trend.

Raw Influent

The average raw TDS did not increase significantly over the 8 week pilot study. Raw TDS average increased to 679 mg/l which is approximately 16% over the baseline of 584 mg/l. Raw chlorides averaged 239 mg/l which is approximately 67% more than the baseline of 143 mg/l. These increases are most likely due to seasonal fluctuations within the collection system as a result of user operations or seasonal runoff from spring rains. (Raw does not have any Patriot Influence or plant return flows)

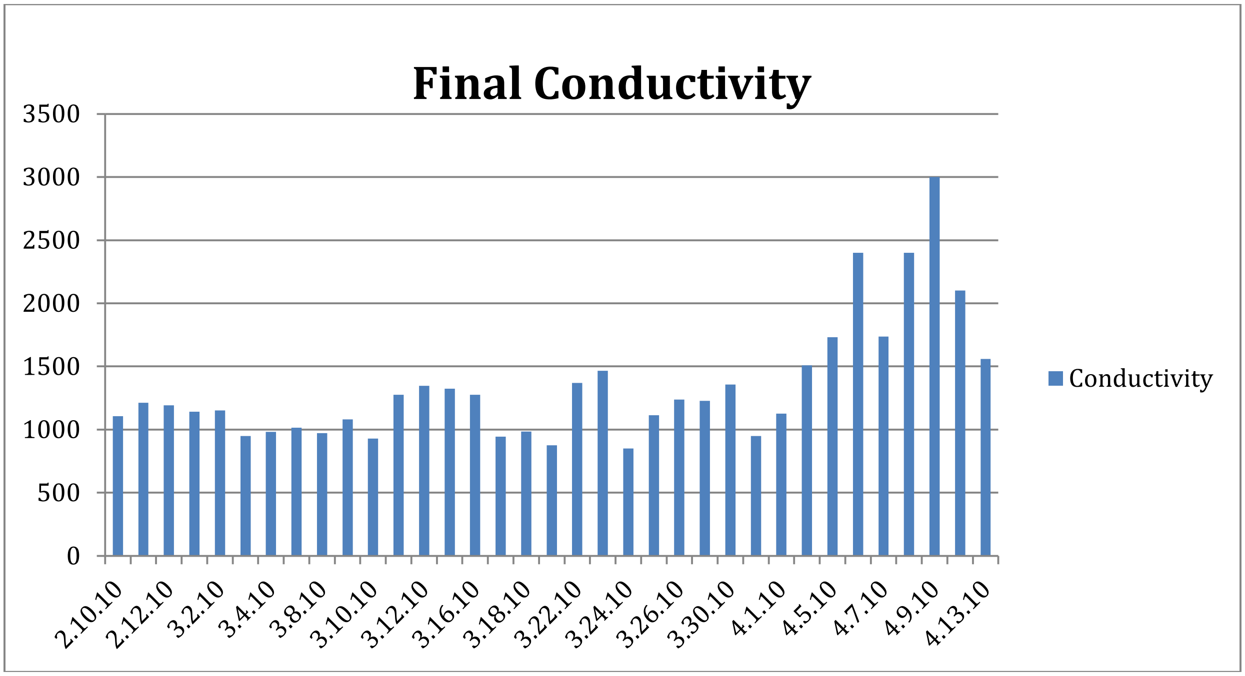


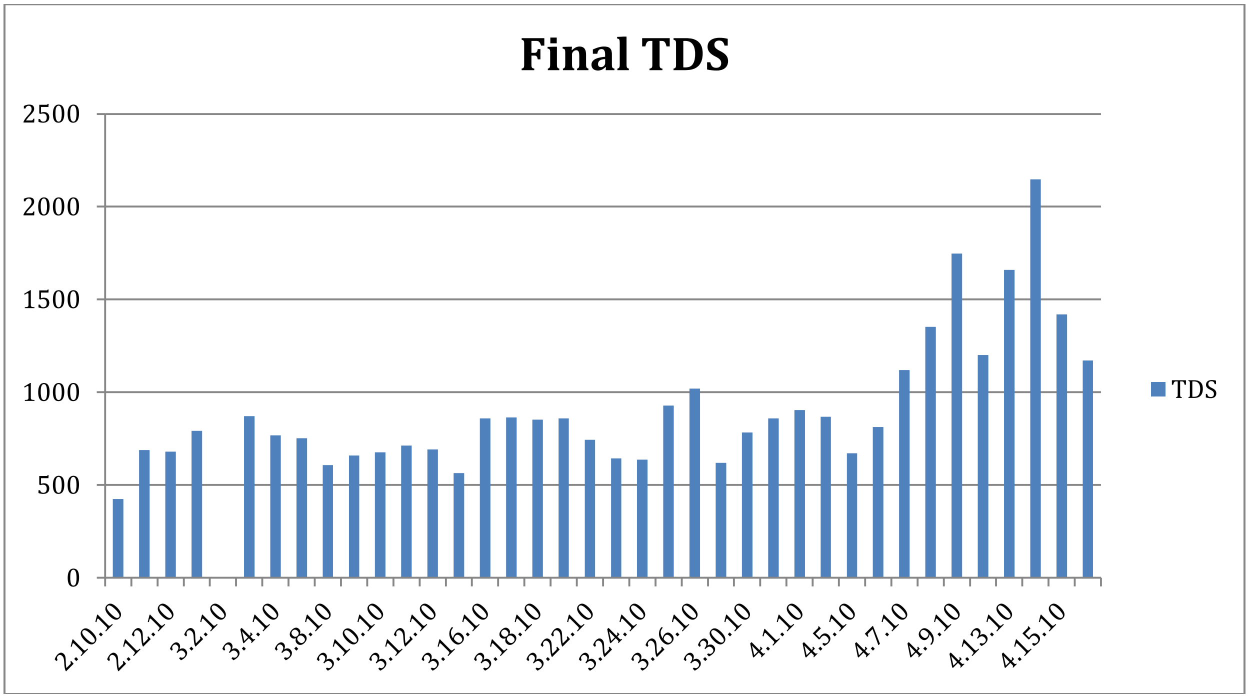


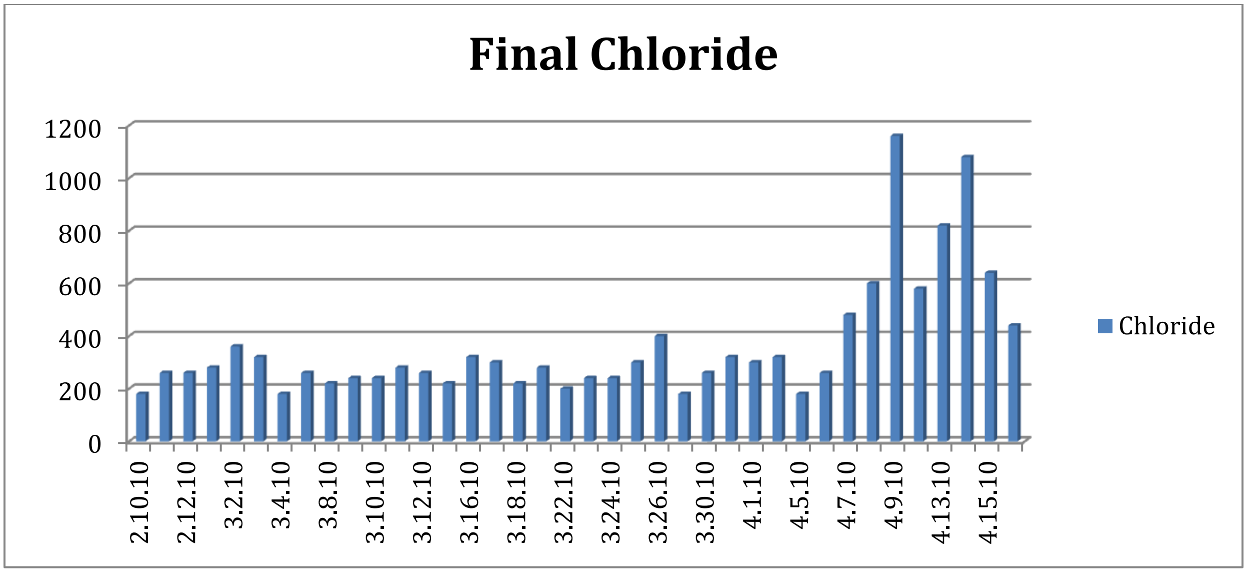


Final Effluent

The average final effluent TDS increased by 47.8% above the baseline to 885 mg/l and the average final effluent Chlorides increased by 122% over the baseline to 348 mg/l. This was expected as most of the TDS would pass through the system. However, since raw chlorides increased at a greater percentage than raw TDS, it cannot be ruled out that seasonal fluctuations within the collection system, as a result of user operations and spring rains, may be causing these increases. The higher increases in chlorides in both the raw and final could have resulted from runoff water from the roads entering the collection system during early spring rains. These rains would have carried additional salt that had acuminated from winter de-icing procedures and was washed off the roads with the spring rains. Infiltration and Inflow into the collection system would have allowed this additional source of salts to add to the overall total. While the timeline, as demonstrated by the graphs below, suggest that this hypothesis may be accurate, it also coincides with the increase to 100,000 gallons per day discharge of brine. Additional observations, during this critical period of time, will help to establish if the hypothesis is accurate.

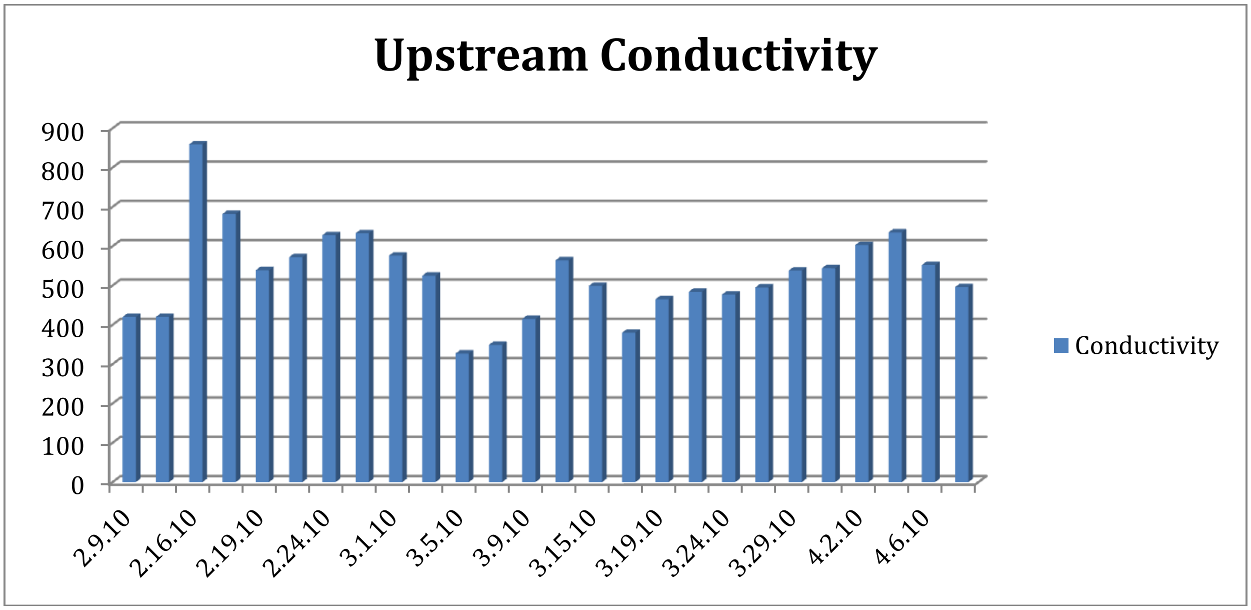


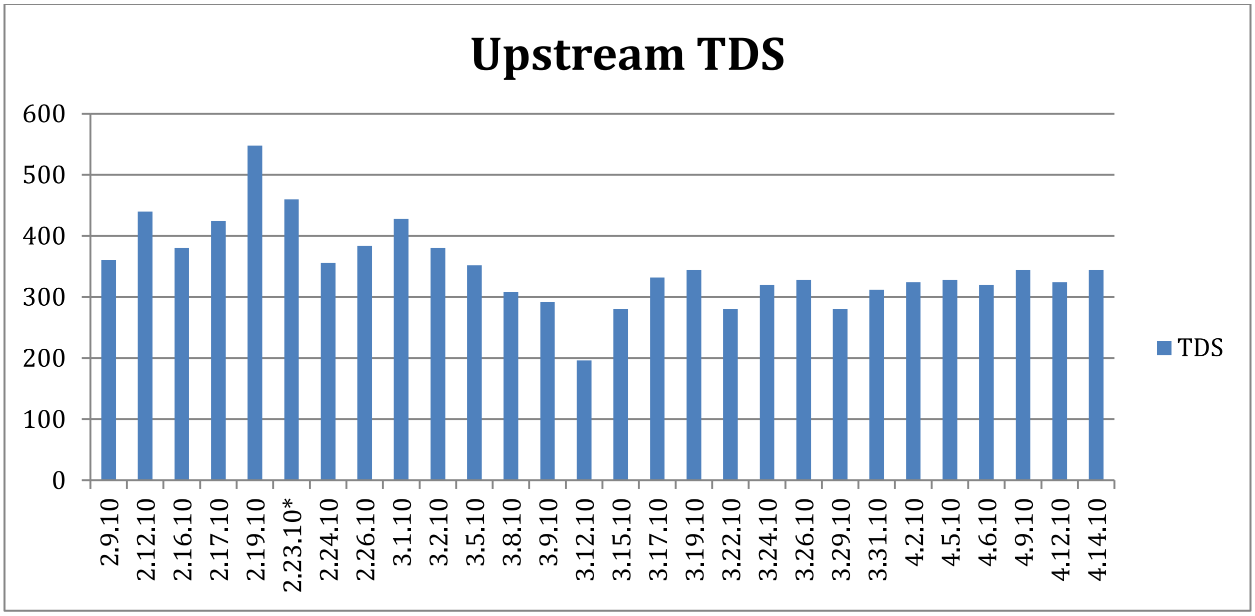


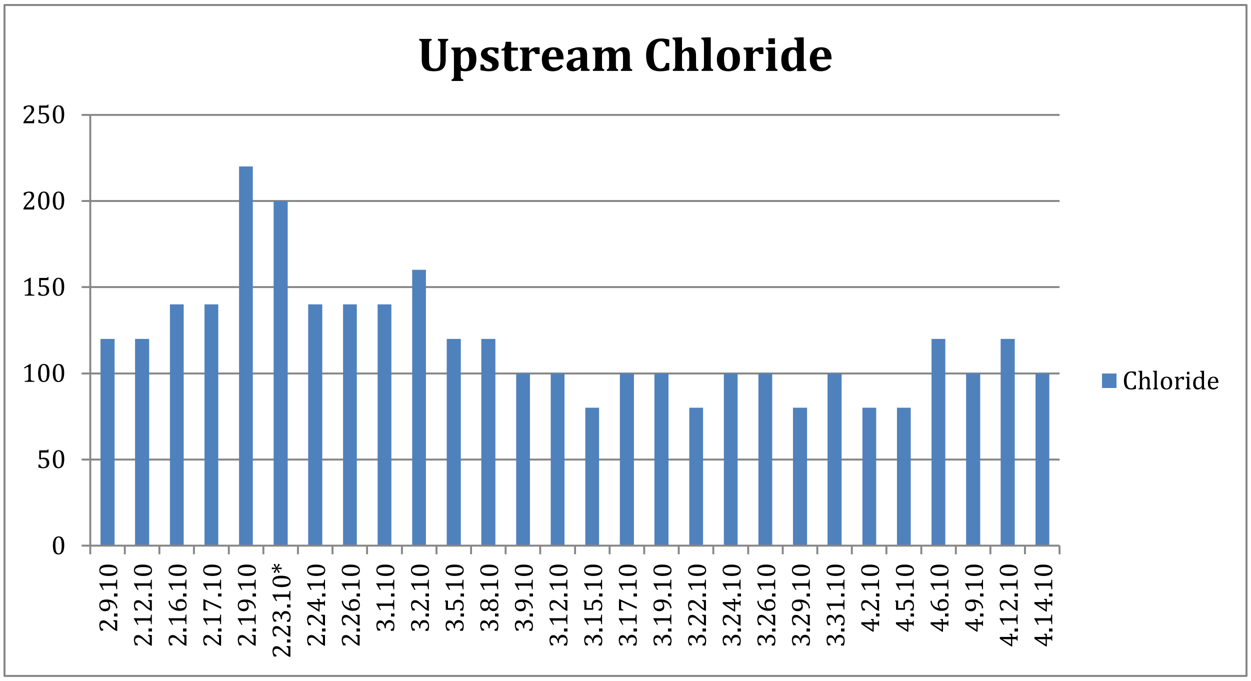


River - Upstream

The average Upstream River TDS of 348 mg/l remained close to the baseline value of 336 mg/l. This represents an increase of 3.6%. However, the average chlorides, at 123 mg/l, were 76% higher than the baseline of 70 mg/l. This is most likely due to seasonal de-icing practices where salts applied to roadways were washed into the river from storm outlets.

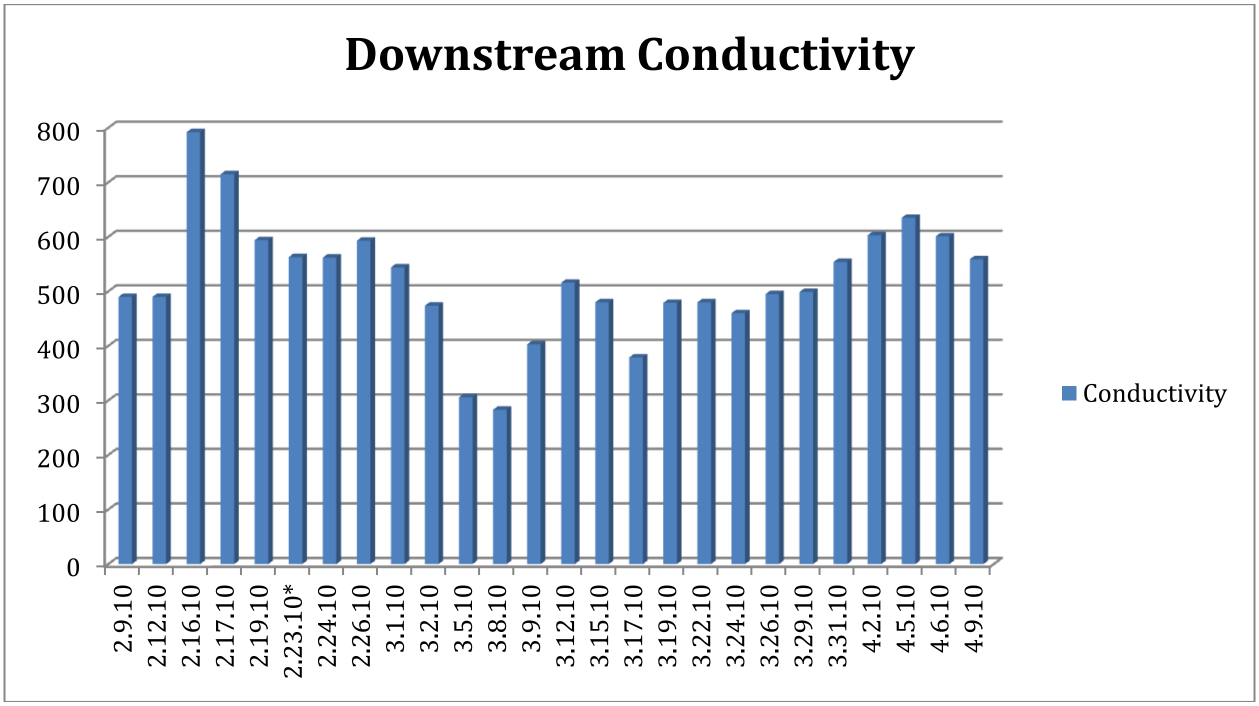


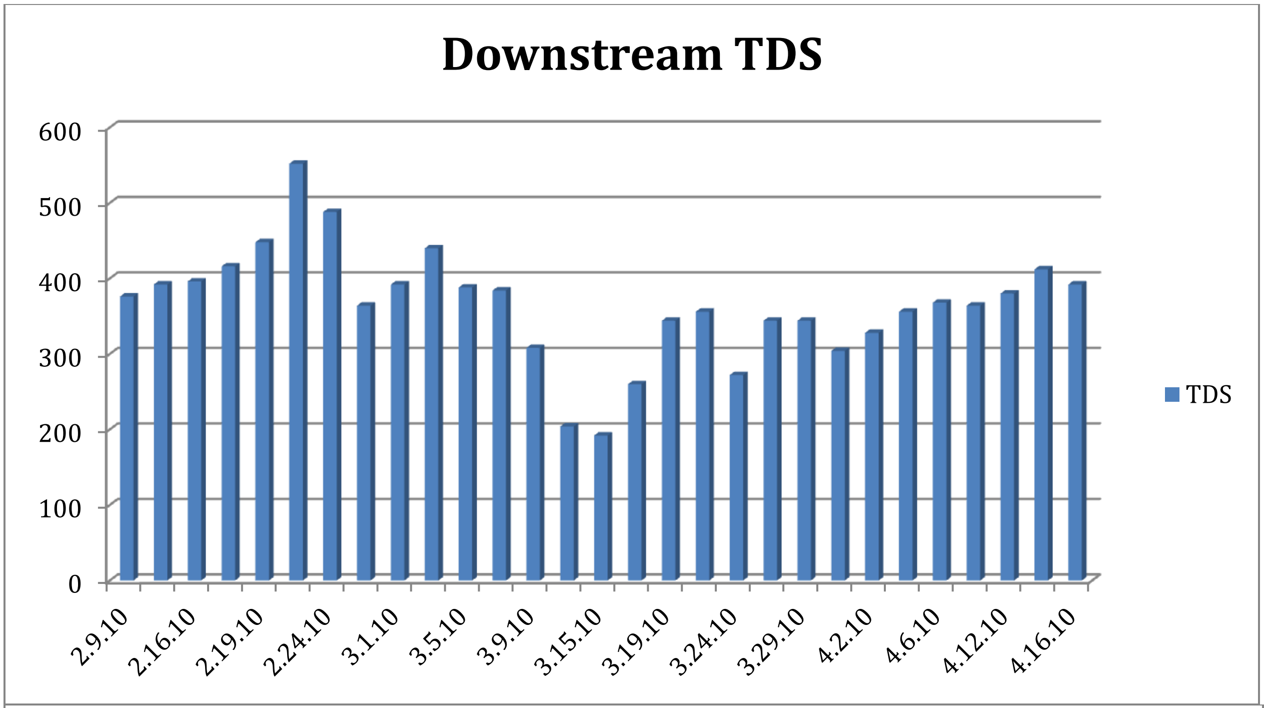

Upstream TDS
600
500
400
300
200
100
0
2.9.10
2.12.10
2.16.10
2.17.10
2.19.10
2.23.10*
2.24.10
2.26.10
3.1.10
3.2.10
3.5.10
3.8.10
3.9.10
3.12.10
3.15.10
3.17.10
3.19.10
3.22.10
3.24.10
3.26.10
3.29.10
3.31.10
4.2.10
4.5.10
4.6.10
4.9.10
4.12.10
4.14.10
TDS

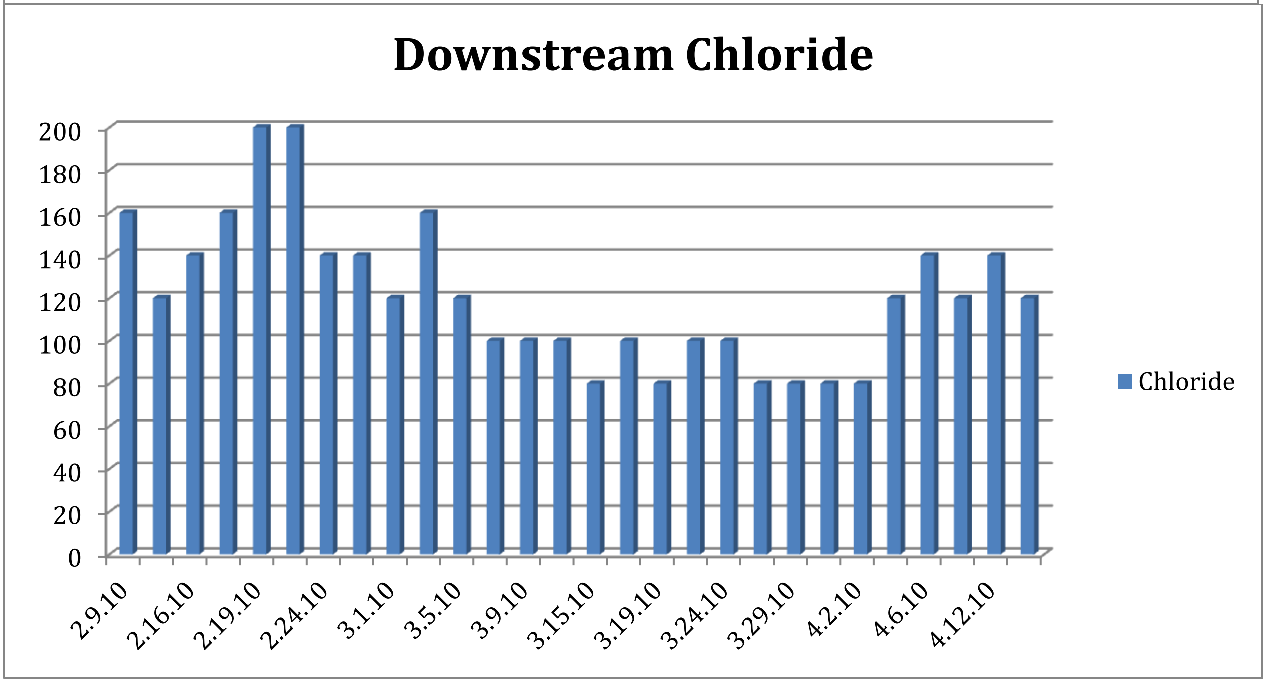

Upstream Chloride
250
200
150
100
50
0
2.9.10
2.12.10
2.16.10
2.17.10
2.19.10
2.23.10*
2.24.10
2.26.10
3.1.10
3.2.10
3.5.10
3.8.10
3.9.10
3.12.10
3.15.10
3.17.10
3.19.10
3.22.10
3.24.10
3.26.10
3.29.10
3.31.10
4.2.10
4.5.10
4.6.10
4.9.10
4.12.10
4.14.10
Chloride

River – Downstream

The average Downstream River TDS of 364 mg/l remained close to the baseline value of 332 mg/l. This represents an increase of 9.7%. However, the average chlorides, at 121 mg/l, were 81% higher than the baseline of 67 mg/l. The majority of this increase is most likely due to seasonal de-icing practices where salts applied to roadways were washed into the river from storm outlets. This is evidenced by the deviation as already noted in the Upstream Chlorides. The additional increase of 5% from Upstream to Downstream would include chlorides from non-point sources along the river way and the introduction of chlorides from the brine water study.




Downstream TDS
600
500
400
300
200
100
0
2.9.10
2.16.10
2.19.10
2.24.10
3.1.10
3.5.10
3.9.10
3.15.10
3.19.10
3.24.10
3.29.10
4.2.10
4.6.10
4.12.10
4.16.10
TDS


Downstream Chloride
200
180
160
140
120
100
80
60
40
20
0
2.9.10
2.16.10
2.19.10
2.24.10
3.1.10
3.5.10
3.9.10
3.15.10
3.19.10
3.24.10
3.29.10
4.2.10
4.6.10
4.12.10
Chloride

Toxicology

Date	**Ceriodaphnia dubia**		**Pimephales promelas**	
	TUa	**TUc**	**TUa**	**TUc**
February 20, 2010	AA	AA	-	-
March 6, 2010	AA	AA	-	-
March 13, 2010	AA	AA	-	-
March 20, 2010	AA	AA	-	-
March 27, 2010	AA	AA	-	-
April 3, 2010	AA	1.8	-	-
April 10, 2010	AA	AA	-	-
April 17, 2010	AA	AA	AA	AA

Patriot Water Treatment in conjunction with Warren WWTP performed 8 weeks of chronic toxicity testing to determine whether the release of brine from Patriot Water Treatment would impact the water quality of Warren WWTP effluent discharged from Outfall 001. Due to the fact that increased salt concentrations impact *Ceriodaphnia dubia* more readily than the *Pimephales promelas*, the water fleas were the primary species used in this study, however, during the last week of testing the minnows were subjected to the brine water also to investigate any potential impacts. The largest impacts were observed in the upstream water which is outside of the influence of the effluent. These effects are not indicative of toxicity as a result of Warren's effluent or Patriot's brine water. The two testing events that indicated toxicity in the upstream receiving water showed that the toxicity was reduced or no longer present in the far field water samples. Overall the results of this study have indicated that if Patriot Water Treatment discharges a consistent amount of brine water over an extended period of time then there will be no adverse changes in the water quality of Warren WWTP or in the Mahoning River downstream of outfall 001.

Daily Chloride Loading to the River

This information provides a better model of loading in terms of pounds of chlorides to the river. To achieve this, I obtained the chart from USGS that shows the Mahoning River flow in cubic feet per second. I than broke out the dates that the study occurred and totaled the flow, dividing by the total number of days to establish an average daily flow in cubic feet per second. I converted this number to million gallons per day and used this to calculate pounds applied. The following tables demonstrate the results of these calculations.

BASELINE DAILY CHLORIDE LOADINGS

Avg River Flow MGD	Upstream Avg Daily Load lbs/day	Downstream Avg Daily Load lbs/day	Plant Avg Daily Load lbs/day
867.27	506,314.39	484,615.20	20,439.42

STUDY RESULTS - DAILY CHLORIDE LOADINGS

	Upstream		Downstream			Plant Effluent	
Avg River Flow MGD	Avg Daily Load lbs/day	Peak Daily Load lbs/day	Avg Daily Load lbs/day	Peak Daily Load lbs/day	Avg Plant Flow MGD	Avg Daily Load lbs/day	Peak Daily Load lbs/day
867.27	852,488.76	1,612,972.97	873,134.10	1,446,612.53	15.61	46,867.46	118,995.12
% Over Baseline	168.37	318.57	180.17	298.51		229.30	582.18
Lbs. Over Baseline	346,174.38	1,106,658.59	388,518.90	961,997.33		26,428.04	98,555.70

This information demonstrates that the river was able to assimilate a peak daily load of chloride 318% greater than the baseline loading without any toxicology issues. In total pounds applied this means that an additional 1,106,658 pounds of chlorides over baseline was assimilated without adverse effects to the river biology. Warren's highest peak daily loading of chloride was only 118,995 pounds.

2010 Pilot Study Conclusion

The 8 week Pilot Study demonstrated that a controlled discharge of brine water into Warren's WWTP did not have adverse water quality impacts to the treatment facility or receiving stream. The Study supports the initial toxicology test that indicated that Warren would be able to accept up to 664,000 gallons per day of brine water at a maximum limit of 50,000 mg/l TDS at 8 MGD daily plant flows. The 8 MGD is set as the low flow limit that can occur in mid-summer at 3:00am..

Based on the results of the Pilot Study, Warren should be able to accept brine water at the initial rate of 100,000 gallons per day at a concentration of 50,000 mg/l TDS (41,700 lbs. TDS) and increase flow at a controlled rate, while sampling, to determine final ceiling concentration.

The Pilot Study was completed in April of 2010 and the report provided to OEPA by May of 2010. OEPA did not issue a modified NPDES to Warren to allow for treatment of flowback brine until December of 2010.

Daily Processing

Ohio's whole model for the treatment of low TDS flowback brine wastewater is based on the observance of issues that was witnessed during 2009 through 2010 by treatment plants that was processing brine wastewater in Pennsylvania. The following matrix highlights the differences between Pennsylvania and Ohio for acceptance and treatment of Hydraulic Fracturing Wastewater Treatment:

Pennsylvania	Ohio
Direct discharge to the municipal wastewater treatment facility	Direct discharge to a municipal wastewater treatment plant will not be allowed
No limit set on volume of brine water being discharged	A limit will be set on the total volume of brine water that can be treated daily
No limit set on total suspended solids (TDS) in the brine water	A limit of no greater than 50,000 mg/l of TDS in the flow will be allowed
No testing of the brine water	All brine water will be regularly tested
No toxicity testing on combined flow discharge	Quarterly toxicity testing will be accomplished
No baseline testing initiated	Baseline levels will be established

Pennsylvania had been accepting Oil & Gas Well Industry brine water since approximately 1984. This initial water was not from the Marcellus Shale Play but from traditional vertical drilling processes where hydraulic fracturing was not being used. Some of this early process water was being discharged into local municipal wastewater treatment facilities.

The practice continued throughout the 80's, 90's and early part of 2000 without incident, oversight or concern. When the boom occurred on the Marcellus Shale Play in 2008, the volume of brine water that needed to be disposed of increased significantly. As a result of this increase, 35 municipal wastewater treatment plants began directly accepting brine water. Because of over 20 years of practice accepting brine water without incident, no limits on volume or pollutants were set and no additional testing requirements were initiated. The practices that were employed were:

- Direct discharge to the municipal wastewater treatment facility.
- No limit set on volume of brine water being discharged.
- No limit set on total suspended solids (TDS) in the brine water.
- No screening of the brine water for heavy metals, radiation, organic or volatile compounds.
- No toxicity testing on combined flow discharge.
- No baseline testing initiated to determine facility of receiving stream current levels of pollutants.

Ohio's approach was completely different. In 1985, USEPA mandated the requirement of Industrial Pretreatment. Prior to 1985, large amounts of heavy metals, volatile and organic compounds were routinely discharged into a municipal wastewater facility. The mandate for pretreatment required an industry to develop treatment practices that removed pollution of concern at the point source to a level that was set through federal categorical and local limits. These limits were designed to allow a municipal treatment facility to safely discharge wastewater into a receiving stream with pollutant concentrations at or below acceptable levels. The implementation of this procedure substantially improved water quality.

This is the method that Ohio employed for the handling of brine water. Ohio initiated the 8 week, live process, pilot study to determine the feasibility of brine water treatment. The pilot study led to the treatment practices as follows:

- Only Flowback, muddy and brackish brine water will be allowed for treatment. No Produced water will be allowed.
- Direct discharge to a municipal wastewater treatment plant will not be allowed. Brine water must go to a centralized waste treatment facility (CWF) for pretreatment prior to discharging to a municipal wastewater treatment facility (MWTF). The CWF will remove heavy metals, suspended solids and other pollutants to categorical and local limits and adjust pH prior to discharge.

- A limit will be set on the total volume of brine water that can be treated daily. This limit will be established based on the ability of the treatment facility to assimilate without toxic conditions or water quality conditions occurring.
- A limit of no greater than 50,000 mg/l of TDS in the flow will be allowed to be discharged from the CWF into the MWTF.
- All brine water will be regularly tested for heavy metals, radiation and volatile compounds and will be summarized in a daily operational report.
- Quarterly toxicity testing will be accomplished by the MWTF.

Ohio's method uses the time proven technique of centralized point source pretreatment with structured limits and testing requirements where Pennsylvania's method basically had no controls at all.

In October of 2010, OEPA issued a PTI to Patriot Water Treatment LLC to install and operate a centralized waste treatment facility for brine water treatment. In September of 2010, OEPA issued a draft NPDES modification to Warren that would allow for the acceptance and treatment of low TDS flowback brine wastewater from a CWF. The limits set did not take into consideration the data accumulated from the Pilot Study and appeared to be an arbitrary number set by the confines of the final limits used in the Pilot Study; 100,000 gallons per day at a concentration of 50,000 mg/l. However, the Pilot Study did not run for a full 24 hr. day but was constrained to the hours when Warren management was on site. This resulted in an 8 hour "day." Therefore the Pilot Study had clearly demonstrated that Warren could accept 300,000 gallons of flowback brine at a concentration of 50,000 mg/l TDS during a 24 hr. period without upset to the plant or receiving stream.
This was pointed out to OEPA in a series of letters between the months of September – December 2010. Another issue of concern was that while the NPDES permit was limiting the volume of flowback brine that could be treated to 100,000 gallons at 50,000 mg/l TDS, the restriction was based on gallons accepted not pounds of pollutant received.

The fundamental problem with this is the discharge limit of 100,000 gallons per day had no referential scientific or reasonable basis. If a finite number was being assigned to a facility, the number should be pounds applied not volume. OEPA did not accept these concerns and without explanation, issued a final NPDES permit revision on December 1, 2010 to allow the POTW to accept brine waste water generated during oil and gas well drilling, development and production. The brine waste water must be discharged from a Centralized Waste Treatment (CWT) facility. The waste water discharged from a CWT to the Warren POTW had the limitations set at a total acceptance of 100,000 gallons of flowback brine per day at a maximum concentration of 50,000 mg/l TDS.

TDS levels in the receiving stream would be a major concern to the overall acceptance and success of the treatment model. Warren's receiving stream, the Mahoning River, flowed into Pennsylvania where the state had recently enacted new in-stream TDS limitations. These limitations required OEPA to ensure that river levels at the Ohio/PA border remain at or below 500 mg/l TDS. Realizing that the overall success of this program depended on how TDS would impact river quality, Warren initiated a self-imposed river sampling program that monitored TDS levels throughout the watershed. The initial program sampled locations upstream and downstream of New Castle, PA, a community just across the state border that was receiving gas & oil well brine water for treatment at their Wastewater Plant which discharged into the Mahoning River and locations on the Shenango River which flowed immediately east of New Castle and joined with the Mahoning south of the community to form the Beaver River. This sampling program was initiated on November 1, 2010 before OEPA had even issued Warren the NPDES modification to allow for brine water treatment.

Additional locations upstream and downstream of Warren were added to better model point and non-point source river levels throughout the watershed. Over the course of the last two years, more locations were added that extended into PA and eventually down to the Ohio River which the Beaver River is tributary to. A total of 8 locations were finally part of the sampling regiment. This allowed for a more complete modeling of the watershed. Initially only TDS was being analyzed as a whole but we began to analyze for both Chlorides and Sulfides to better develop origination sources of the TDS. Pennsylvania has a very developed and active Mining Industry that contributes to the overall load of TDS in the rivers. The dominant dissolved mineral from this activity would be Sulfides whereas Chlorides would constitute the majority of dissolved solid from oil & gas brine waste.

In May of 2010 we began to analyze for Bromide when it was determined that it was a potential pollutant of concern from oil & gas brine wastewater due to the development of Trihalomethanes in the presence of Chlorine in drinking water treatment facilities. All of these testing regimens are self-imposed and not required by OEPA. All sampling is conducted once a week by our Industrial Pre-treatment Coordinator. With the monitoring protocol in place Warren began accepting 100,000 gallons per day of pre-treated flowback brine water with a maximum concentration of 50,000 mg/l TDS from Patriot Water Treatment LLC on December 27, 2010. This process has continued to date uninterrupted except for a 3 month period in 2012 when OEPA issued a new NPDES Permit that removed Warren's ability to accept brine water.

In December 2010, Warren filed an appeal with the Environmental Review Appeals Commission (ERAC) to the NPDES modification challenging the 100,000 gallon per day limit as the controlling parameter. In May of 2011, OEPA issued a letter to the Ohio Department of Natural Resources (ODNR) indicating that the permits issued to Warren and Patriot were in violation of ORC 1509.22 and would not renew the modification when Warren's current permit expired on December 31, 2011. This resulted in a legal battle that raged for the remaining part of 2011 but at no time did either OEPA or ODNR issue an order to Warren or Patriot to stop treatment. During the next year and 4 months, Warren continued to accept pre-treated brine water from Patriot without any plant or receiving stream violations or upsets. OEPA did not issue a new NPDES to Warren until April 1, 2012 where OEPA inserted a new Section BB that stated:

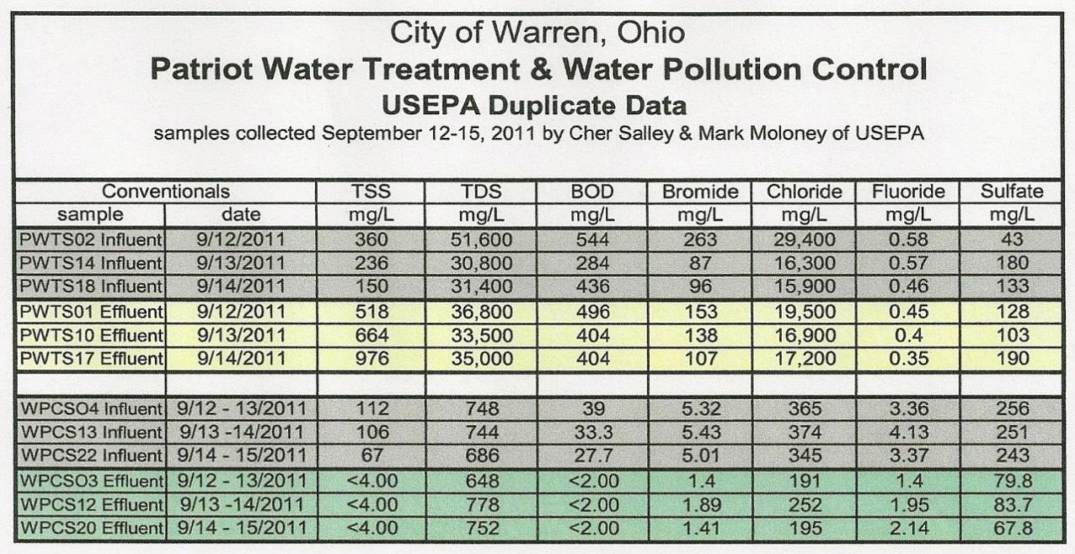
> *Beginning on the effective date of this permit, the permittee shall stop accepting brine wastewater from oil or gas drilling, exploration or production. Disposal of brine wastewater from oil or gas drilling, exploration or production through a wastewater treatment plant and discharge to waters of the state is not an authorized method of disposal under R.C. 1509.22(C)(1) unless and until it is approved by the Chief of the Division of Oil and Gas Resources Management for testing or implementing a new technology or method of disposal. If such an approval is granted under R.C. 1509.22(C)(1) by the Chief of the Division of Oil and Gas Resources Management, the*

> *permittee must submit an NPDES Permit Modification application to Ohio EPA for approval prior to acceptance of brine wastewater. The permittee may not accept brine wastewater from oil or gas drilling, exploration or production until after an NPDES Permit Modification authorizing acceptance of the material is approved.*

This caused Warren to order Patriot to cease discharging brine water to its Municipal Wastewater Plant effectively shutting down Patriot. Warren immediately appealed the new NPDES to ERAC and asked them to enjoin it with the existing appeal. ERAC denied the enjoinment based on the previous appeal was for a modification that did not exist and rendered the appeal mote, but allowed the appeal of the new permit to be placed into proceeding schedules already established for the previous appeal. This allowed a hearing on the new NPDES permit to begin in April of 2012 and was completed in early May of 2012. On July 3, 2012 ERAC determined that Section II, BB of the 2012 Warren NPDES was both unlawful and unreasonable. In so holding, ERAC unilaterally modified Warren's NPDES to remove Section II, BB in its entirety. ERAC also upheld Patriot's 2010 PTI which contained an express provision allowing Patriot to send oil and gas waters to Warren. Warren issued a letter to Patriot to start up operations in July of 2012 and Warren has continued to receive daily discharges from Patriot since that time without a single water quality violation or facility upset.

On September 12, 2011 through September 16, 2011, USEPA Region 5 conducted a compliance inspection to determine that the Warren WPCC was only accepting brine waste water generated from the oil and gas industry from one CWT facility (Patriot), and that the POTW had not experienced any of the following conditions since accepting the brine waste water:

1. Diminished or inhibited performance of the biological treatment processes,
2. Adverse impacts to the downstream water quality,
3. Adverse impacts to the quality of the facility's biosolids.



City of Warren, Ohio

Patriot Water Treatment & Water Pollution Control

USEPA Duplicate Data

samples collected September 12-15, 2011 by Cher Salley & Mark Moloney of USEPA

Conventionals		TSS	TDS	BOD	Bromide	Chloride	Fluoride	Sulfate
sample	date	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
PWTS02 Influent	9/12/2011	360	51,600	544	263	29,400	0.58	43
PWTS14 Influent	9/13/2011	236	30,800	284	87	16,300	0.57	180
PWTS18 Influent	9/14/2011	150	31,400	436	96	15,900	0.46	133
PWTS01 Effluent	9/12/2011	518	36,800	496	153	19,500	0.45	128
PWTS10 Effluent	9/13/2011	664	33,500	404	138	16,900	0.4	103
PWTS17 Effluent	9/14/2011	976	35,000	404	107	17,200	0.35	190
WPCSO4 Influent	9/12 - 13/2011	112	748	39	5.32	365	3.36	256
WPCS13 Influent	9/13 -14/2011	106	744	33.3	5.43	374	4.13	251
WPCS22 Influent	9/14 - 15/2011	67	686	27.7	5.01	345	3.37	243
WPCSO3 Effluent	9/12 - 13/2011	<4.00	648	<2.00	1.4	191	1.4	79.8
WPCS12 Effluent	9/13 -14/2011	<4.00	778	<2.00	1.89	252	1.95	83.7
WPCS20 Effluent	9/14 - 15/2011	<4.00	752	<2.00	1.41	195	2.14	67.8

Both Warren and Patriot were inspected and numerous tests were conducted. Overall, approximately 950 pages of documents were generated from the report. A summary of the key constituents of concern is shown below:

In addition to a complete metals analysis, radiological screening was accomplished. The inspection included sampling of the influent and effluent at the Warren POTW and Patriot and sludge press samples from Patriot and Warren were analyzed for RCRA levels. The report concluded that all sampling indicated the discharge for Warren's POTW was in compliance with the NPDES permit limitations for Final Outfall – 001and that none of the sludge sample results were above the RCRA Regulatory Toxicity Levels.

Daily Processing Summary

`The waste treatment model used in Warren has almost 2 ½ years of operational data that demonstrates that it is a safe and viable alternative disposal that compliments other disposal options including deep well injection. The model requires both a CWT and a POTW. It requires extensive testing by both entities which are mandated and voluntary. It only allows for a small percentage of hydraulic fracturing wastewater to be accepted. The water that this model accepts; low TDS, pit, flowback, muddy and storm waters are also the waters that are most problematic for deep well injection.

Not all POTWs will be able to develop a program that will allow this model to be implemented. A POTW must have dilution capacity, historical low TDS influent levels, receiving stream assimilation capacity and a very capable Pretreatment Program. It must also be willing to submit itself to mandatory and voluntary testing beyond typical NPDES requirements. While this model uses dilution as a control mechanism, it is the same mechanism currently used to handle like waste loads for other industrial sources such as Steel Mills, Food Processing Facilities, Pharmaceutical manufactures, paper producers and other high TDS dischargers. None of these industrial flows are fully treated in a conventional POTW.

Properly implemented, this model can become a catalyst for enhanced TDS treatment that all other industries could benefit from. Enhanced treatment technologies are available but are currently very costly to implement and operate. Working in partnership with the private sector, this model can be a bridge to better treatment. As has already occurred in other industrial treatment areas, this model provides a revenue stream that can support research and development. Developing programs with targeted goals for waste load reduction over a determined timeline can create the synergy necessary to achieve enhanced waste recovery systems that will be economical to install and operate.

Reducing Fresh Water Use in Upstream Oil and Gas Hydraulic Fracturing

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The statements made during the workshop do not represent the views or opinions of EPA.
The claims made by participants have not been verified or endorsed by EPA.

Hydraulic fracturing (HF) uses water as a carrier fluid for the sand or ceramic that props open the fractures. Typically, fresh groundwater or fresh surface water is used as a source of this water. Pioneer Natural Resources embarked on a multi-year initiative to conserve fresh water by reducing its use in HF.

Key definitions of water types include:

1. Fresh water – surface or ground water with total dissolved solids (TDS) less than 1,000 milligrams per liter (mg/l)
2. Produced water – naturally occurring water that is produced with the oil and gas and is normally high in TDS. This includes the initial water production that is occasionally referred to as flowback water.
3. Brackish Water – naturally occurring groundwater with TDS greater than 1,000 mg/l (not from an oil and gas reservoir)

The primary components of the study address:

1. Water quality needed for HF if using treated produced water or blended water
2. Water treatment technologies currently available that effectively treat produced water for reuse or recycling
3. Logistics of transporting produced water from its source to treatment site and on to the well for HF
4. Economics and environmental aspects of storing, transporting and treating water
5. Naturally occurring brackish water as a substitute for fresh water
6. Prevention of evaporation from storage

The variable natural of the formation rock and formation fluids requires different technical and economic solutions to conserve fresh water. This abstract evaluates some of the factors impacting HF and the potential solutions.

Water quality needed for HF

A third-party consultant was contracted to study the types of waters being used, types of fracture treatments being performed and possible fresh or brackish waters which could be used with treated produced water for three areas operated by Pioneer in Texas. The type of fracture design may dictate the quality of the water needed for the fracture fluid. For example, hydraulic fracturing technologies can vary between slickwater (mostly water-like fluid) and gels (fluids that create a gel-based fluid that holds the proppant.

The three areas used a variety of hydraulic fracturing designs, had varying water qualities that included higher concentrations of some naturally occurring minerals than optimal for the HF design. The solutions for all of the areas included removal of the total suspended solids (TSS).

The individual minerals needed to be addressed in some cases before the water could be re-used effectively.

The overall conclusion is water treatment levels need to be evaluated based on specific hydraulic fracturing design and available water quality. None of the recommended solutions require removing total dissolved solids (TDS) to replicate "fresh" water. The optimal solution may vary within a state or even within the basin or field.

Water treatment technologies

Pioneer has tabulated over 100 companies marketing water management and water treatment technologies. The technologies are generally established methods applied for use in water treatment operations which can be applied to oil field applications. Some technologies/systems include electrocoagulation (EC), flocculation, membrane filtration, chemical treatments and evaporative/distillation systems.

Pioneer tested the technologies employed by twelve companies during 2011 and 2012. Six of the representative pilot treatment results are shown in Table 1 below. The companies' names and certain identifying factors are hidden for confidentiality purposes. This data demonstrates most technologies removed some analytes, but effectiveness varied significantly. The red highlighted cells indicate effluent did not meet Pioneer's requirements for use in a HF application, while the green highlighted cells indicate treatment results were sufficient for HF use.

Table 1. Water Technologies Tested during 2011 and 2012.

		Membrane	Chemical, Forward Osmosis	Chemical	coagulation	Osmosis, Nanofiltration	coagulation	coagulation
Constituent	**Units**	**Avg. Change Inf to Eff**	**Avg. Change Inf to Eff**	**Avg. Change Inf to Eff**	**Avg. Change Inf to Eff**	**Avg. Change Inf to Eff**	**Avg. Change Inf**	**Avg. Change Inf to Eff**
Barium	**mg/L**	9%	-27%	-92%	-9%	-86%	217%	-7%
Boron	**mg/L**	8%	-15%	-54%	-4%	-25%	3%	-12%
Calcium	**mg/L**	20%	-12%	-97%	1%	-79%	58%	-8%
Chloride	**mg/L**	-4%	63%	-38%	-4%	-28%	42%	-5%
Iron	**mg/L**	-24%	-44%	-100%	71%	-98%	-100%	-100%
Magnesium	**mg/L**	18%	-22%	-44%	2%	-92%	45%	-8%
Oil & Grease HEM	**mg/L**	-87%	-83%	0%	48%	0%	0%	-100%
SiO2, Silica	**mg/L**	2%	-19%	-80%	-5%	-45%	-72%	-84%
Sodium	**mg/L**	19%	64%	-4%	0%	-24%	38%	-1%
Strontium	**mg/L**	2%	-15%	-81%	3%	-85%	140%	-5%
Sulfate	**mg/L**	-15%	148%	33%	-30%	426%	-10%	-18%
Total Dissolved Solids	**mg/L**	0%	46%	-28%	-3%	-51%	58%	17%
Total Suspended Solids	**mg/L**	**-48%**	**-44%**	**-93%**	**113%**	**-98%**	**-81%**	**-49%**

Treatment Passed PXD Guidelines	🟩
Treatment Failed PXD Guidelines	🟥

Analyte guidelines are set to prevent interference with hydraulic fracturing gels. This table suggests quality control of water treatment is difficult and variable. TSS, the most significant component, had observed reductions of 44% to 98% from influent TSS.

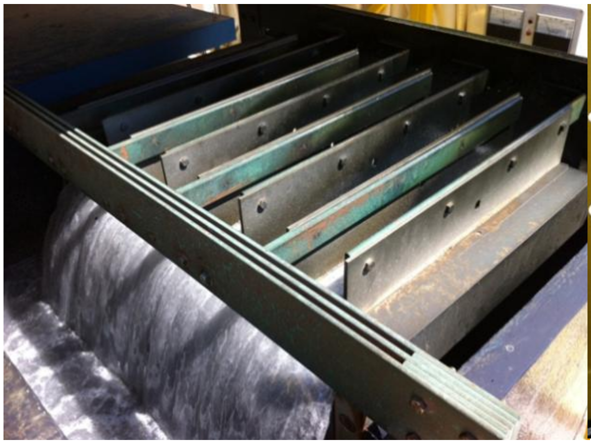

Figure 1. Electrocoagulation unit

Figure 2. Membrane Unit

Logistics of transporting produced water

Logistics of transporting and storing produced water is a significant portion of operations of water recycling in oil and gas operations. In a typical centralized treatment scenario, produced water must first be gathered from individual wells or to the centralized location where treatment occurs. Gathering water to a central location allows a critical mass which often translates to lower treatment costs. However, additional collection lines must be installed before recycling may commence. Alternatively, trucking of produced water is often employed for smaller volumes of water.

Once produced water is collected at a central site, treatment should immediately commence, so this water can be stored and available for immediate reuse. Typically, the HF process requires water at high rates and may use a majority of stored water in a short time. Often, temporary lines are used to transport treated produced water from central storage to a new well to be fractured. Produced water requires lines which do not leak, but can also be easily installed and moved to a new site at the end of HF treatment.

Economics and environmental aspects

Economics of recycling produced water in oil and gas operations are highly variable depend on:

1. Quality of water needed for planned HF design,
2. Quality of produced water,
3. Concentration of planned new HF wells to nearby produced water, and
4. Availability/accessibility to water disposal wells.

Typically, based on an available volume of water, produced water must first be accumulated in a central site where it can be treated. Small volumes of water are generally very expensive to treat; thus the desire to accumulate larger volumes in a central location makes sense. Often, additional water pipelines are needed to transport produced water to a central location. Capital cost increases with increasing distance and size of the pipeline, and can be highly variable. Whereas, operating cost of the pipeline is usually minimal. Alternatively, produced water can be trucked to a central site for treatment. Trucking costs may range from $1 to $3 per barrel depending on local conditions and distance transported.

At a central site, produced water may be treated by a variety of technologies designed to remove bacteria, eliminate any residual hydrocarbons and suspended solids, reduce potential scaling (a solid precipitation when minerals combine) caused by mixing different types of water, and, in some cases, removal of the majority of minerals through desalination. The type of fracture design may dictate the quality of water needed for fracture fluid. For example, hydraulic fracturing technologies can vary between slickwater (mostly water-like fluid) and gels (fluids under certain temperatures, pressures and chemical combinations, create a gel-based fluid that holds the proppant). The volume of water processed per day highly influences the cost to treat produced water to usable levels. This is partly due to a need to have operating personnel on location for water treatment. This effectively limits minimal volume of daily throughput for recycling to be economically viable to thousands of barrels of water per day; which can be the production from 10's to 100's wells. This reinforces why the accumulating phase of this process is so important. Treatment cost for minimal water treatment (not desalination) may range from $2 per barrel for high volumes to multiples of $2 per barrel for smaller volumes of water (which is more common). To desalinate produced water to a drinking water standard, costs may vary from $4 to multiples of $4 per barrel depending on the volume per day and the quality of inlet water being treated.

Once produced water is treated, it needs to be stored in tanks or a pond. An earthen pond is often more practical than having a large number of tanks. For saline water storage, water ponds often have more stringent construction criteria to assure safe storage of more environmentally sensitive water. The saline water ponds may cost $500,000 to an order of magnitude higher, compared to one third to one tenth for an equivalent sized storage designed for fresh water.

The last stage of the recycling process is to transport treated produced water from a central storage area to a HF site. Transportation of water is normally accomplished with a temporary no-leak line to the HF site which can stretch to five or more miles. Landowner approval is required and would typically include a payment for temporary access which could last two to four weeks. Because recycling involves produced water, the pipeline cost is typically twice the cost of fresh water pipeline transport.

An economic decision to recycle produced water is often driven by the cost of a next best alternative, which is typically disposal into a class 2 injection well. The cost of trucking water to a disposal well and the cost of disposing of fluid into a class 2 well vary depending on regional geology, availability of roads and the distance involved in trucking. Trucking and disposal costs may range from $1 per barrel of water to an order of magnitude higher in various parts of the United States.

Environmental factors, such as availability of water for HF, are very important in consideration for recycling produced water. If water is limited in an area, a company may decide to recycle produced water for strategic reasons, even if it costs more than sourcing fresh water. Additional environmental factors may need to be considered if recycling involves increased environmental exposure due to the storage or transport of produced water. Often, additional environmental risk can be mitigated by higher design standards and practices.

Naturally occurring brackish water as a substitute for fresh water

In some areas where HF is being employed, recycling produced water is significantly more costly than disposal of produced water into class 2 injection wells. In an effort to conserve fresh water, naturally occurring brackish water is sourced. Brackish water is generally defined as groundwater, not produced water, from an oil or gas reservoir, having a concentration of total dissolved solids (TDS) over 1,000 milligrams per liter (mg/l). Brackish water can be used directly for HF source water, in some cases. Although sometimes, it is blended with fresh water depending on the HF design and water quality.

Brackish water is not found everywhere. Usually brackish water is found deeper than fresh groundwater, and often produces at lower rates than shallower fresh groundwater. Because of these factors, brackish water may be more costly to source than fresh groundwater. The oil and gas industry has significantly increased use of brackish water in Texas[i].

Estimated at more than 2.7 billion acre-feet, brackish groundwater constitutes an important water supply option in Texas[ii]. "Much of the water in the state's aquifers is fresh; however, brackish groundwater is more common than fresh groundwater in the southern Gulf Coast area and in large parts of West Texas[iii]."

Prevention of evaporation from storage

Large numbers of water storage ponds are used for HF operations. The majority of water in Texas is fresh water stored in lined ponds to prevent leakage/loss. In hot dry climates, evaporation from water storage can be significant. The Texas Water Development Board (TWDB) estimates evaporation by county by month in Texas[iv].

Pioneer verified the evaporation rate in North Texas in July 2012 and found good agreement with the data on the TWDB website. Figure 4 shows the primitive, yet effective, evaporation testing bucket. Figure 5 is an installed pond cover in west Texas with a pump to move rainwater from above the cover to below the cover in an attempt to reduce/eliminate evaporation of water.

Figure 3. Testing a pond for evaporation

Figure 4. Pond Cover over freshwater storage

Subsequent economic evaluation indicates that the potential cost of covering a water pond may save enough water in some cases to pay back the cost of covering it. Cost of water and estimated life of the storage pond are significant inputs to the results. Operationally, the covers must float on the surface and have a method to prevent water, including rain, from accumulating on top of the cover. Pond covers must also be durable enough to withstand high winds and provide a practical operational solution. Assuming an operational and economic solution is found, current thinking indicates that storage covers may become one component in the effort to conserve fresh water.

Conclusions

Oil and gas uses a significant volume of water for HF. Until recently, the vast majority of water utilized for HF activities has been fresh surface water and fresh groundwater. The variable natural of the formation rock and formation fluids requires different technical and economic solutions to conserve fresh water. Although the most practical solutions to vary by region, the oil and gas industry is making strides to reduce fresh water consumption by reusing/recycling produced water, sourcing brackish water and preventing evaporation.

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[ii] Texas Water Development Board (2012) *Brackish Resources Aquifer Characterization System (BRACS)* funded by the 81st Texas Legislature, 2009.

[iii] George, Peter G., Ph.D., P.G., Mace, Robert E, Ph.D., P.G. and Petrossian, Rima, P.G., (2011*)* *Aquifers of Texas*, *Report 380* for the Texas Water Development Board.

[iv] Texas Water Development Board and the National Weather Service data collected from 1954 through 2011. *Precipitation & Evaporation* (2012)

Treatment for the Beneficial Reuse of Produced Water and Hydraulic Fracturing Flowback Water

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The statements made during the workshop do not represent the views or opinions of the EPA. The claims made by the participants have not been verified or endorsed by the EPA.

Introduction

Reuse of produced water and hydraulic flowback water will be a significant issue as the United States develops its oil and gas shale plays. Water is an essential component of the development of oil and gas wells, both in the development of the well and through the increased use of hydraulic fracturing techniques. Well development typically utilizes 60,000 to 650,000 gallons of water for the use of cuttings control and lubrication of the drill bit. Currently, 3 to 5 million gallons of water are utilized per hydraulic fracturing event per well.[8] One issue is the source of this water and its impact on the environment. The Colorado Division of Water Resources, Colorado Water Conservation Board, and the Colorado Oil and Gas Conservation Commission did a study on the amount of water used by energy companies. This amount was shown to be 0.14–0.8 percent of the annual flow of water in Colorado.[5] However, this would be close to what the City of Denver would use in 6 to 12 months. So, while this is a small percentage, it is a large volume of water, especially in drought conditions.

Several exploration and production (E&P) companies are embracing water reuse and recycling as part of their overall corporate structure.[6] Energy companies that wish to conserve and reuse water will require methods of wastewater treatment developed to allow for reuse and recycling. This paper discusses the water treatment facilities we have developed for produced and flowback water and what considerations are important in the feasibility of this water reuse opportunity.

To discuss the reuse of produced water or hydraulic fracturing fluids, we must first define these terms. Produced water is the water that originates in an oil or gas well and is developed with the oil and/or gas resource. Hydraulic fracturing flowback (flowback) water is defined as the water that is released from the well after a hydraulic fracturing process. This flowback water normally will return between 50 to 80 percent of the water that was originally used in the hydraulic fracturing process and is returned over a 60- to 90-day period. Produced water will follow the flowback water after the initial 60- to 90-day period. Therefore, if 5 million gallons are used in the hydraulic fracturing process, then 2.5 to 4 million gallons will be returned as flowback water.

Another important issue in the reuse of produced and flowback water is water quality. Water quality is important due to the components of the produced or flowback water and the interaction of these components with either the hydraulic fracturing fluids or the formation water. In addition, water quality determines the ability to treat and eventually discharge produced or flowback water to the surface. The regulations that affect these water quality components are also discussed. However, E&P companies need to be aware that the compounds used in their

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[8] Matthew E. Mantell, "Produced Water Reuse and Recycling Challenges and Opportunities Across Major Shale Plays," Chesapeake Energy Corporation, March 29, 2011.

operation can add to issues in treatment; therefore, any component added to their exploration fluids should be evaluated for its removal in wastewater treatment.

Water Quality

Produced and flowback water include water naturally occurring alongside hydrocarbon deposits as well as constituents injected into the formation. The following are the main contaminants of concern in produced and flowback water:[7]

- Total dissolved solids (TDS), ranging from brackish water (>1,000 mg/l) to saturation levels (>300,000 mg/l)
- Oil and grease
- Suspended solids
- Dispersed oil
- Dissolved and volatile organic compounds (VOCs)
- Heavy metals
- Radionuclides
- Dissolved gases and bacteria
- Chemical additives, such as biocides, scale and corrosion inhibitors, guar gum, and emulsion/reverse-emulsion breakers

The amounts of these constituents vary considerably from the formation water to the mixture of chemical additives.[8] In the early development of the production well there will be higher concentrations of the chemical additives, and later in the well development the produced water will be closer to the formation water. A more detailed listing of the typical flowback water chemical additives is found in Attachment A.[9]

Facilities for the Beneficial Reuse of Produced Water and Hydraulic Flowback Water

One of the first facilities constructed for the beneficial use of produced water was conceived in 2001 and constructed in 2005. The Wellington Water Works Produced Water Treatment Facility in northern Colorado, with a capacity of 5,000 bbl/day, has operated continuously since 2006 and has provided water for agricultural use, hydraulic fracturing makeup water, and municipal drinking water supply augmentation. This facility is dedicated to the Wellington Oil field.

A similar facility was developed for Harley Dome 1, LLC in Westwater, Utah. This facility is slated to start operation in June 2013 and has a capacity of 5,000 bbl/day with the potential to increase to 15,000 bbl/day. The facility is designed to discharge water to the Colorado River system but likely will sell most of the water as hydraulic fracturing makeup water.

We have worked on the design of treatment facilities for tight gas sand in Wyoming, coal bed methane (CBM) facilities in Wyoming and Colorado, and also oil production facilities in the Eagleford Field in Texas. All of these facilities have several common concepts for treatment.

Impacts on the Water Market

Sixteen energy-related constituents (energy companies, federal and state agencies, academia, environmental NGOs) were surveyed regarding hydraulic fracturing operations.[10] The top concerns from this survey were (1) water availability, (2) truck traffic, (3) surface spills and leaks, and (4) air pollution. These are the same issues identified by the EPA in their hydraulic fracturing studies. All of these issues can be resolved with proper water reuse facility treatment methods.

Treatment Issues

In the past, most companies have either used fresh water or a blend of produced water and fresh water with limited treatment. However, the growing need or desire for a higher percentage of water for reuse or recycling necessitates higher levels of treatment. The areas that need to be considered are as follows: (1) the final use of the water, (2) difficult treatment issues, (3) chemicals used in hydraulic fracturing, (4) air pollution issues, (5) brine disposal, and (6) potential for harvesting of elements from water.

1.0 Final Use of the Produced Water or Hydraulic Flowback Water

There are several areas that will fit into the recycling or reuse of produced water or hydraulic flowback water. These include (1) makeup water for hydraulic fracturing fluid, (2) stream discharge of the water, and (3) augmentation of municipal water supplies. A good summary of this type of treatment evaluation is found in Figure 1. This chart indicates the type of treatment required for the removal of various constituents.

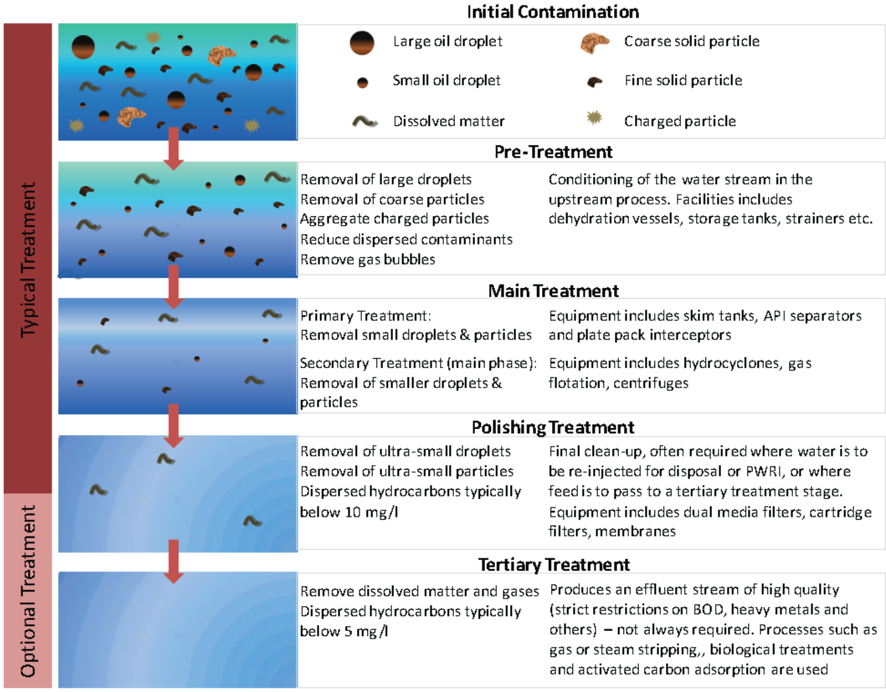


Figure 1. Treatment Requirements

Makeup Water for Hydraulic Fracturing Fluid

An excellent reference for makeup water treatment and criteria is found in Attachment B, the PTAC Water Decision Tree.[11] As noted on the chart, the items that need to be controlled are bacteria, scale formers, iron, corrosion parameters, and total dissolved solids. As long as these items are addressed, you can normally provide chemistry for the hydraulic fracturing fluid makeup to allow for successful operation.

Water Discharge to Surface Water or Groundwater

Water reuse for either agricultural or municipal water augmentation will require discharge to a surface water or tributary groundwater, which will require a discharge permit. Under 40 CFR 435, the EPA is allowed to regulate the discharge of wastewater from E&P operations under the Clean Water Act for industrial pretreatment categorical dischargers. However, currently the EPA only regulates discharge of produced water from offshore platforms. In 2010, Mr. Carry Johnston, of the EPA, investigated the potential for this regulation in the control of CBM waters. However, at this point, it appears to be a low priority for the agency.[12] We worked with the State of Colorado to develop a statewide permit system for the discharge of produced water or hydraulic flowback water. The statewide permit allows for the discharge of water with a known discharge value from a treatment facility. The compliance point is at the point of discharge and therefore in-stream mixing is not allowed as part of the permitted process. The time line for obtaining this type of permit is approximately 2 months. In particular, the sodium absorption ratio (SAR, the ratio of sodium to calcium and magnesium) is typically below a value of 3, which will require the control of sodium in the discharge. The other items of concern are typically metals and some organics. In addition, the discharge needs to meet the Toxicity Effluent Limits testing protocol. However, if the discharge is controlled for SAR, then meeting the toxicity limits is normally not an issue.

2.0 Difficult Treatment Constituents

We break the area of difficult treatment constituents into two areas: organics and inorganics. In the organic area, we have found that waters containing asphaltines, heavy oils, and paraffins require a special treatment process. The inorganics are normally controlled through the use of membrane filtration.

Organic Treatment Techniques

The organics are classified in two types. The first type is volatile organic compounds (VOCs). The VOCs are normally determined by benzene, toluene, ethyl-benzene, and xylene (BTEX). Of these compounds, the most difficult to treat for is benzene, due to the discharge limit of 0.001 mg/l. The techniques of air stripping and activated carbon adsorption have worked well at the Wellington facility.

The second type, the heavy organics such as the asphaltines, is removed utilizing a walnut shell filter (WSF). This is a process that is typical to the oil fields and has been used for decades. If there is any type of membrane treatment in the process, it is necessary to remove these heavy organics prior to treatment.

One of the most significant issues in the reuse of produced water and especially flowback water is guar gum. The values that we have seen in the field range from 100 mg/l to over 20,000 mg/l of guar gum. Guar gum is a thixotrophic material that is used to move the silica sand or proppant to the end of the

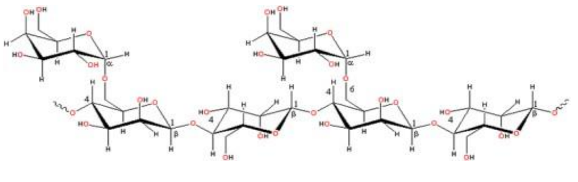


Figure 2. Guar Compound

fracture zone. This material is a significant hindrance to any filtration of this water.

Treatment of the guar gum, which is a natural polymer, will require either a breakdown of the polymer by enzyme chemistry or a reaction of the polymer with a cation, such as iron. Therefore it is extremely important to understand the levels of guar gum in the flowback water, how these different concentrations react to filtration, and to be able to test for this chemical additive in the field as well as the laboratory.

The control of microorganisms is also very important. Microorganisms can be abundant (more than 1×10^9 organisms per 100 ml) in produced water, depending on the formation. It is very important when considering reuse to control sulfate-reducing bacteria.

Inorganic Treatment Techniques

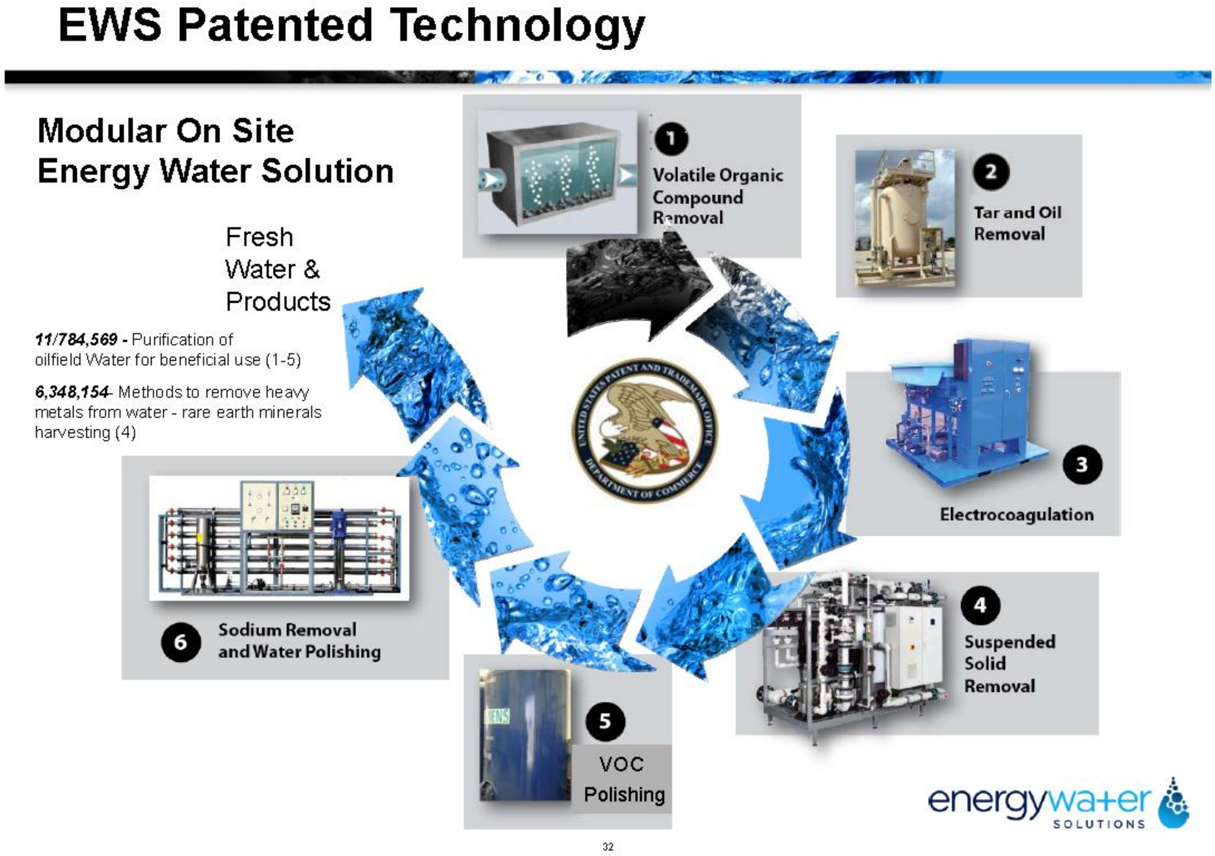
Inorganic treatment is typically controlled by precipitation chemistry. The use of ion exchange for this type of treatment is normally not used due to the brine stream that is created. The exception is the use of the Higgins Loop technology in CBM waters. This has been used extensively in the Powder River basin area of Wyoming and Montana. However, it normally requires a water in which the majority of the TDS is in the form of carbonates. In the areas that we have been involved in, we have found that the produced water is normally sodium chloride–laden water. The Higgins Loop is not useful for this type of water.[13]

We have found that the most useful treatment for inorganics is precipitation chemistry followed by ceramic microfiltration (CMF) and then either nanofiltration (NF) or reverse osmosis (RO). The precipitation chemistry can be performed utilizing the adjustment of pH and solubility or can also be accomplished by electrocoagulation (EC). Due to the concern of handling solids in the facility, the lowest pH possible to meet the NF/RO feed water criteria for precipitation is desired. This can normally be accomplished with the use of EC.

3.0 Overall Treatment Process

With the constraints identified above, we have developed the following treatment process stream:

- VOC removal with air stripping
- Oil/heavy organic removal with WSF
- Precipitation chemistry utilizing EC
- Removal of precipitated multivalent ions utilizing CMF
- Removal of remaining VOCs with activated carbon
- Monovalent ion removal utilizing NF/RO



EWS Patented Technology

Modular On Site
Energy Water Solution

Fresh
Water &
Products

11/784,569 - Purification of oilfield Water for beneficial use (1-5)

6,348,154- Methods to remove heavy metals from water - rare earth minerals harvesting (4)

Figure 3. EWS Treatment Process

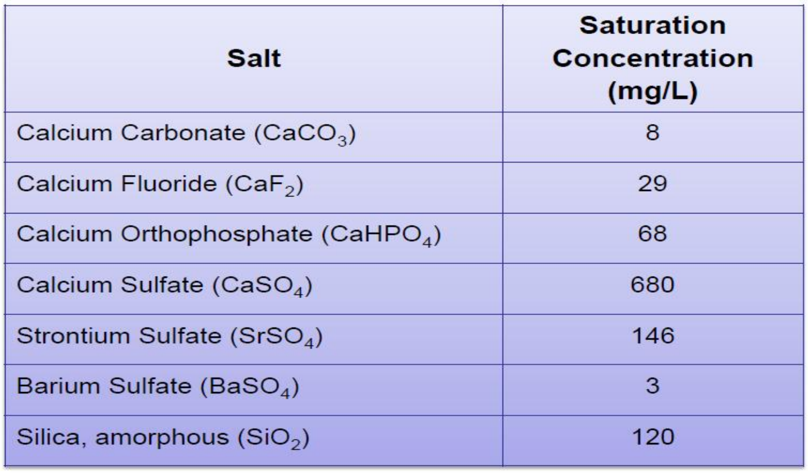
The flowchart in Attachment B provides the criteria for which water quality parameters need to be examined and also provides the type of treatment required. The areas that we have found to be critical for reuse of water in hydraulic fracturing are:

- pH
- Boron
- Barium
- Iron
- Calcium
- Magnesium
- Silica
- Strontium

These parameters will determine the chemistry precipitation and also address the scale-formation chemicals.

The other issue of concern is the scale-formation chemistry. As shown in Table 1, there are significant scale-formation constituents. These include barium sulfate, silicates, calcium, and magnesium. Therefore, if reuse is a consideration, the constituents that could form scales in the formation need to be removed so as not to impact the production well.

Table 1. Scale Formation Concerns



Salt	Saturation Concentration (mg/L)
Calcium Carbonate ($CaCO_3$)	8
Calcium Fluoride (CaF_2)	29
Calcium Orthophosphate ($CaHPO_4$)	68
Calcium Sulfate ($CaSO_4$)	680
Strontium Sulfate ($SrSO_4$)	146
Barium Sulfate ($BaSO_4$)	3
Silica, amorphous (SiO_2)	120

In addition to the above issues, it is important to consider which compounds can lead to interference issues with the hydraulic fracturing chemistry. An example of this is boron, which is an accelerant of the fracturing fluids. Therefore, the boron concentration must be below 1 mg/l in the hydraulic fracturing fluid makeup water.

These three components—guar gum, scale-forming chemistry, and hydraulic fracturing chemical accelerants—are difficult items to remove and will be a challenge as the industry moves forward with water recycling and reuse. An example of the water quality goals for hydraulic fracturing fluid makeup water is provided in Table 2.

Table 2. Water Quality Goals for Hydraulic Fracturing Fluids

Bacteria	100,000 per 100 ml
Barium (mg/l)	< 2
Bicarbonates (mg/l)	250 to 100,000
Calcium (mg/l)	300
Chlorides (mg/l)	2,000 to 40,000
Iron (mg/l)	10
Hydrogen sulfide (mg/l)	ND
Magnesium (mg/l)	100
pH	6.5 to 8.0
Phosphates (mg/l)	10
Radionuclides (pCi/l)	<15
Reducing agents (mg/l)	ND
Silica (mg/l)	<20
Strontium (mg/l)	<10
Sulfate (mg/l)	400 to 1,000
Total Dissolved Solids (mg/l)	500 to 5,000

4.0 Air Pollution Issues

The control of VOCs is important for the discharge of water to surface water or groundwater. The suggested treatment is air stripping. However, air stripping will require an air permit for this discharge. At the Westwater, Utah facility, we have found that capturing these VOCs for energy reuse is a cost-effective way of handling this material and results in the facility's being exempt from air permitting, except for the notification process.

5.0 Control of the Brine Stream

The control of the brine stream is currently the most challenging aspect in the overall reuse of produced water. The brine stream can have a TDS that ranges from 50,000 to 300,000 mg/l. This type of water can be reinjected into a Class II injection well. However, it appears that there can be other uses of this water if the scale-formation chemistry has been removed from the water stream, such as utilizing the brine as a makeup water for 10-pound brine used in the drilling process and the manufacturing of chemistry (hydrochloric acid or bleach solution and sodium hydroxide) in the chlor-alkali process. This area requires additional research, but would allow for a waste stream to become a usable by-product.

6.0 Potential for Harvesting of Elements from Water

We have also found potential for harvesting metals from this water. For example, in the CBM waters of southern Wyoming, the produced water contains a significant concentration of lithium. This lithium can be precipitated and captured for sale as a by-product. Additional research needs to be done to determine viability, but based on preliminary calculations, lithium recovery could be significant.

Lessons Learned from the Treatment of Produced Water and Hydraulic Flowback Water

The lessons learned from the treatment of produced water and hydraulic flowback water are as follows:

1. Economics is the primary driver for any type of reuse or recycling effort. If the energy company cannot process this water at a cost less expensive than the current disposal method, the likelihood of success is small. Therefore, it is important to take into account all of the costs, such as trucking, impact to the environment, water sourcing, etc. If these items are taken into account, the likelihood of reuse and recycling increases dramatically.
2. Organic removal, including microorganisms, is very important to the overall process. If membrane filtration is required, then the removal of heavy organics is necessary as well. We have found WSF is critical to this type of treatment process.
3. Organic removal of benzene will be required if the water is to be discharged from the facility. This will require air stripping and activated carbon.
4. Inorganic removal, for the control of scale formers and SAR, will be required if reused or recycled or discharged to the environment.
5. If these steps are taken in the treatment of produced water or hydraulic fracturing flowback water, then reuse or recycling is certainly possible. This will also address the

primary concerns—water sources, truck traffic, spills, and air pollution—of the industry, regulatory agencies, and environmental groups.

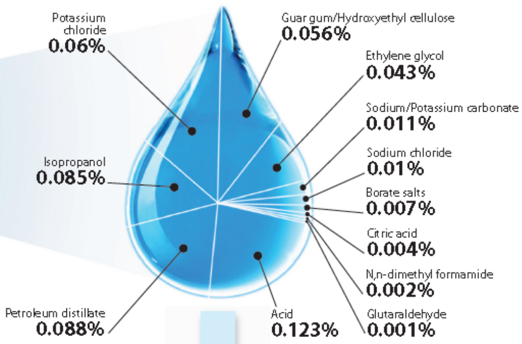
Conclusions

Water reuse and recycling will become one of the controlling factors for hydraulic fracturing of oil and gas wells in the United States. It will be crucial for the energy industry to develop the criteria for water recycling and reuse and to develop the treatment technologies and testing techniques to implement these recycling and reuse projects.

Attachment A. Typical Solution Used in Hydraulic Fracturing

A FLUID SITUATION:

TYPICAL SOLUTION* USED IN HYDRAULIC FRACTURING



Compound*	Purpose	Common application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant; Sterilizer for medical and dental equipment
Sodium Chloride	Allows a delayed break down of the gel polymer chains	Table Salt
N, n-Dimethyl formamide	Prevents the corrosion of the pipe	Used in pharmaceuticals, acrylic fibers and plastics
Borate salts	Maintains fluid viscosity as temperature increases	Used in laundry detergents, hand soaps and cosmetics
Polyacrylamide	Minimizes friction between fluid and pipe	Water treatment, soil conditioner
Petroleum distillates	"Slicks" the water to minimize friction	Make-up remover, laxatives, and candy
Guar gum	Thickens the water to suspend the sand	Thickener used in cosmetics, baked goods, ice cream, toothpaste, sauces, and salad dressing
Citric Acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice
Potassium chloride	Creates a brine carrier fluid	Low sodium table salt substitute
Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Washing soda, detergents, soap, water softener, glass and ceramics
Proppant	Allows the fissures to remain open so the gas can escape	Drinking water filtration, play sand
Ethylene glycol	Prevents scale deposits in the pipe	Automotive antifreeze, household cleansers, deicing, and caulk
Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, and hair color

On average, **99.5%** of fracturing fluids are comprised of freshwater and compounds are injected into deep shale gas formations and are typically confined by many thousands of feet or rock layers.

Source: DOE, GWPC: Modern Gas Shale Development In the United States: A Primer (2009)

*The specific compounds used in a given fracturing operation will vary depending on source water quality and site, and specific characteristics of the target formation. The compounds listed above are representative of the major material components used in the hydraulic fracturing of natural gas shales. Compositions are approximate.

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PTAC Water Decision TREE

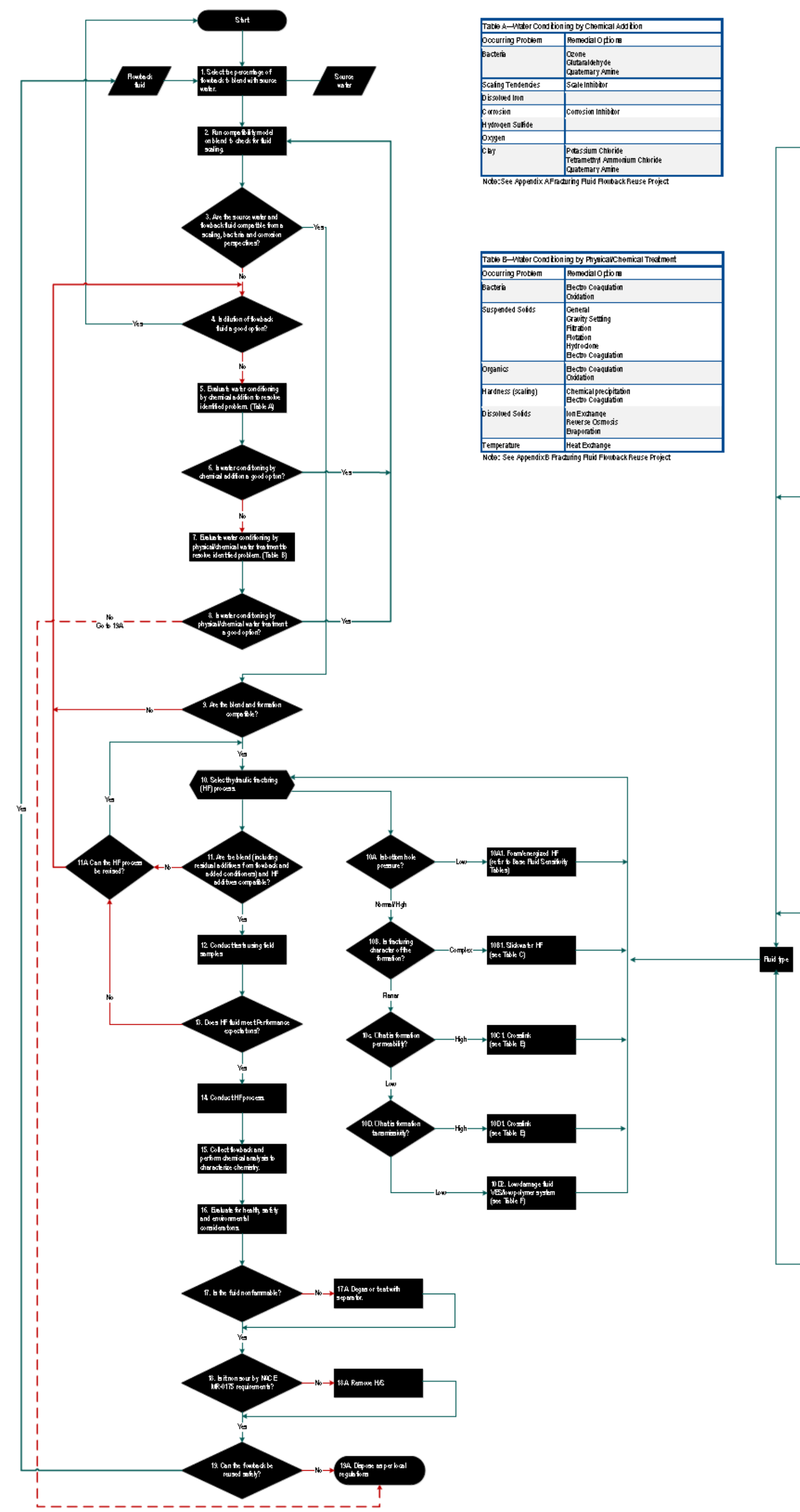

Table A—Water Conditioning by Chemical Addition

Occurring Problem	Remedial Options
Bacteria	Ozone Glutaraldehyde Quaternary Amine
Scaling Tendencies	Scale Inhibitor
Dissolved Iron	
Corrosion	Corrosion Inhibitor
Hydrogen Sulfide	
Oxygen	
Clay	Potassium Chloride Tetramethyl Ammonium Chloride Quaternary Amine

Note: See Appendix A Fracturing Fluid Flowback Reuse Project

Table B—Water Conditioning by Physical/Chemical Treatment

Occurring Problem	Remedial Options
Bacteria	Electro Coagulation Oxidation
Suspended Solids	General Gravity Settling Filtration Flotation Hydroclone Electro Coagulation
Organics	Electro Coagulation Oxidation
Hardness (scaling)	Chemical precipitation Electro Coagulation
Dissolved Solids	Ion Exchange Reverse Osmosis Evaporation
Temperature	Heat Exchange

Note: See Appendix B Fracturing Fluid Flowback Reuse Project

Table C—Slickwater

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	3–40	Temp for safe handling of fluid at surface lower temperatures may cause freezing problems	Use a hydration unit for mixing of water and friction reducer
pH	5.0–8.0	pH < 5 may cause prolonged hydration pH > 8.0 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	<90,000	High chloride concentration inhibits hydration. Greater amounts of friction reducer maybe required.	Mechanical vapour recompression, ionization, reverse osmosis, electrocoagulation
Hardness (mg/L $CaCO_3$)	<15,000	Divalent cations inhibits hydration	flocculation and coagulation, ion exchange, electrocoagulation
Concentration Factor for Residual Additive Ingredients	2	Friction reducer impact on formation	Breaker
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to reservoir	Settling or filtration

Table D—Linear Gels

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	15–40	Lower temperatures may prolong the hydration of gel polymers	Passive cooling in tanks or ponds Heat exchanger
pH	6.0–8.0	A pH < 6 may cause prolonged hydration of gel A pH > 8 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	<50,000	High chlorides concentration destabilizes the fluid and hydration	Mechanical vapour recompression (MVR), ionization, reverse osmosis (RO), electrocoagulation
Iron (mg/L)	<25	Iron degrades and breaks polymers in gels, causing premature breaking and crosslinking	Iron sequestration, oxidization
Sodium (mg/L)	<1000	Excess sodium destabilizes the fluid	Ion exchange, MVR, RO
Bacteria (CFU)	0	The presence of bacteria degrade the gel viscosity	Biocide, ozone
Concentration Factor for Residual Additive Ingredients	2	Polymer impact on formation and fresh additive	Breaker
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to Reservoir	Settling or filtration

Table E—Cross link Fluids

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	15–40	Temperature range for safe handling of fluid at surface and hydration of gel.	Passive cooling in tanks or ponds. Heat exchanger.
pH	6.0–8.0	pH < 6 may cause prolonged hydration of gel pH > 8 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	<30,000	High Cl- concentration destabilizes the fluid and creates problems with crosslinking	Mechanical vapour recompression (MVR), ionization, reverse osmosis (RO), electrocoagulation
Iron (mg/L)	<25	Iron degrades and breaks polymers in gels, causing premature breaking. Iron can also create premature crosslinking	Iron sequestration, oxidization
Alkalinity (mg/L $CaCO_3$)	<600	Acts as a pH buffer, so high concentrations of crosslinking activator may be needed	Ionization, mechanical vapour recompression, scale inhibitor
Sodium (mg/L)	<1000	Excess sodium destabilizes the fluid	Ion exchange, MVR, RO
Silica (mg/L)	<35	Excess silica may inhibit the crosslinking of polymer gels	
Bacteria (CFU)	0	The presence of bacteria degrade the gel viscosity	Biocide, ozone
Concentration Factor for Residual Additive Ingredients	Field Tests Required	Borate impact on control of crosslinking	Disposal of flowback or physical/chemical water treatment for dissolved solids
	2	Polymer impact on formation and fresh additive	Breaker
	Field Tests Required	Buffers impact on control of crosslinking	Disposal of flowback or physical/chemical water treatment for dissolved solids
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to reservoir	Settling or filtration

Table F—Viscoelastic Fluids

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	20–40	Temperature range for safe handling of fluid at surface	Passive cooling in tanks or ponds Heat exchanger
pH	5–12	Outside this range can effect properties of surfactants. Testing required	
Chloride (mg/L)	<33,000	Being outside of this range could affect the fluid quality and performance of standard chemistry. Alternative blends can be tested above this concentration.	Blending, mechanical vapour recompression, reverse osmosis, ionization, electrocoagulation
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to reservoir	Settling or filtration

Notes

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[7] "Challenges in Reusing Produced Water," SPE White Paper, 2012.

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Marcellus Wastewater Treatment: Case Study

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Natural gas represents an important energy source for the United States (US). According to the US Department of Energy's (DOE's) Energy Information Administration (EIA), over 20% of the country's energy needs are provided by natural gas. Thanks to the development of new nonconventional technology, the development of huge pools of oil and gas reserves, once thought to be too deep and held too tightly in shale rock formations, is now happening at a feverish pace in several areas of the US and the world. One of the most prominent of these "basins" in the US is the Marcellus Shale Basin – underlying large swaths of New York, Pennsylvania, Ohio, West Virginia, and Maryland. In the highly competitive US shale gas market, it is important for oil and gas (O&G) exploration and production (E&P) companies to find efficient solutions to one of the high-cost aspects of production; treatment of development and produced waters. Due to scarcity of water resources as well as regulatory constraints and expensive treatment technologies, E&P companies must develop and implement innovative methods for re-use and adopt more localized and centralized water management systems. E&P companies in various shale plays across the US are now consistently seeking out new methods to transport, dispose, and reuse development and produced water to maximize the profitability of shale gas production and remain competitive in a fast-growing market.

This paper covers the following topics with a focus on the Marcellus Shale Gas play in Pennsylvania:

- History of Eureka
- Future Plans
- Reuse Strategy
- Process Description
- Co-Product Reuse Studies
- Conclusions/Takeaways

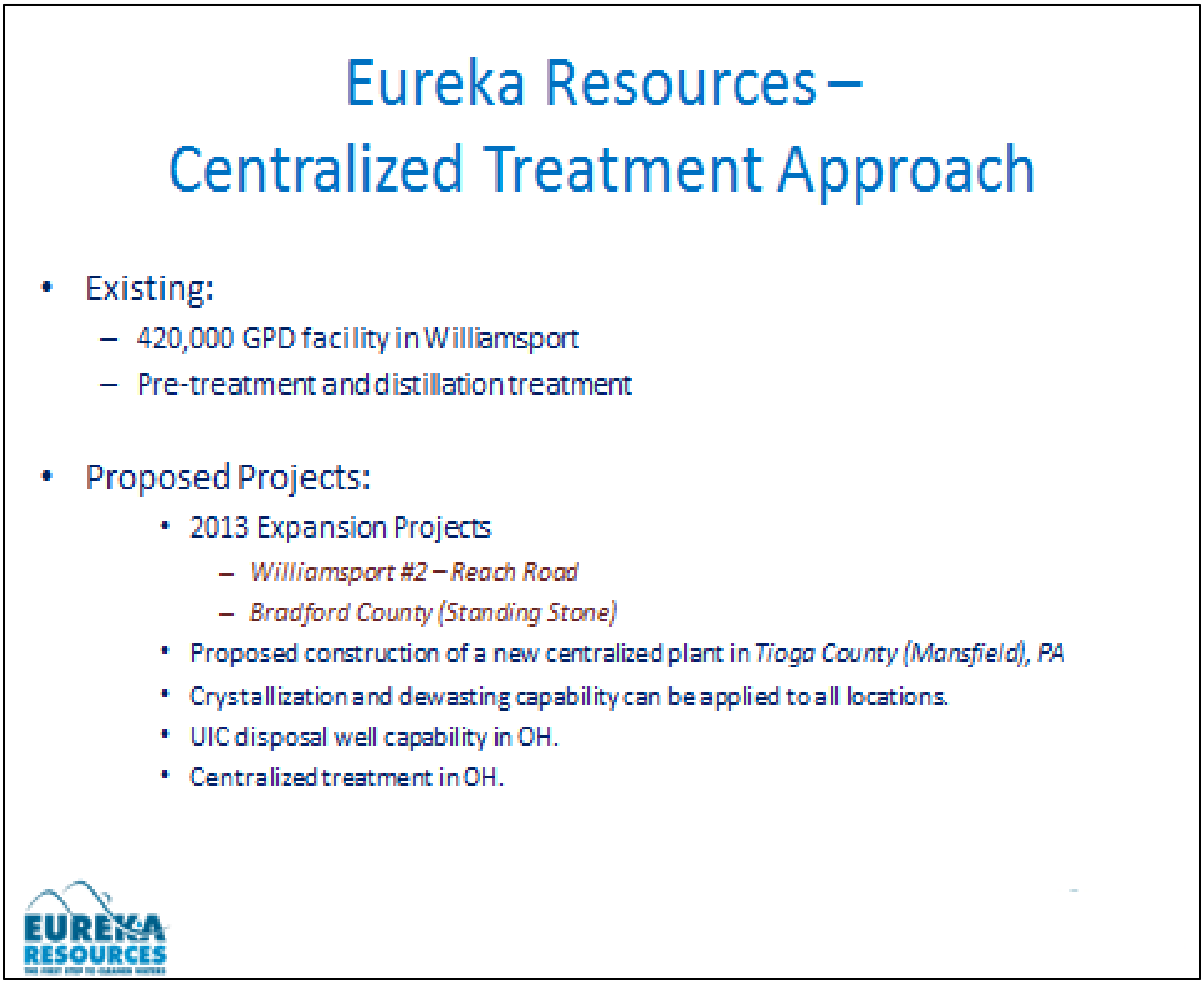
History of Eureka

Eureka Resources, LLC (Eureka) currently provides centralized treatment, recycling and/or disposal of flowback/produced waters (wastewaters), as well as waste drilling fluids generated as a result of nonconventional natural gas exploration and development activities in the Marcellus play. Eureka placed its first centralized pretreatment facility in operation in November 2008 in Williamsport, PA with a capacity of approximately 4,800 barrels per day (bpd) or 200,000 gallons per day (gpd). The facility was originally permitted by the PADEP Bureau of Waste Management under WMGR119. In 2010, Eureka opened an expanded centralized treatment facility which is currently capable of treating/recycling up to 10,000 bpd (420,000 gallons) of flowback/produced wastewater daily. The facility permit was converted to a WMGR123 permit at this same time, as authorized by the PADEP Bureau of Waste Management.

Eureka has the most comprehensive centralized wastewater treatment capabilities in the Marcellus play. Eureka's customers currently have the choice of requesting various levels of treatment with the goal of maximizing recycle of:

- Pretreated Water - water treated to reduce the suspended solids and heavy metals content and readily-settleable dissolved constituents.
- Distilled Water – water treated to remove more soluble dissolved solids,
- Concentrated Brine – water very high in TDS which can be reused as a drilling fluid additive.

Figure 1. Eureka Oil and Gas Wastewater Facility



Eureka Resources –
Centralized Treatment Approach

- Existing:
  - 420,000 GPD facility in Williamsport
  - Pre-treatment and distillation treatment
- Proposed Projects:
  - 2013 Expansion Projects
    - *Williamsport #2 – Reach Road*
    - *Bradford County (Standing Stone)*
  - Proposed construction of a new centralized plant in *Tioga County (Mansfield), PA*
  - Crystallization and dewasting capability can be applied to all locations.
  - UIC disposal well capability in OH.
  - Centralized treatment in OH.

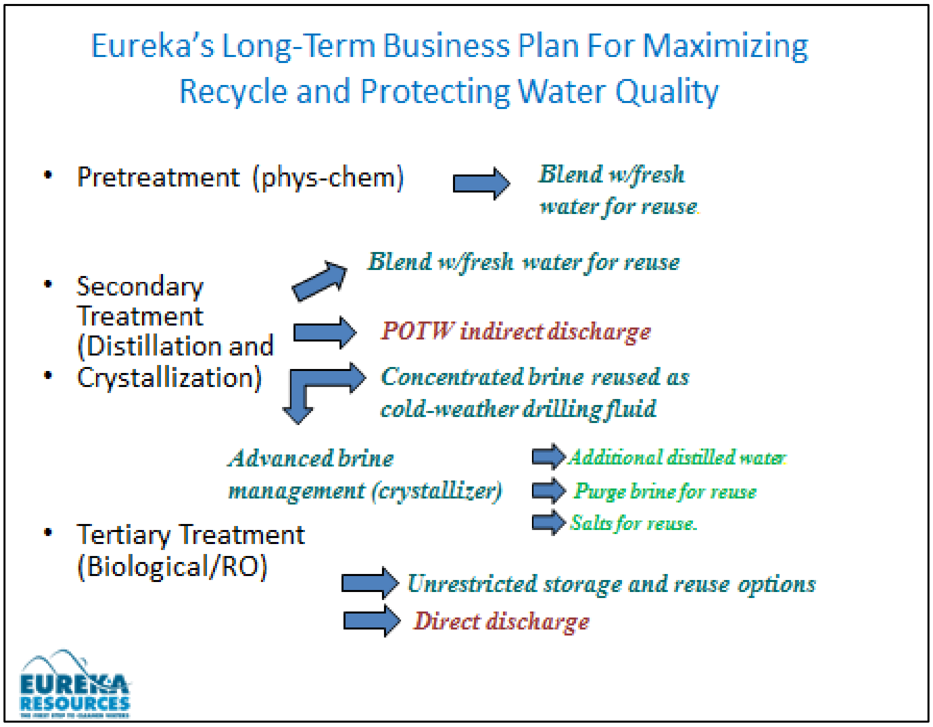
EUREKA RESOURCES

Figure 2. Eureka's Expansion Plan

Future Plans

Eureka is in the process of planning, permitting, designing, and constructing facilities to provide the following additional wastewater treatment/disposal services in support of nonconventional E&P activities below and on Figure 2:

- Concentrated Brine Management Options:
  - Further centralized treatment using mechanical vapor recompression (MVR) crystallizers, with beneficial reuse of a dewatered sodium chloride, calcium chloride and other purge stream byproducts
  - Deep well injection in Ohio and/or West Virginia
- Tertiary treatment of distilled water using membrane biological reactors (MBR) followed by reverse osmosis (RO) to generate dewasted water for unrestricted reuse [Patent Pending].
- Establishment of three more centralized treatment facilities in Pennsylvania, as well as possible additional centralized treatment facilities in Ohio and West Virginia.
- Dedicated producer centralized or satellite treatment and/or storage facilities.



Eureka's Long-Term Business Plan For Maximizing Recycle and Protecting Water Quality

- Pretreatment (phys-chem) → *Blend w/fresh water for reuse*
- Secondary Treatment (Distillation and
- Crystallization)
  - → *Blend w/fresh water for reuse*
  - → *POTW indirect discharge*
  - → *Concentrated brine reused as cold-weather drilling fluid*
  - *Advanced brine management (crystallizer)*
    - → *Additional distilled water*
    - → *Purge brine for reuse*
    - → *Salts for reuse.*
- Tertiary Treatment (Biological/RO)
  - → *Unrestricted storage and reuse options*
  - → *Direct discharge*

EUREKA RESOURCES

Figure 3. Eureka's Business Plan

Reuse Strategy

Eureka's long-term business strategy focuses on providing a centralized treatment facility for development and produced wastewaters that allows maximum flexibility for applying the level of treatment necessary to promote reuse of the treated water (see Figure 3). Using this approach, Eureka is able to provide the following for potential reuse by E&P companies:

- Pretreated Water
- Distilled Water
- Dewasted Water (meeting WMGR123 declassification effluent standards)
- Concentrated Brine Purge
- Dry Salt – Sodium Chloride (NACl) (< 3% moisture)
- Calcium Chloride (CaCl2) Brine or Dry Prills

All of the Eureka facilities are permitted such that we can install all or some subset of our anticipated unit processes. Our existing Williamsport Facility has oil recovery, pretreatment and mechanical vapor recompression distillers (See Figure 4). Eureka's Standing Stone facility (currently under construction) will have pretreatment and first phase (generating commercial grade sodium chloride) crystallization in 2013 and is expected to have second phase (generating commercial grade calcium chloride brine) crystallization and membrane biological reactor/reverse osmosis treatment capability in 2014 (See Figures 5 and 6). Descriptions of the unit processes employed by Eureka are summarized below:

PROCESS DESCRIPTION

Pretreatment:

- **Receiving Water Tanks**– Before any received water is unloaded into the partially below grade concrete receiving water storage tanks, it is first evaluated by one of the Eureka operators. The water is tested for total dissolved solids (TDS), barium, settleable solids, and also visually inspected for oil. If it passes the visual inspection, the truck is unloaded into one of the three concrete receiving water storage tanks at the direction of the plant operator.

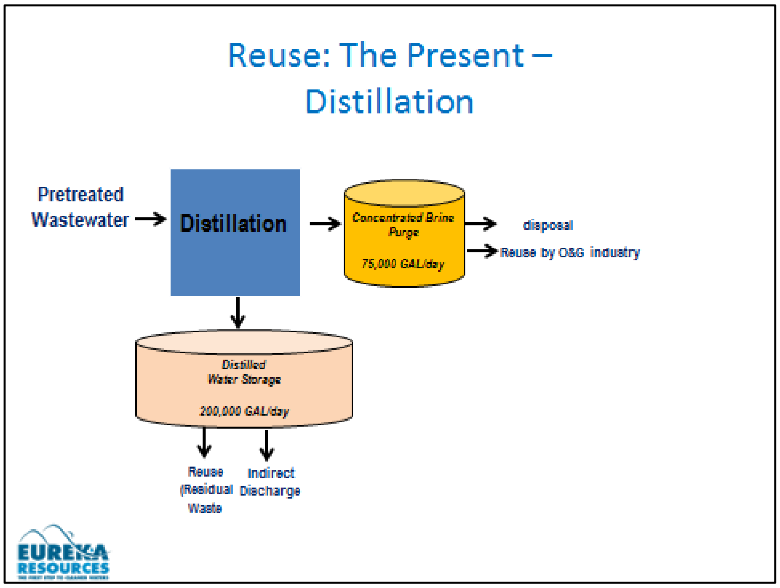


Figure 4. Eureka Existing Williamsport Unit Processes

- **Primary Settling Clarifiers/Oil Skimmers** – Situated above the concrete receiving water storage tanks are three steel clarifiers which are used to collect and remove any rapidly settling solids and trap oil. Prior to pumping water into these tanks, the large mixers in the concrete receiving water tanks are turned on to fluidize the contents. The slurry is then pumped into one of the overhead clarifiers. The heavy solids settle in these clarifiers, and the liquid overflows a weir and pours into a partially below grade concrete raw water transfer tank by gravity. The pump in the raw water transfer tank is used to transfer the water into one of the indoor storage tanks. The overflow weirs on the primary clarifiers are setup such that any free oil in the clarifier is collected at the surface of the tank by skimmers and stored in portable totes, and thus prevented from entering downstream treatment processes.

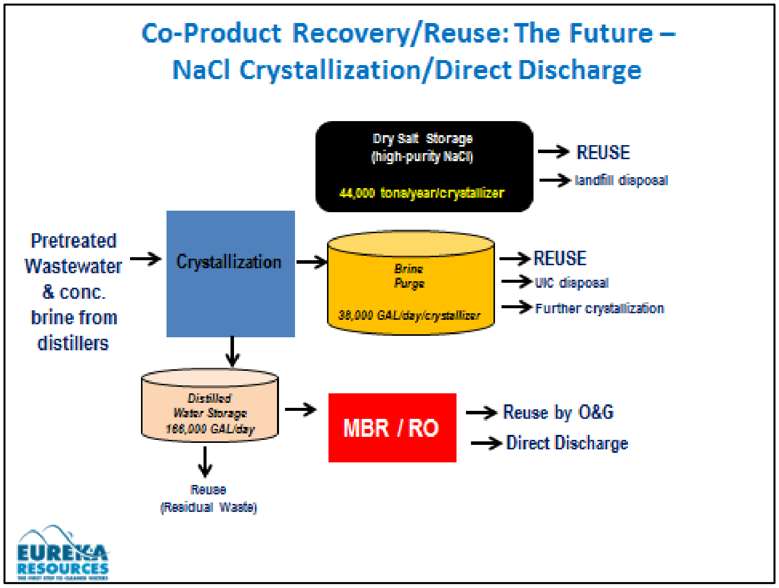


Figure 5. Planned Standing Stone Unit Processes

- **Oil Separation/Recovery Facilities** – The oil recovery system consists of a dedicated treatment process to treat oil-containing wastewater. A series of aboveground storage tanks are used to separate/recover waste oil material that is incorporated into certain types of incoming oil and gas wastewater received at the plant. Incoming oil and gas wastewater known to contain oil material is not discharged to the concrete receiving tanks like other wastewaters brought to the facility. Instead, it is directed to one of two receiving tanks located in the interior space immediately adjacent to the receiving water tanks. As the material in the tanks is allowed to equilibrate, the oil and water components begin to separate. Free water is drawn off of the bottom of the tanks by pumps and recycled back to the concrete receiving tanks.

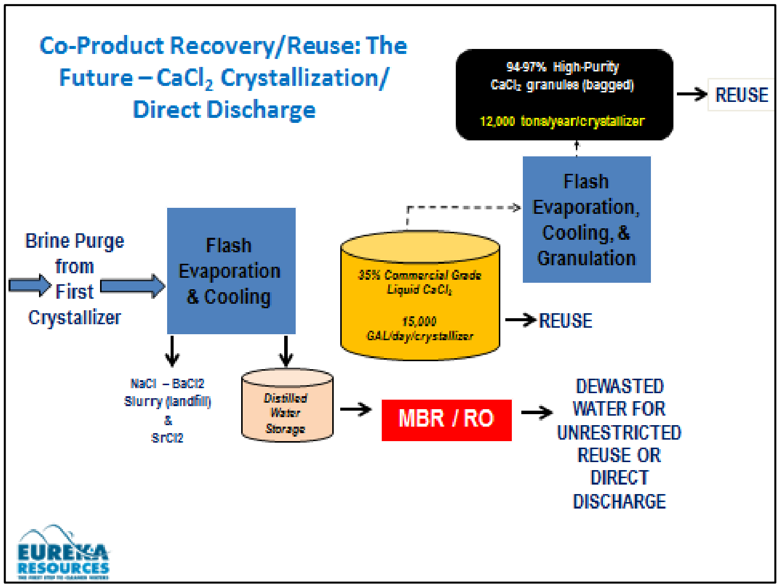


Figure 6. Future Standing Stone Unit Processes

  The remaining oil/water emulsion is conveyed to a heated tank. Free water forming on the bottom of the tank is drawn off by pumps and recycled back to the concrete receiving tanks. The remaining oil in the tank is pumped to a recovered oil storage tank. The recovered oil is offloaded into tanker trucks and sold. A pre-engineered heater-treater system is utilized to provide additional throughput and heat treatment capacity when necessary. Oil recovered in the heater-treater is pumped to the recovered oil storage tank, and subsequently offloaded into tanker trucks and sold. Water from the heater-treater is recycled back to the concrete receiving tanks.

- **Indoor Raw Water Storage Tanks** – Each of the 10 indoor above grade steel raw water storage tanks is equipped with a designated fill line from an overhead manifold that allows operators to select which tank to fill from the pump in the raw water transfer tank. When in operation, these tanks can also be isolated from the process along a common header that supplies a process feed pump. These two features enable operators to selectively fill and draw from a given tank or set of tanks in order to manage variable water quality. The process feed pumps deliver water from the specified raw water tank into pH adjustment/chemical addition tank No. 1 in either Pretreatment Train A or B, where chemical treatment begins.

  Over time, some solids settle/accumulate in the raw water storage tanks. There are two diaphragm pumps connected to the header at the bottom of the raw water storage tanks that can be used to transfer solids from the tanks directly into the sludge holding tanks.

This is done periodically in order to prevent the accumulation of unmanageable solids levels in the tanks.

There is a third header that can be used to put water into each tank individually from the final equalization tank in the process. If there is a process upset, this allows operators to recycle water from the end of the process back to the raw water tanks in order to manage out of spec water.

Chemical Precipitation:

- **pH Adjustment/Chemical Addition Tanks –** Prior to the secondary clarifiers, there are three pH adjustment/chemical addition tanks. Acid (hydrochloric) or alkali (caustic soda) can be added to each of these tanks in order to lower or raise the pH when necessary to achieve proper metals removals/settling. The second pH adjustment/chemical addition tank is used for pH polishing only. In the third pH adjustment/chemical addition tank, a coagulant can be added in order to aid in the removal of suspended particles.
- **Secondary Clarifiers –** Following pH adjustment and chemical addition, the process water flows into a clarifier. The settleable particles fall to the bottom of the clarifier before being pumped into sludge holding tanks. The resultant clarified pretreated water rises to the top of the clarifier from which it flows directly to a final equalization tank.
- Pretreated water is conveyed to Final EQ/Pretreated Water Transfer Tanks. The EQ tank serves as a wastewater transfer tank, where pretreated effluent is pumped to pretreated water holding tanks.

Sludge Dewatering:

- **Sludge Holding Tanks –** The solids from the bottom of the clarifier drains into a sump and are then pumped into sludge thickening tanks. The clear water that rises to the top of the thickening tanks is decanted by gravity back to one of the pH tanks.
- **Sludge Dewatering –** Thickened sludge is dewatered using either a plate-and-frame filter press, a rotary press or a centrifuge. The dewatered sludge cake is stored in sludge roll-off containers, which are hauled away for disposal when filled. The filtrate from the dewatering system is recycled back to one of the pH adjustment processes.

Secondary Treatment - Distillation:

- **Pretreated Water Holding Tanks –** Above grade steel pretreated water storage tanks are equipped with a designated fill line from an overhead manifold that allows operators to select which tank to fill from the pump at the pretreated EQ tank. Process feed pumps deliver water from the pretreated water tanks to NOMAD units. Eureka designs each facility with the option to use the process feed pumps to pump the pretreated effluent to tanker trucks to allow for reuse of pretreated effluent (i.e., physical-chemical treatment only without additional treatment through the NOMAD mechanical vapor recompression units) by gas drillers and producers for the extraction of natural gas from various shale gas drilling operations. Over time, some solids settle/accumulate in the pretreated water storage tanks. Two diaphragm pumps connected to a header at the bottom of the pretreatment tanks are used to transfer solids from the tanks directly into the existing sludge holding tanks, as necessary.

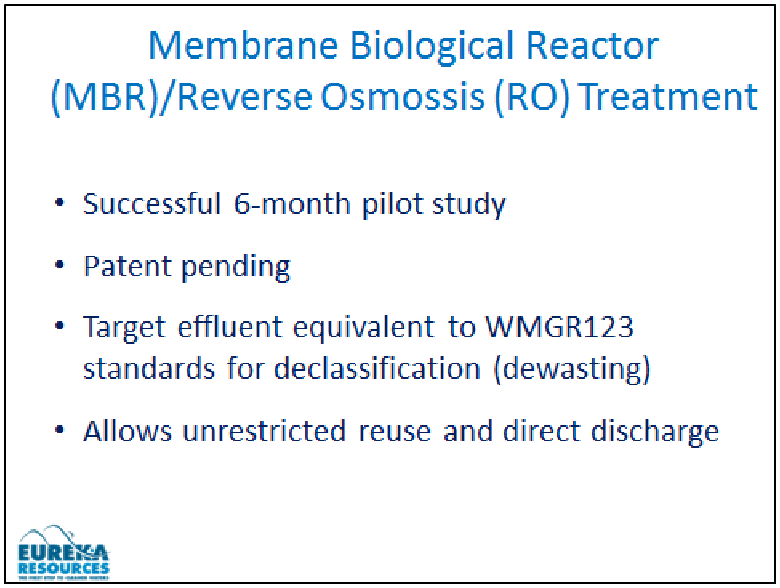
- **NOMAD Units** – If distillation treatment is needed, pretreated water is pumped from the Pretreatment Tanks into the NOMAD units. The feed water passes through the Feed Filter where any residual solids are removed. The feed water flow is then split into two streams and directed to the Feed/Distillate Preheat Exchanger and Feed/Concentrate Preheat Exchanger with the Feed Control Valves. The feed water heats up to near boiling as it recovers sensible heat from the hot distilled water and hot concentrate leaving the NOMAD. After the Preheat Exchangers, the two feed water streams combine to a single stream and the feed water enters the De-Aerator where non-condensable gases are stripped from the feed water and vented to atmosphere.
  The feed water drops to the bottom of the De-Aerator column where it combines with a large volume of hot re-circulating concentrate. The feed water blends with the re-circulating concentrate and then pulled out of the Separator Vessel through a nozzle beneath the De-Aerator by Recirculation Pumps. The hot re-circulating concentrate is driven from the Recirculation Pumps up through the Evaporator Exchanger where approximately 5% of the liquid is vaporized into steam on the outside of the exchanger cassettes. The mixture of steam and hot concentrate exits the top of the Evaporator Exchanger and flows into the Separator Vessel through the inlet nozzle. Inside the Separator Vessel, the hot concentrate separates from the steam by gravity. A vane pack type mist eliminator inside the vessel removes small particles of liquid from the steam. The steam is drawn from the Separator Vessel through the steam discharge nozzle by the Compressor. The Compressor boosts the pressure and temperature of the steam by approximately 6 to 8 psi and 18 to 23 F. The hot, high-pressure steam is driven from the discharge of the compressor to the Evaporator Exchanger. The steam enters the Evaporator Exchanger through the top. As the steam moves down through the inside of the exchanger cassettes it condenses into distilled water. The latent heat energy given up by this compressed steam as it condenses transfers to the circulating brine vaporizing an equivalent amount of brine. The amount of energy required to vaporize the brine are equal to the energy needed to compress the steam.
  The hot distilled water is collected in the Distillate Receiver. The discharge pressure of the Compressor and steam is determined by the temperature approach required to maintain boiling in the exchanger. Operating pressure in the Separator Vessel is maintained by regulating the excess steam from the distillate receiver to hold separator pressure between 0.75 and 1.5 psi.
- **Concentrated Brine Holding Tanks -** To maintain a constant specific gravity of re-circulating concentrate, a concentrate (or blow down) stream is drawn from the Separator Vessel with the Concentrate Pump. The hot concentrate flows to the Feed/Concentrate Preheat exchanger, where the concentrate cools down, passing its sensible heat to the incoming feed. The cool concentrated brine then flows out of the NOMAD and is pumped to concentrated brine holding tanks.
- **Pretreated Effluent/Distillate Storage Tanks –** The water stored in the distillate tanks is either trucked offsite by licensed/permitted haulers for beneficial reuse by gas well developers or, if reuse is not an option or under emergency conditions or during periods of low demand for treated effluent for reuse, discharged via indirect discharge permit.

Secondary Treatment - Crystallization

- **Crystallizer Unit -** The crystallizer unit is used to further process/dewater the brine concentrate currently produced by the NOMAD vapor compression distillation units or to process pretreated, high TDS wastewater. Brine stored in the concentrated brine holding tanks will be pumped to the crystallizer unit for treatment. The crystallizer is operated much the same way the distiller is operated using mechanical recompression technology. The crystallized salt material and possibly calcium chloride brine produced by the crystallization processes will be recovered and packaged for beneficial reuse or hauled to a landfill for disposal.

Tertiary Treatment:

- **Membrane Biological Reactor (MBR)/Reverse Osmosis (RO) treatment [Patent Pending] –** The MBR/RO system will allow Eureka to further treat the distilled water produced by distillers or crystallizers using biological treatment processes similar to those that are typically used at most municipal wastewater treatment plants (See Figure 7). Following treatment via these processes, the treated water will meet the declassification (dewasting) treatment standards set forth in Appendix A of the revised WMGR123 regulation recently issued by the PADEP (i.e., it will no longer be regarded as a residual waste). In Pennsylvania, this will allow for storage of the effluent in an impoundment or other facility under the control of an oil and gas producer prior to reuse as hydraulic fracturing water, without required compliance with storage and transportation requirements in 25 PA Code Chapter 299. The distilled, dewasted effluent will either be immediately trucked offsite by licensed/permitted haulers for unrestricted beneficial reuse by gas well developers, or temporarily stored onsite to be hauled offsite for unrestricted beneficial reuse at a later date, or discharged directly to surface water via a direct discharge permit.



Membrane Biological Reactor (MBR)/Reverse Osmossis (RO) Treatment

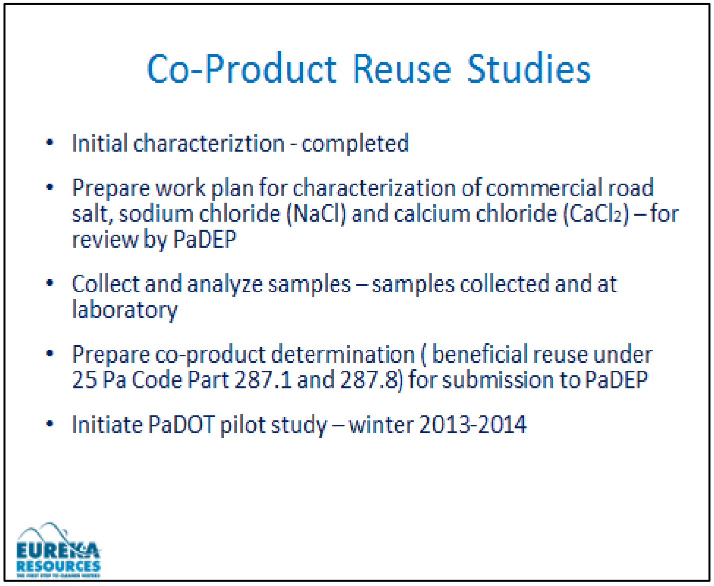
- Successful 6-month pilot study
- Patent pending
- Target effluent equivalent to WMGR123 standards for declassification (dewasting)
- Allows unrestricted reuse and direct discharge

Figure 7. MBR/RO Implementation Status Summary

  - **Membrane Biological Reactor (MBR) -** The MBR system is designed to provide biological removal of chemical oxygen demand (COD) and ammonia in the distilled water feed. The MBR system consists of feed pumps, a mixed anoxic tank, two aeration tanks, the membrane separation system, sludge recycle pumps, an automatic sludge wasting system, and final effluent pumps.

  - **Reverse Osmosis (RO) -** The RO system is used as a polishing step downstream of the MBR system to remove residual nitrate and sodium that may be in the MBR effluent.

In the RO process, water under pressure will be forced across a membrane element, with a portion of the feed permeating (by diffusion) the membrane ("permeate"), and the balance of the feed water sweeping along the membrane surface and exiting without passing through the membrane ("reject"). During the diffusion process, the membrane will freely pass the water molecules but will reject most of the dissolved salts and metal ions, the small particles as well as organic compounds and some bacteria. The reverse osmosis process will typically convert, or "recover", a certain percentage, approximately 80%, of the initial incoming feed water into "RO permeate". The remaining by-product, or the "RO concentrate", will contain/concentrate the salts rejected by the membrane.



Co-Product Reuse Studies

- Initial characteriztion - completed
- Prepare work plan for characterization of commercial road salt, sodium chloride (NaCl) and calcium chloride ($CaCl_2$) – for review by PaDEP
- Collect and analyze samples – samples collected and at laboratory
- Prepare co-product determination (beneficial reuse under 25 Pa Code Part 287.1 and 287.8) for submission to PaDEP
- Initiate PaDOT pilot study – winter 2013-2014

Figure 8. Co-Product Reuse Study Status

The main single-pass RO system components include a pre-RO membrane cartridge skid (with one stainless steel membrane housing), a RO membrane cartridge skid (with six FRP membrane housings), one RO feed pump, permeate and reject storage tanks, chemical injection systems (for anti-scalant, acid, and sodium bisulfite feed), and a clean-in-place system, which will use an FRP tank and a centrifugal pump to circulate any one of a number of cleaning solutions used to remove either biological and/or salt scaling from the RO membranes.

CO-PRODUCT REUSE STUDIES

Eureka has initiated a co-product determination study designed in accordance with 25 PA Code Parts 287.1 and 287.8 (See Figure 8). The study which focuses on beneficial reuse of commercial grade dry sodium chloride and liquid calcium chloride is underway and is expected to be completed in early 2014.

CONCLUSIONS/TAKEAWAYS

Actual experience treating development and produced wastewaters generated in Pennsylvania as a result of the Marcellus Shale Gas play has indicated the following:

- Eureka's business plan focuses on locating centralized treatment facilities (employing technologies that maximize potential for recycle and beneficial reuse) in close proximity to major fairways of development activities to minimize logistics and associated costs.
- Eureka has over four years of successful experience treating complex unconventional Marcellus play flowback and produced waters generated in Pennsylvania, by providing the following to their customers:
    - Wide range of treatment levels available; allows for flexible wastewater treatment strategy.
    - Focus on selecting the level of treatment to optimize reuse options and reducing impact on hydrologic cycle.
    - Forward-thinking strategic position to stay at forefront of emerging regulatory requirements; close dialogue with state regulators regarding the development of regulations and standards.

REFERENCES

General Permit WMGR123, Pennsylvania Department of Environmental Protection, March 24, 2012.

"Permitting Strategy for High Total Dissolved Solids (TDS) Wastewater Discharges", Pennsylvania Department of Environmental Protection.

"Modern Shale Gas Development in the United States: A Primer", U.S. Department of Energy, April 2009.

Appendix B.

Extended Abstracts from Session 2: Current and Future Trends in Hydraulic Fracturing Wastewater Management

Successful Oilfield Water Management: Five Unique Case Studies

Brent Halldorson
Fountain Quail Water Management

The statements made during the workshop do not represent the views or opinions of EPA.
The claims made by participants have not been verified or endorsed by EPA.

Summary

Oilfield water management includes sourcing fresh water, recycling, disposal, water impoundment, conveyance (trucking or pipeline) while also taking into consideration environmental, public and regulatory issues. There are also potential reservoir and production impacts resulting from fracturing shale formations with different water compositions. Every shale play has unique water management issues.

Recycling wastewater associated with shale gas development is challenging due to the varying composition of the wastewater. The traditional solution has been to dispose of the wastewater via injection wells. While forming part of the solution, disposal alone is not sustainable and recycling is required to allow the industry to grow. Fountain Quail pioneered commercial oilfield water recycling in the Barnett (TX) and has since expanded into the Marcellus (PA) and Eagle Ford (TX). Results and challenges associated with recycling water from various shale plays will be discussed.

The ultimate water management plan for shale gas development will include variations of (1) on-site water re-use including TSS removal to allow re-fracturing of wells using saltwater; (2) desalination of brine using NOMAD or similar technology; and (3) disposal or beneficial re-use of residual wastes such as concentrated brine or salt. Success will require participation and cooperation between industry and regulators, a range of technology solutions and common sense.

Introduction

Fountain Quail Water Management ("FQWM") pioneered shale water recycling in the Barnett Shale and has worked continuously in this field to date. Additional experience has been gained through operations in the Marcellus (PA), Eagle Ford (TX) and Permian Basin (TX). Throughout this 10 year period water recycling has grown from an emerging new industry into a recognized component of developing unconventional oil and gas plays. Recycling has gone from a pilot project to an ever-more integral part of oilfield operations.

In this paper FQWM experience will be summarized and five very different case studies will be reviewed. For the sake of simplicity "unconventional oil and gas" development will simply be referred to as "shale" development, even though this is not strictly accurate. When "shale" is referred to in this paper it refers to any unconventional oil and/or gas play where large volume hydraulic fracturing is being utilized, regardless of whether it is a true shale or other formation (limestone, conglomerate, etc.) being developed.

Water Management – A Complicated Issue?

Water management can prove challenging in shale plays due to the variable nature of the water and the dynamic nature of shale development.

In early stage shale plays the drilling program is often chaotic as production companies are forced to "drill-to-hold" acreage in order to meet lease commitments. Water management is very difficult when there is no structured completion program. Once out of the early "drill-to-hold" pattern producers settle into a more structured development program and water management becomes easier.

There are five main areas that dominate water management. These are far from all-encompassing, however they give the reader an idea of the "big picture" forces at work when considering water management in particular shales.

1. Disposal. What is the availability and cost of disposal in the region (typically saltwater disposal wells hereafter referred to as "SWD"s)? Is there a possibility of induced seismicity due to the depth and formation used for saltwater disposal?

2. Freshwater. What is the availability and cost of freshwater? Often there are competing needs from other industries (agriculture) or municipalities.

3. Regulatory and Community. Shale development is occurring in areas that are unfamiliar with oil and gas development (PA, OH and possibly NY). Media and public opinion have often impacted development in these areas, despite gross misinformation and fear-mongering. This is a very real issue that needs to be dealt with and it impacts how water is managed in these regions.

4. Recycling and Re-Use. Due to the varying subsurface geology, the composition of flowback and produced water is radically different from shale to shale. Certain plays exhibit very high TDS wastewater (Marcellus, Bakken) and others have relatively low TDS wastewater (Fayetteville). The different levels of TDS, hardness and other factors impact the relative cost and efficiency of different types of treatment.

5. Transport. This is a simple but often overlooked component of water management. Trucking is much more expensive than pipelines (on a per-bbl basis) for handling water. The local terrain and weather have a large impact on the transportation and storage options open to producers in that region.

The above factors have different impacts depending on the shale. To demonstrate,

- The Marcellus Shale (PA) has very limited disposal, however it has abundant freshwater. In this shale the predominant water management strategy generally involves re-using saltwater in new hydraulic fracturing stimulations in order to avoid costly disposal. This

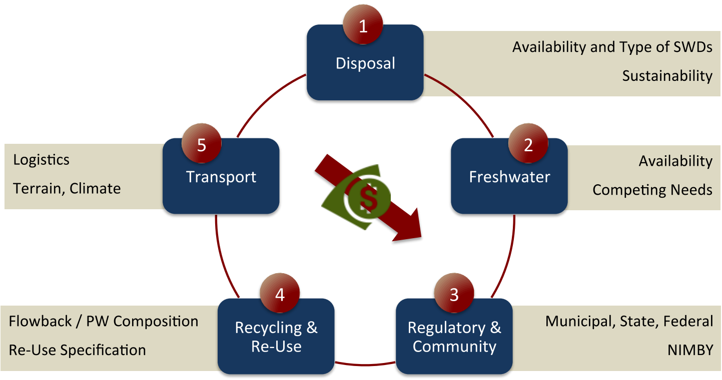


Figure 1. Dominant Water Issues

works well for early stage development where water is always in deficit (the volume to be disposed of can go into a new hydraulic fracturing stimulation), however as more and more wells are drilled the volume of produced water ("PW") will eventually become a very real issue due to the limited disposal availability in this region.

- The Barnett Shale in north Texas is the polar opposite of the Marcellus. The Barnett has abundant low cost disposal due to the Ellenburger formation (immediately below the Barnett Shale). The Barnett often struggles with freshwater availability, especially during times of prolonged drought as are inevitable in the region.

Coupled with the big picture water issues are the multitude of other water related issues. Certain producers may opt for the lowest cost and simply re-use flowback and produced water with minimal, if any, treatment. Experience has shown that re-using water with no treatment will negatively impact the decline curve of the well due to downhole scale deposition and/or plugging of the formation. The question becomes whether the impact on the well decline curve justifies water treatment or not. This is a question being addressed by the individual producers and is not a topic for this paper.

Other issues include permits for storage and withdrawal of water, NORM management, liability for potential saltwater leaks or spills, road damage from trucking water, pit closure costs, odor issues, downhole scaling, microbial control, etc. Many more could be listed.

These questions and many more can lead to paralysis and producers become bogged down in evaluating the details. It sometimes feels like an "endless DO Loop" with no resolution. Another complicating factor is water treatment companies that bombard the energy producers with ridiculous unscientific claims, often that make no sense at all or involve "black boxes".

The point of this paper is to try to simplify these issues and chart a logical water management path.

The Big Question: Saltwater or Freshwater?

The fundamental question in shale water management is whether the producer wants to deal with (1) saltwater, or (2) freshwater. Once this question is addressed the decisions going forward become much easier to deal with. Case studies involving both saltwater and freshwater will be discussed later in the paper.

(1) Saltwater.

Freshwater	**Saltwater**
• Higher cost (thermal distillation).	• Lower cost (minimal treatment).
• Lower risk – store and transport freshwater.	• Difficult logistics (storage + transport)

Figure 2. The Big Question: Saltwater or Freshwater?

On the surface, the re-use of saltwater is a much lower cost alternative if it is practical. FQWM offers basic TSS removal utilizing its ROVER clarification system for the range of $1/bbl of water treated. Other service providers offer technology such as electrocoagulation, dissolved air flotation (DAF) or filtration to meet customer needs for saltwater re-use. These are generally high capacity, low cost systems that give back a certain quality of saltwater. FQWM prefers the ROVER as it can easily adapt to varying water composition and also can provide targeted treatment objectives (i.e.: it can selectively precipitate certain species the producer wants to eliminate). Saltwater can be re-used regardless of the TDS of the feed – the goal is generally to remove TSS and polymers so that the clean brine can be blended with make-up water for new fracture stimulations.

While the treatment options for saltwater are varied and generally low cost, the storage and handling of large volumes of saltwater can become very challenging. For example, in Texas the producer is required to have an H-11 approved pit to store large volumes of saltwater. The permitting and construction of such pits becomes significant for large volume fracs. Case studies 'C' and 'D below show examples of saltwater re-use scenarios.

(2) Freshwater.

There are very limited technology options for converting shale wastewater into freshwater for re-use. It is often deemed to be impractical and many customers feel it is too costly to consider as an option.

The two established technologies for TDS removal include (1) membrane based systems, and (2) thermal based systems. Membrane systems have generally struggled to prove effective in oilfield wastewater due to poor recovery coupled with susceptibility to membrane damage from organics. New developments such as Forward Osmosis ("FO") show promise for addressing some of these issues. The traditional alternative to membranes is thermal distillation, which has often been misrepresented as being too costly.

As an example, FQWM offers its patented NOMAD treatment, which is a compact and efficient thermal evaporator, for a cost range of \$3-\$4/bbl (including power, labor, chemical and equipment). This is 3-4X the cost of ROVER treatment, however it returns freshwater to the customer for re-use rather than saltwater. Despite the higher treatment cost, the customer has (1) a predictable hydraulic fracturing water composition (freshwater), and (2) much less headache with water storage and transportation. Examples of areas where freshwater makes sense are shown below in case studies 'A', 'B' and 'E'.

A by-product of NOMAD treatment is clean, heavy brine (the leftover solution after maximum water recovery has been achieved). This "concentrate" often has value to producers that need 10# brine for drilling and completions. In areas where re-using this heavy brine stream is advantageous it makes the freshwater scenario more cost effective. Once the decision as to saltwater or freshwater re-use has been made, the remaining decisions on how to implement a water management strategy become easier.

Charting a Logical Path Towards a Water Management Strategy

On either path, freshwater or saltwater, simple and achievable goals must be set. It may be desirable to start with very basic goals and expand them over time depending on the level of success achieved. This should not be considered as "pilot" or "demonstration" treatment, but rather a phased in level of treatment starting with the very simple.

Regardless of the plan, both the producers and the treatment provider need to be adaptable and flexible. Solutions need to be capable of scaling up in size as the need increases.

Examples of water management goals include the following:

- Reuse as much flowback and PW as possible in new fracs (saltwater example).
- Eliminate the need for saltwater pits and allow the use of aluminum fastlines (freshwater example) without concern for environmental liability.

The overriding goals for each case study will be highlighted below.

Beware of Black Boxes

A complicating factor which has delayed the implementation of water recycling has been the entry of new technology solutions which are not based on real science. Often these gadgets make promises which cannot be delivered on or which contravene the laws of thermodynamics. For example, there are several companies today promoting that their solution is chemical free, uses no energy (some create energy!) and have no waste byproduct. In essence they are promoting dirty water in and clean water out without having any science behind it. Unfortunately many producers have tried these systems and it has left a bad taste for water recyclers in general. The old axiom holds true: "if it sounds too good to be true, it probably is."

Experience trumps wild promises every time. Water recyclers must invest the time and energy in learning to treat this highly variable wastewater and customers should stop listening to vendors that cannot explain how their systems work.

Some producers are content to run an endless stream of pilot projects. This can gain some insight for the producer, however it makes more sense to work with a treatment company that has a real product based on real science and together work through the issues. Often the knowledge gained through a pilot leaves and has to be re-learned by the next vendor in line.

Case Study A – Freshwater, Devon Barnett Shale

In the early days of the Barnett Shale (north Texas), all the producers were fraccing with freshwater and that was the goal for treatment – to get back to freshwater. Fountain Quail was fortunate to begin work with Devon Energy in 2004 with the NOMAD evaporator system which was developed specifically for shale wastewater. The NOMAD was designed to achieve the highest possible recovery of freshwater from shale flowback and PW, while still being easily transportable. Devon Energy were pioneers in shale development (formerly Mitchell Energy), and their input was valuable in developing the technology.

The objectives for this case study include the following:

(1) Move the recycling to be near the drilling activity. This essentially cuts the transportation of both the saltwater and freshwater by placing both in the midst of the current drilling activity.

(2) Hydraulic fracturing with freshwater alone. This allows for predictable hydraulic fracturing chemistry and reduced hydraulic fracturing costs (using saltwater requires slightly more hydraulic fracturing hp and additional chemical cost).

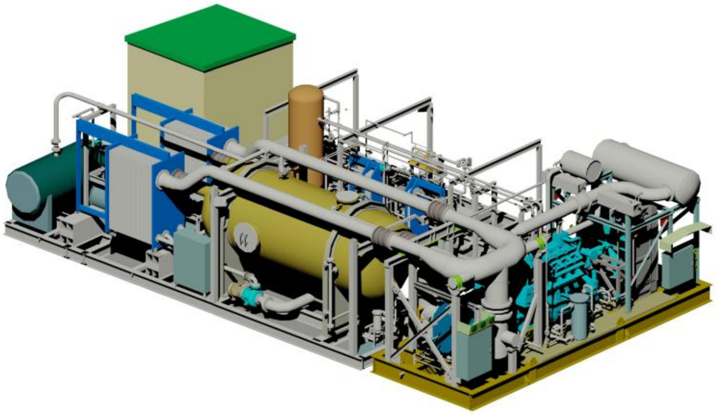


Figure 3. NOMAD Mobile Evaporator System

(3) Avoids the transport and storage issues associated with saltwater. All hydraulic fracturing fluid can be stored in freshwater pits (un-lined, non H-11) and can be transported via aluminum irrigation pipe.

(4) Water leaks are not a concern and there is no liability from animals drinking the water (NOMAD distilled water far exceeds EPA secondary drinking water), water fowl landing in the pits or odor issues.

(5) By placing the recycling in the midst of drilling activity, flowback and PW from nearby wells can be tied into the mobile recycling center via welded surface poly pipe (rather than trucking).

The operation continues today and the nearly 10 years of experience have been valuable to both Devon Energy and FQWM. There have been over a dozen different locations throughout this time. With low cost disposal available in the Barnett Shale, FQWM learned to become very efficient so that recycling could remain competitive with low cost disposal.

In March 2012 the Gas Technology Institute ("GTI") completed a third party evaluation of the NOMAD technology at a Devon Barnett Facility utilizing a RPSEA grant.[1.] This report demonstrates the technical and cost effectiveness of the NOMAD treatment system on shale wastewater.

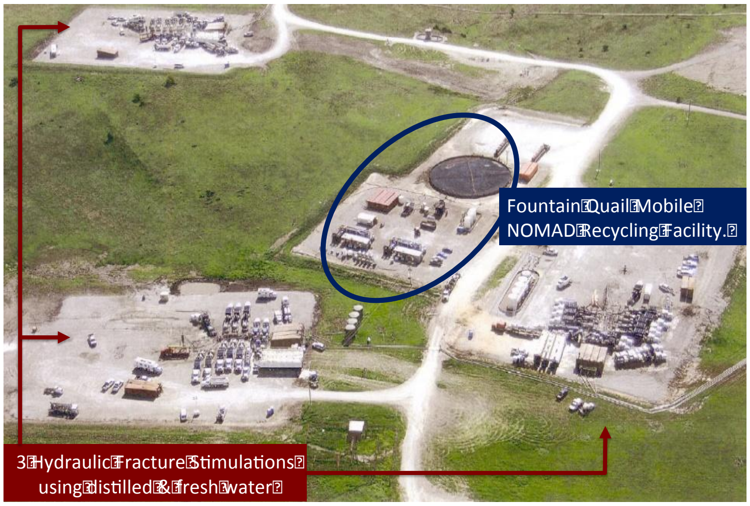


Figure 4. Devon Energy Recycling Site, Barnett Shale TX

Case Study B – Turning PW into Freshwater in West Texas

West Texas contains some of the best oil-producing formations in North America. One of the challenges in this area is a lack of available freshwater resources. This client has taken the bold approach of using their existing PW as the feedstock for a NOMAD system to create freshwater.

The objectives for this case study include the following:

(1) Reduce and even eliminate the producer's reliance on groundwater. Use existing PW as the source water for development in the region.

(2) Reduce the SWD volume and extend the SWD life. This SWD is owned and operated by the producer. By recycling the majority of the PW back into freshwater, the existing SWD can now serve for disposal of the NOMAD concentrate alone (clean, nearly saturated brine without polymers or TSS).

(3) Utilize a portion of the NOMAD concentrate as 10# brine for drilling and completions in the region.

(4) Recover additional oil that is currently going down the SWD well.

(5) Have the ability to recycle high solids flowback from the local area that is currently being hauled long distance for disposal.

Disposal of brine and recycling are often viewed as two completely separate options. This case study demonstrates that recycling and disposal can be combined to (1) maximize the recovery of value-add products such as freshwater, heavy brine and oil, while simultaneously (2) protecting and extending the life of the disposal well.

Case Study C – Saltwater Re-Use, Eagle Ford Shale TX

New shale plays initially follow chaotic development as producers "drill-to-hold" their acreage positions. This requires a highly flexible and adaptable water management strategy. The Eagle Ford Shale in south Texas offers an example of this type of play.

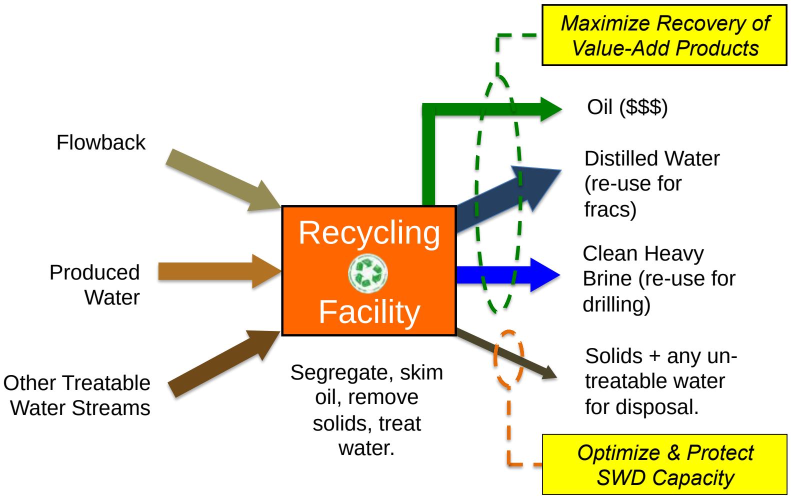


Figure 5. Recycling "Hub" Combining Disposal and Recycling

FQWM developed the ROVER for this purpose – to allow customers to re-use their brine in a highly mobile package at a very low cost. In its more basic form it is removing TSS and polymer using a high pH clarification process. This is the same pre-treatment that FQWM has used ahead of its NOMAD systems for close to a decade. The system has proven capable of handling highly variable wastewater influent and delivering consistent, clean brine for re-use. Solids are de-watered on the system utilizing a built-in sludge thickener and filter press. One of the key benefits to a system like this is the flexibility. If the producer wants to remove a certain scale forming species, then FQWM can usually precipitate it by varying the chemical addition or softening. The cost may go up slightly, however it is still targeting the specific treatment needs of the customer at the lowest possible cost. In this case study the customer wanted to treat flowback and produced water. The goal was to effectively remove polymer, TSS and iron. The ROVER system was delivered to site and was completely rigged up and operational within 12 hours of arrival. The system treated all of the flowback and PW available. Results from the recycling are shown in the figures below.

Figure 6. ROVER Mobile Clarifier

Eagle Ford Flowback				
Parameter	Metric	Influent to ROVER (Feed)	Effluent from ROVER	Removal
Alkalinity	mg/L CaCO3	406	206	49%
Iron (Fe)	mg/L	83	trace	100%
Manganese (Mn)	mg/L	1.2	trace	100%
Total Hardness (Ca+Mg)	mg/L	1025	602	41%
Silica (SiO2)	mg/L	148	27	82%
Total Suspended Solids (TSS)	mg/L	180	19	89%
Turbidity	NTU	>100	3	n/a
pH	pH	6.8	6.8	n/a
Total Dissolved Solids (TDS)	mg/L	32,835	34,610	n/a

Figure 7. Case Study C, ROVER Flowback Results

Eagle Ford Produced Water				
Parameter	Metric	Influent to ROVER (Feed)	Effluent from ROVER	Removal
Alkalinity	mg/L CaCO3	340	101	70%
Iron (Fe)	mg/L	26.2	trace	100%
Manganese (Mn)	mg/L	1.5	trace	99%
Total Hardness (Ca+Mg)	mg/L	2,027	1,563	23%
Silica (SiO2)	mg/L	169	18	89%
Total Suspended Solids (TSS)	mg/L	277	32	88%
Turbidity	NTU	44	3	n/a
pH	pH	7.1	7.1	n/a
Total Dissolved Solids (TDS)	mg/L	46,501	48,365	n/a

Figure 8. Case Study C, ROVER PW Results

Case Study D – Saltwater Re-Use, Woodford/Cana OK

This case study shows how inventive producers have become at managing flowback and PW. In this case the producer drills all their wells in linear "rows". As the wells are drilled and hydraulically fractured, the flowback is hard-piped along the row back to a tank. This flowback is blended with make-up water (fresh) and used to hydraulically fracture the next well (without treatment).

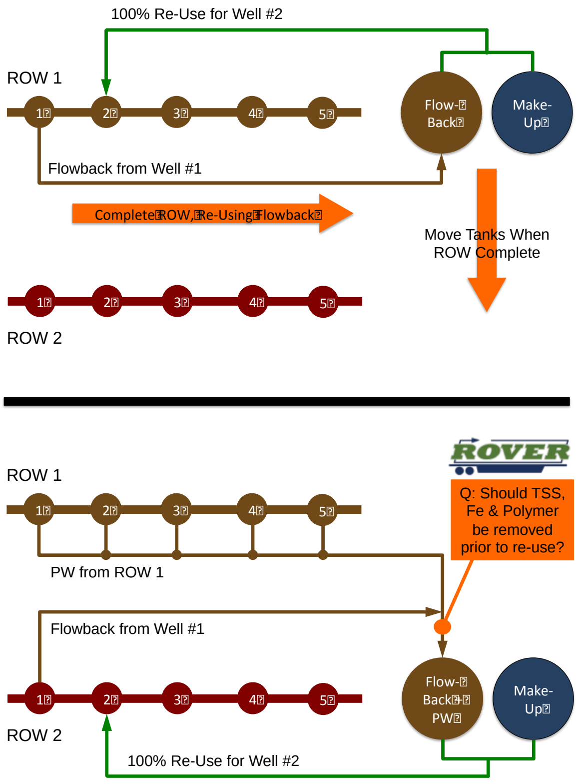


Figure 9. Case Study D, "Row" Development

The objective of this case study was to evaluate whether or not to remove the TSS and polymer from the flowback prior to re-use. After studying the water, it was determined that the water was easily treatable with a ROVER mobile clarification system. The turbidity could be dropped from 600 to 5 NTU. The ROVER treatment could achieve this goal for a budget price of $0.79/bbl. The customer struggled to quantify whether the removal of the TSS and polymer (and reduced scaling index) would have a significant impact on their oil production.

In this case the customer opted to do nothing and continue without treatment. Sometimes this is the answer and recyclers need to understand and accept that "no treatment" might be part of a successful water management strategy.

Case Study E – Brackish Water Study, Wise County TX

This case study demonstrates a unique challenge and creative solution. The customer has limited freshwater in this Barnett Shale county (Wise county), however they do have "brackish" saltwater wells. Despite this, the customer still prefers to hydraulically fracture wells with freshwater.

In this case it makes sense to look at membrane technology to desalinate the brackish saltwater (consistent composition, no hydrocarbon). FQWM came up with the following "hybrid" solution utilizing an RO system to treat the brackish water and also using a NOMAD evaporator to treat the RO reject combined with flowback and PW in the region.

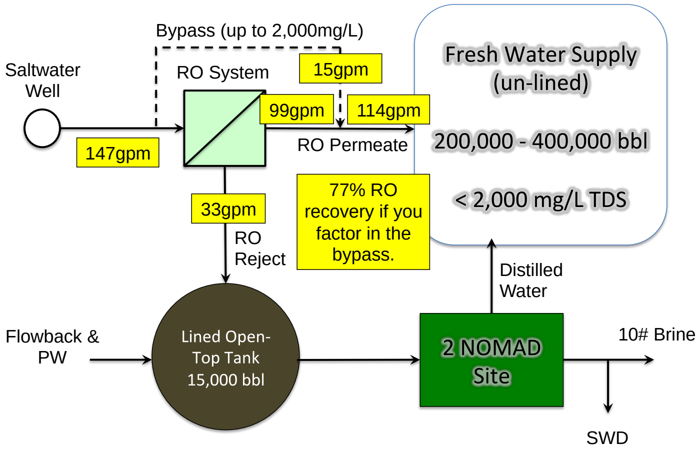


Figure 10. Case Study E, Brackish RO + NOMAD

The customer continues to study this idea and may set up a small scale system initially. This demonstrates how different technologies can be combined to arrive at a solution. Texas has ample brackish water and there are many ways that it can be incorporated into a water management plan, either by using it directly or treating it to freshwater as demonstrated in this case study.

Conclusions

These case studies demonstrate how both freshwater and saltwater re-use can be successfully incorporated into an energy producer's water management strategy. To arrive at a solution the customer must be prepared to answer the initial question: freshwater or saltwater? After this it is a matter of laying out simple and achievable goals and selecting a treatment partner or technology that is based on real science and has actual oilfield experience.

Both the producer and the treatment company must be committed to working jointly through the issues as they arise, and success will inevitably follow.

Acknowledgments

Devon Energy has been invaluable as a resource and partner for FQWM. Not only has Devon helped launch FQWM as a recycling service provider, it has tested dozens of other technologies and continues to be an example of pioneering new and better ways of developing oil and gas [2.].

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Nomenclature

DAF	*Dissolved Air Flotation.*
FQWM	*Fountain Quail Water Management, LLC.*
GTI	*Gas Technology Institute*
NORM	*Naturally Occurring Radioactive Material.*
NTU	*Nephelometric Turbidity Unit, Turbidity Measurement*
RRC	*Texas Railroad Commission*
TSS	*Total Suspended Solids (stated in mg/L or ppm).*
TDS	*Total Dissolved Solids (stated in mg/L or ppm).*

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Produced Water Management in the Marcellus

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Controversy continues to surround the deployment of horizontal drilling and hydraulic fracturing technologies for natural gas extraction from sub-surface shale. Comparative life-cycle assessment has demonstrated reduced CO_2e/mmBTU emissions from electricity produced from shale gas compared to coal, while highly localized impacts of hydraulic fracturing have been reported for fresh water aquifers within one mile radius of a wellhead. While global and local analyses are important for strategic management and regulation of shale gas resources, regional level impacts and benefits often drive state-level policy in resource extraction. Quantifying these regional impacts by summing over a set of regional wells also helps to define variance in single well impacts, which can hinge both on exogenous variables as well as on the management decisions, experience, risk aversion, and commitment of the operators. Determining the origins and magnitude of this variability is valuable to operators, regulators, land-holders, and environmental advocates alike.

We find significant variation in the waste management practices and drilling patterns of Marcellus firms. A large portion of this variance is attributed to waste disposal method, company experience operating in the Marcellus, and drilling practices suggesting that impact minimization is a function of firm-level decision making on a highly localized scale. Among the most important strategic interventions is the practice of synchronizing drilling operations in time and space, or clustering. Companies that drill their wells in clusters reuse a larger percentage of waste and minimize total waste transport.

Mid-Continent Water Management for Stimulation Operations

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction: Water, its use and management is critical to the petroleum industry. It is the most common and heavily used fluid in the oil and gas business. In every jurisdiction in this country its use is regulated in some manner. The regulations and ownership of water is different in each area in which the industry works. In many areas of the country the use and handling of water have become emotionally charged. For this presentation, I will be concentrating on the water use and reclamation for the stimulation of the Granite Wash tight gas reservoirs in the Anadarko Basin and the shale oil reservoirs of the Cana Woodford Shale in the Anadarko Basin. Both areas have evolved as the drilling activity increased and changed. In each area an infrastructure has been created to support Newfield's completion operations and the need for water.

Water Management Cycle:

Source: Granite Wash – ground water
Woodford Shale – surface ponds
Cana Woodford – ground water, surface ponds, lakes, and streams

Transport: Fresh water is pumped through aluminum, poly pipe, PVC pipe, lay-flat hose or trucked. Recycled water is pumped through poly pipe, lay-flat hose or trucked to the well site.

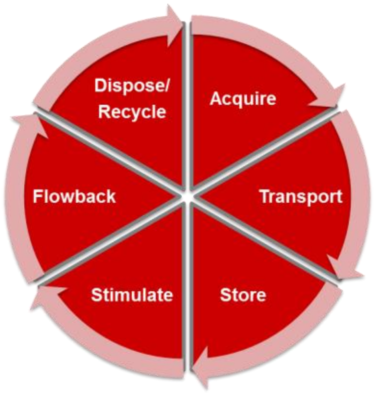

Figure 1. Water Management Cycle

Store: Fresh water is stored in ponds or lined pits.
Recycled water is stored in lined pits or hydraulic fracturing tanks.

Stimulate: Halliburton, Schlumberger, BJ or other companies mix the water with proppant and other chemicals and pump it into the well to stimulate the reservoir.

Flowback: Flowback water is separated from any hydrocarbons at the well's test or production facilities. It is then pumped or trucked to a recycle pit or a disposal well.

Recycle or Disposal: Once at the recycle facility the flowback and/or produced water is processed and cleaned up for reuse. The water that is not reused will be taken to a disposal well.

NFX Granite Wash Operations: Newfield's Britt Ranch and Briscoe fields were originally drilled for deep Morrow gas during the 1980's. The Morrow is a conventional gas condensate reservoir. The Granite Wash is very tight laminated reservoirs in Western Oklahoma and the Texas Panhandle. From 2001 until 2008, Newfield drilled over 150 vertical Granite Wash wells. Beginning in 2008, all of the wells Newfield drilled in the Granite Wash have been horizontal. Initially, hydraulic fracturing tanks or hydraulic fracturing pits were used at each well site for the completion operation. It soon became apparent that having central water supply pits was more economical. As the amount of water being used increased and the cost of potassium chloride went way up, it made economic sense to begin recycling flowback water. When Newfield started drilling and completing horizontal wells in this area the water usage went from approximately 80,000 barrels per completion for vertical wells to over 250,000 barrels per completion for horizontal wells.

Figure 2. Map of Anadarko Basin

Figure 3. HDPE

Although in most areas 10" aluminum irrigation pipe is used to transport fresh water, Newfield uses its own HDPE (high density polyethylene) to move it from the water storage pits to the completions. The recycled water is transported through either 8" or 12" HDPE pipe.

Figure 4. Recycle Pump

Newfield owns 38 miles of 8" poly, 4 miles of 12" and 10 miles of 4" poly to move water from pit to pit, from the pits to the wells being stimulated and from the wells back to the recycle pits. Generally three or four lines are used to deliver water from the hydraulic fracturing pits to the well being completed. Once the completion is finished and the well begins to flow back one poly line is left in place to pump the water back to the pit. Newfield also owns 6 water transfer pumps to move water from the flow back or production tanks to the recycle pits.

The water being produced into the recycle pits contains approximately the same TDS as the water used during the completion operation (15,000 to 20,000 mg/l) and is relatively clean. Any solids produced with the water will drop out in the flow back pits. By reusing the water, Newfield saves over $30 million per year in reduced water disposal costs, $8 million per year by not purchasing potassium chloride and another $1 million a year by not purchasing additional fresh water. The hydrocarbons not caught in the production equipment (less than 500 mg/l) are skimmed from the pits as is necessary and recycled through our disposal facilities.

Currently, Newfield recycles approximately 80% of the water it uses. The company would recycle more however not all of the wells produce back their entire load. In addition, the pits are permitted only for fresh or flowback water, so once the entire load is recovered the produced water must be trucked or piped to a SWD well. In the Britt Ranch area, the company has seven recycle pits with a total capacity of 2.4 million barrels and ten fresh water pits with a total capacity of 1.3 million barrels. In the Briscoe area there are two recycle pits with a total capacity of 900,000 barrels. Due to the soil conditions and to protect the environment all of the pits are lined with geomembrane liners.

The Texas Railroad Commission permits each of the recycle pits. The pits are inspected before they are used and then drained at least once a year and re-inspected. Some of the pits have been in use for more than five years without a leak or failure.

As stated above, Newfield has a long history of drilling vertical wells in the Granite Wash. Since the Granite Wash has multiple pay zones the focus had been on drilling vertical wells and completing all of the zones using multiple hydraulic fracturing stages. Using this approach the best vertical well in the area had an initial production rate of 9.2 MMCFD and 48 BOPD with over a 90% initial decline rate when completing eight of the zones. An average vertical well initially produces at a rate of approximately 5 MMCFD with multiple zones completed. After much work, a horizontal well was drilled and completed in the upper member of the Granite Wash during the fall of 2008. That well initially produced at a rate of 25 MMCFD and 1500 BOPD and produced 2 BCF and 100,000 BO in its first four months. Since that time eleven individual zones have been tested in the Granite Wash with horizontal completions. The average initial production of 17 MMCFD and had a much lower decline rate than the vertical wells. As can be seen with these numbers, horizontal wells have substantially improved both the initial productivity and recoverable reserves from the Granite Wash.

With the horizontal wells has come the demand for much more water. The average vertical well was completed using 80,000 to 100,000 barrels of water. The average horizontal well is using 250,000 barrels of water or 25,000 barrels per hydraulic fracturing stage. Experiments have been conducted using different perforating schemes, water volumes (from 5,000 barrels to up to 55,000 barrels per stage) and pumping rates (from 60 to over 100 barrels per minute). Since some of the zones are up to 600 feet thick, attempts have been made to see if the zones could be drilled with just one lateral and get sufficient height from the hydraulic fracturing to recover the reserves efficiently. Based on the hydraulic fracturing mapping, we have not been able to achieve the hydraulic fracturing height desired. These attempts to intentionally increase the hydraulic fracturing height have proven that in most cases getting more than 250 feet of height growth is very difficult. The probability of fracturing into a USDW zone more than 10,000 feet above the reservoirs being stimulated is very implausible.

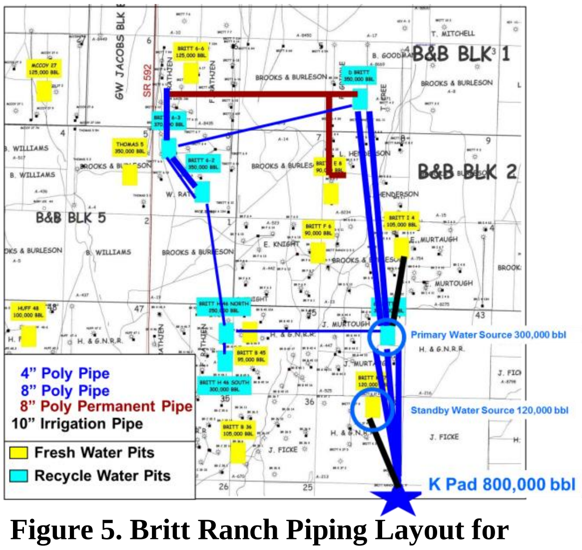

Figure 5. Britt Ranch Piping Layout for 800,000 bbl completion of 2 wells

Due to the large amount of water required to complete some of the wells, the pits have been "daisy chained" together using poly pipe so that water can be moved from pit to pit. Using this approach two wells were recently completed on the same pad using over 800,000 barrels of water with the fracs being pumped at over 100 barrels per minute and water moved up to nine miles. The figure to the left depicts the pipe system used to connect the pits to each other and the wells being completed.

The approach Newfield has taken in its Granite Wash water management is being used as the model for new projects in Western Oklahoma, the Eagle Ford in South Texas, the Wasatch in Eastern Utah and the Marcellus. Other operators in the area are also copying Newfield's model.

Figure 6. Arkoma Basin

NFX Woodford Shale Operations: Newfield's Woodford Shale operations are conducted over a 900 square mile area in the Arkoma Basin. The Woodford Shale was initially developed with vertical wells with the best initial production being 1,600 MCFD and the average well's initial production ranged from 300 to 400 MCFD. Newfield began drilling and completing horizontal Woodford wells during the spring of 2005. During the last eight years the lateral lengths increased from 2500 feet to over 10,000 feet with corresponding increases in initial production rates. The average initial producing rate for Newfield's Woodford wells is 7.0 MMCFD. At this time, operations in this play have been suspended due to low gas prices.

Fracturing volumes on the vertical wells were generally small (less than 10,000 bbl) and could be done from hydraulic fracturing tanks or a small fresh water pond. To achieve higher producing rates from the Woodford wells, much larger fracture stimulations with volumes increasing up to 300,000 barrels per well were required. Some of Newfield's four well pads have used up 1.2 million barrels of water during the completion operations.

Figure 7. Fresh Water Hydraulic fracturing Pond

As the horizontal play developed Newfield built over 60 fresh water ponds to collect run off from rainwater. The ponds ranged in size from 50,000 to over 750,000 bbls with a total capacity of over 8 million barrels. Fresh water was transferred from the pond to the well sites through 10" aluminum irrigation pipe. In cases where there was not enough fresh water in one pond they would be connected together using irrigation pipe and the water moved from pond to pond. Fresh water has been moved up to 2.5 miles during the hydraulic fracturing operations. Recycled high chloride water was trucked from our Ecosphere water treatment facility to the well site where it was stored in hydraulic fracturing tanks. Fresh water was then mixed with the recycled water through the hydraulic fracturing blender to make an equivalent of one percent potassium chloride water.

Ecosphere is a company Newfield used to clean its flowback water for use as a potassium chloride substitute. The technology provided by Ecosphere Energy Services, LLC, uses ozone to oxidize hydrocarbons, residual chemicals and heavy metals in the flowback water. This process also kills any bacteria in the water, reduces the surface tension of the water and reduces sulfate and carbonate scaling tendencies. Their process also uses hydrodynamic cavitation, electro chemistry, acoustic cavitation and various types of filtration. Should it be desired to reduce the salinity the unit is equipped with reverse osmosis units. Newfield saved over $13 million per year in reduced chemical usage by using Ecosphere to clean its recycled water.

Once the completion was finished and the well flowing back, the produced water was trucked to a salt water disposal facility. The Ecosphere equipment is located at one of Newfield's salt water disposal wells and uses the water there as its source. The processed water was stored in hydraulic fracturing tanks until it is needed. At the time, only six percent of the hydraulic fracturing water in Newfield's Arkoma Basin operation was recycled.

Figure 8. Fresh Water Hydraulic fracturing Pit

Until Newfield suspended its operations in the Arkoma Basin, it was working on locating a place for recycle pits and being able to use higher chloride water as a hydraulic fracturing fluid so that more water could be recycled.

NFX Cana Woodford Operations: For the last two years Newfield has been in the exploration phase of a program in an oil rich area covering 10,000 square miles in Central Oklahoma. Only fresh water is currently being used for its hydraulic fracturing fluids. Newfield has been able to cut its water use by 2/3 by changing from slick water hydraulic fracturing's to cross-linked gel hydraulic fracturing's. With the drought it is quite apparent that another source of water must be found and used. Newfield is working toward recycling the hydraulic fracturing water in areas where its infrastructure has grown to a point that it makes economic sense. Reuse of the cross linked gel water presents greater challenges than reuse of the slick water. Newfield and its vendors are in the process of working out the hydraulic fracturing fluid chemistry, water cleanup technology, and getting pits permitted for the use of recycled water.

Conclusion: Newfield has recycled over 50 million barrels of water and saved over $200 million in completion costs in its Britt Ranch operations. Newfield's Granite Wash operation is a prime example of where recycling hydraulic fracturing water is environmentally responsible and economically feasible at the same time. This is a win-win for the landowners, the community, and the company.

Utilizing Models Developed for Water Management and Risk during Carbon Storage to Improve Water Management during Unconventional Gas Exploration and Production

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Introduction

The extraction of produced water during carbon storage is used to control subsurface reservoir pressure gradients and the flow of stored CO_2 plumes as a risk management strategy. Treatment and repurposing of this water creates a useful resource and reduces the volumes that must be disposed. Models have been developed to assist decision-making and acceptable risk policy making related to water production, treatment, and use during the carbon storage process [1-5]. Likewise, similar models are needed to support decision making and management related to water extraction and use during unconventional gas exploration and production.

Existing models (e.g., water treatment modules in CO_2-PENS) derive their processes and substantiating data extensively from produced water databases, brackish and seawater treatment processes, enhanced oil recovery data, and other published literature and engineering studies related to oil and gas production. Many of the processes, including pretreatment, treatment, concentrate disposal, and transport, are applied to water qualities similar to or the same as those of oil and gas produced water and/or hydraulic fracturing fluids (collectively referred to here as PW). The resulting information informs us about the feasibility of the treatment and management systems chosen and the cost versus risk scenarios.

Our current work includes evaluation of transportation and storage costs, improvement and expansion of supporting data for cost values and ranges, and additional sensitivity analyses. Because of the similarities that exist between carbon storage and hydraulic fracturing, including large extracted volumes, high salinities, and potential treatment methods, models used for carbon storage water extraction processes are anticipated to translate well into process models that can assist with volume management, pretreatment and treatment, transport and disposal, and use and reuse of water used in hydraulic fracturing and gas recovery. Utilization of existing models from carbon storage research will allow fast implementation and evaluation of processes, costs, and risks in the rapidly evolving hydraulic fracturing and unconventional energy production industry.

Model types, time scales, and system scales

Pore-scale chemistry and flow models (e.g. PFLOTRAN) can be used for small-scale phenomena on shorter time scales (seconds to years), and can be used to measure mineral-fluid, fluid-fracture, and porous-media interactions. Local or site-scale flow and transport models (e.g. Modflow) can evaluate local well impacts such as well bore leakage or fracturing return flows (days to years). Site- and local-scale system and process models (e.g. CO_2-PENS; GTI spreadsheet model) can be used to integrate processes such as injection, extraction, treatment, and transport (days to years); then can be used to evaluate costs and risk impacts [6, 7]. Field-scale (regional) and basin-scale flow and transport models and model platforms (e.g., Modflow, PFLOTRAN,mASCEM) are used to model water flow and balances, salt or contaminant transport, collective impacts of pore- or local-scale processes, and can be used for short or long time frames (days to years). We note the critical importance of real-time and historical field data to calibrate and verify models [7]. To date, several site-scale models have been developed, but large-scale modeling has not yet been attempted, at least not to the level done for carbon storage projects. Cross-scale linkages of models for carbon storage are feasible and are needed for hydraulic fracturing systems, for near- and long-term time scales [8].

Needs for models to address:

1. Fresh water (drinking water) management and impacts—predict use, reuse, losses via disposal or evaporation, impacts on other energy production (e.g., power plant intakes; ecological impacts; agricultural impacts)[9, 10].

2. Salt water management and impacts-use, reuse, spills, disposal to surface bodies, disposal to wells (volume and time limitations), outcomes, energy use, and costs of treatment; transportation, reuse, and disposal; pipeline network expansion; impacts of regulation [11-14].

3. Salt and inorganic constituent inventories and management—extraction from shale via PW/flowback; treatment; creation of saline concentrate streams and solid salts; disposal to wells and formations; impacts to reuse from chemistry changes over multiple cycles [7, 14].

4. Risk Modeling: similar to that done to evaluate risks for CO_2 storage [8]; must be robust, up-to date, and flexible. Includes reservoir storage and potential leakage pathways, fracture propagation and effects of propagation including seismic and chemical interactions in subsurface; impacts on fresh water reservoirs. Also should include the effects of increased environmental regulation and linkages with economic analyses and the impacts of forecasted climate change [11].

5. Economic and cost analysis: Similar to that done to evaluate CO_2 water management strategies [3]. Effects of system expansion, environmental regulations, impacts on producers and the market, impacts of the market on production, infrastructure costs; transportation costs, life-cycle analysis [11].

Here we discuss the site-scale water management tool within CO_2-PENS, including current uses and future utilization for system modeling for hydraulic fracturing processes; We introduce the ASCEM model (developed for DOE-EM contaminant and environmental studies), and PFlotran (used for ecological and contaminant studies) as possible additional models for large regional scale assessments and linking pore- and fracture-scale phenomena to larger-scale models.

Methods

We use a systems approach to evaluate treatment costs that are reasonable for the chemical and physical qualities (salinity, temperature, pH and turbidity) of water that could be extracted from target geologic carbon storage formations (Figure 1). The temperatures and salinities of water extracted during unconventional gas production fall within ranges evaluated for carbon storage. The system model was developed using the GoldSim© platform linked to a Fortran code [15]. GoldSim© provides utilities that can be used to develop analysis models designed to perform multi-realization, probabilistic simulations. The model also has various data elements to input user-specified parameters including stochastic distributions. The preliminary model captures all decision points (Figure 2).

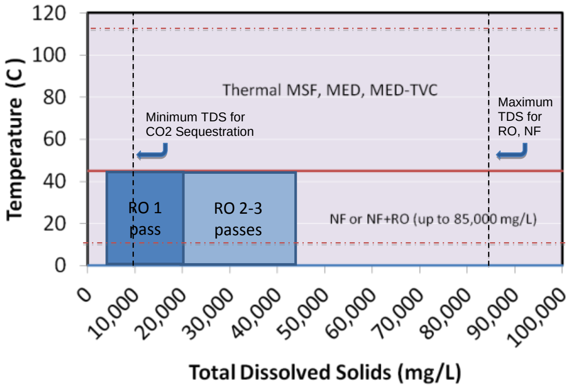


Figure 1. Ranges of temperature and salinity for treatment options.

We evaluated generalized cost scenarios based on data found in the literature for brackish (15,000 mg/L TDS) through highly saline (80,000 mg/L TDS) water qualities, four electricity costs (0.04, 0.07, 0.10, and 0.20 $/kWh), and variable temperatures from 15-120 °C (to account for variation from cool stored surface water to superheated high-salinity waters). Several methods of treatment, including nanofiltration (NF), reverse osmosis (RO) and thermal methods (multistage flash distillation, multiple effect distillation, thermal vapor compression [MSF, MED, TVC]) are included in the model [3, 4] (Figure 2). Recent model additions include organic pretreatment methods (oil/water separation, filtration, adsorption, oxidation) and transportation costs (pipelines, trucks). The user can select various choices of input volume, temperature, salinity, location, and electricity costs to obtain output treatment types and costs, and feasible concentrate disposal methods and costs [3].

Results and Discussion

Our data indicate that for waters extracted from carbon storage sites, salinities and temperatures may often be higher than for municipal seawater and brackish water treatment scenarios (Figs. 1 and 3). The temperatures and salinities of extracted waters are similar to that of unconventional PW. Thus, thermal treatment methods are more cost-feasible than membrane methods in many cases, although pressure recovery methods for RO can mitigate this. Treatment costs including concentrate disposal fall within a range of US\$0.50 to US\$2.50/ton CO_2 injected, although some costs can be much higher (up to US\$30/ton CO_2 under certain concentrate disposal cost ranges). These values can be converted to m^3 of water when CO_2 density is known (Figure 3). A sensitivity analysis

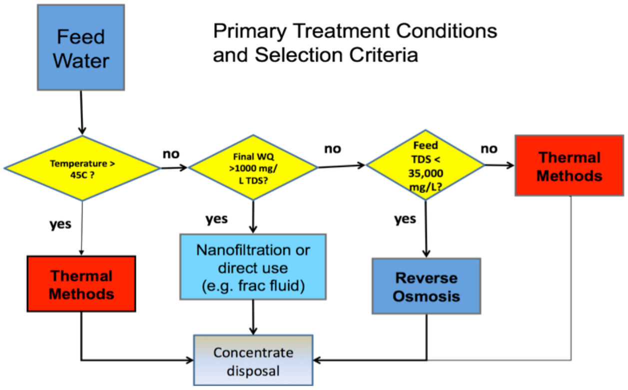
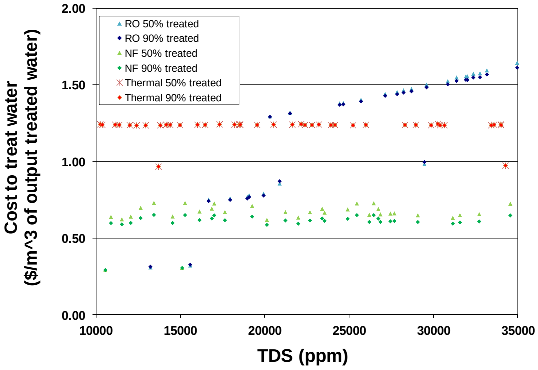


Figure 2. Primary treatment conditions and selection criteria.

showed that temperature is most important in determining costs, followed by selection of concentrate disposal method.

The Rock Springs Madison Fm. (Wyoming, Teapot Dome region) was chosen for modeling because the formation has a higher salinity range (>45,000 mg/L), thus ruling out RO treatment methods in the model. A produced water scenario was evaluated in order to include Class II well disposal costs (Figure 4). The model also selects an evaporation pond scenario for disposal; limiting factors include a humid climate and the availability of land area for ponds. While some high cost ranges are shown (up to \$29/ton CO_2) most costs fell below \$2.50/ton CO_2 using a \$0.10/kWh electric cost input; these can be lowered if thermal energy can be designed to be a larger contributor to the energy costs at these sites.

Figure 3 (right). Cost to treat in \$ per m^3 of output treated water with a constant injected CO_2 density (water volume normalized to 37,854 m^3 or 10 mgd). Variable TDS (<35,000 mg/L) and temperature (15°C to 65°C), desired treated water recoveries=50% and 90% of feed volume, energy cost =\$0.10/kWh, MSF thermal rate, no pressure recovery, no disposal options included, 100 modeled realizations.



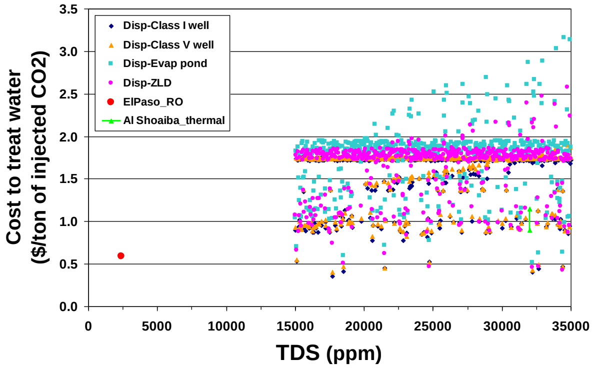


Figure 4 (left). Cost to treat in \$/ton CO_2 injected Formation=Rock Springs Weber Fm., variable TDS (15,000-35,000 mg/L) and temperature (10-117°C), energy costs=\$0.10/kWh, MSF thermal, Pelton pressure recovery included, 500 realizations.

Volumes of extracted water treated after carbon storage are predicted to be very large in some cases, ~1 km^3 over 50 years [16, 17]. The volumes of water extracted are very similar to those projected for fracture flowback during gas recovery phases. The large, and temporally variable, extracted volumes are projected to impact management and treatment costs considerably. We have evaluated volumes up to 10 mgd (37,854 m^3) in our current scenarios. Methods for handling and storing such large quantities should be included in hydraulic fracturing system models to evaluate infrastructure and cost impacts.

While system models are convenient ways to make near-term management decisions, larger scale models are needed to look at longer term, multi-dimensional and multiphysics scenarios. CO_2-PENS provides large scale system transport and pressure/chemistry interactions of gas and fluids. ASCEM is a state-of-the-art physics-based approach for predicting contaminant fate and transport. It is based on a modular, extensible, and open source design that leverages existing high-performance computing capabilities (many developed through DOE SC-ASCR). It currently provides a dynamic and evolving community platform across many DOE sites, for testing and integrating the processes behind large-scale contamination problems. The model integrates key tools into single framework, including simulation, data management, visualization, parameter estimation and uncertainty quantification. PFLOTRAN, a multi-scale chemistry and flow model, can be integrated with ASCEM. These models have been used for contaminant transport at DOE sites and understanding the evolution of permafrost melting and subsurface flow in the Arctic. In combination, the two can be used to promote understanding of the effects of unconventional gas extraction methods on basin scale resource use, while incorporating climate change, regulation, and economics parameters.

Acknowledgement

This work was funded in part by the US DOE's Office of Fossil Energy through the National Energy Technology Laboratory's Carbon Sequestration Program.

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Appendix C.

Poster Abstracts

Sustainable Water Treatment, Recycling & Disposal Practices in the Marcellus Shale Basin

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Altela, Inc.

The statements made during the workshop do not represent the views or opinions of EPA.
The claims made by participants have not been verified or endorsed by EPA.

Introduction

Recent technological innovations in hydraulic fracturing (well-stimulation) have transformed the nation's shale formations from marginal producers of natural gas to substantial contributors to the nation's energy supplies. At the same time, critical water resource problems have developed with respect to managing, treating and disposing of the significant volumes of hydraulic fracturing flowback waters in an environmentally safe manner.

The Marcellus Shale is a thick sequence of Devonian age, sedimentary rocks in the Appalachian Basin that extends from southern New York across Pennsylvania, and into western Maryland, West Virginia, and eastern Ohio. Each Marcellus shale-gas well is hydraulically fractured with approximately five million gallons of water. Following fracturing of each well, significant amounts of hydraulic fracturing flowback water come to the surface and must be managed and disposed of in an environmentally responsible manner[1]. Historically in the Marcellus Shale, natural gas exploration and production companies have relied on either trucking the water to reinjection wells in Ohio where geologic formations support such high volume reinjection or sending the wastewater to commercial treatment facilities including publically owned treatment works ("POTWs") to dilute this wastewater before releasing it into surface water bodies. There are many pollutants of concern in this hydraulic fracturing water which contains significant amounts of salt, metals, sulfates, and chlorides. In addition, certain constituents that are proprietary in nature are not fully disclosed on manufacturer's safety data sheets.

In response to these concerns, the Pennsylvania Department of Environmental Protection ("PA DEP") developed new discharge standards. The PA DEP amended its Chapter 95 Wastewater Treatment Requirements effective August 21, 2010, to ensure that drinking water, waterways, and watersheds in the state were not impacted by high levels of total dissolved solids ("TDS") including chlorides and sulfates[2]. These new discharge and recycling regulations have created challenges for the shale-gas industry due to the lack of proven treatment technologies that are able to economically treat hydraulic fracturing water to discharge water quality standards. Without such technological solutions, these new regulations may have the unintended consequence of curtailing the nation's natural gas development through increased exploration and production costs.

The purpose of this abstract is to provide a brief summary and update on efforts these past three years to develop an integrated water treatment technology solution for sustainable water resource management in the Marcellus Shale Basin.

Discussion

NETL Project DE-FE0000833

The U.S. Department of Energy's ("DOE") Office of Fossil Energy's, National Energy Technology Laboratory's ("NETL") primary goal is to enhance the responsible development of domestic natural gas and oil resources that supply the country's energy. A specific objective is to accelerate the development and demonstration of technologies that will aid our country's independent producers in dealing with use and treatment of water related to natural gas and oil production.

In 2009, NETL selected nine new projects targeting environmental tools and technology for shale gas production. Altela, Inc. was selected as the lead team member with respect to Project DE-FE0000833 titled "*An Integrated Water Treatment Technology Solution for Sustainable Water Resource Management in the Marcellus Shale". * The purpose of the field demonstration project was to provide an integrated approach aimed at addressing the increasing water resource challenges between natural gas production and other water stakeholders in shale gas basins. Specific goals of the project included: 1) deliver field-proof that the water treatment technology and protocol was actually capable of treating this highly challenged Marcellus hydraulic fracturing water to water quality standards required for discharge and/or applicable beneficial re-use, 2) deliver field-proof that the water treatment technology could economically treat the hydraulic fracturing water at a cost equal to or lower than current disposal methods, and 3) demonstrate that the regulatory environment would support implementation of the water treatment technology solution.

The NETL field demonstration project successfully attained its goals. During nine continuous months of operation, the AltelaRain® system placed adjacent to a natural gas well treated 77 percent of the hydraulic fracturing flowback and production wastewater on-site, providing distilled water as the product. The average treated water cost per barrel over the demonstration period was approximately 20 percent lower than the previous total conventional disposal costs at the site. The system also significantly reduced the need for trucking wastewater from the site thereby reducing truck mileage. Based on field data generated from the NETL demonstration, Altela increased the efficiency of its technology by more than 30%. All of the clean water produced at the demonstration site was suitable for beneficial re-use by well operators for additional stimulations and was also suitable to be discharged to surface waterways, thus reducing the economic and environmental impacts of clean water usage. Additional detailed information including complete water analyses, recovery rates and overall economics are included in the project's final report dated June 30, 2011[3].

This DOE demonstration project accelerated the commercialization of the AltelaRain® system which has led to the development of several large centralized wastewater treatment, recycling and disposal facilities in the Marcellus including Casella-Altela Regional Environmental Services, LLC McKean Facility.

Casella-Altela Regional Environmental Services, LLC ("CARES")

In August 2011, Casella Waste Systems, Inc. and Altela, Inc. formed a joint venture, Casella-Altela Regional Environmental Services, Inc., to construct and operate water treatment, recycling and disposal ("TRD") facilities to support the natural gas drilling activity. The first facility is located in Sergeant Township near Mt. Jewett, Pennsylvania. The CARES McKean TRD Facility, ("CARES McKean Facility")[4] is part of a larger initiative to transform the existing McKean County Landfill into a multi-purpose environmental services facility designed to serve the region's evolving recycling and disposal needs, create jobs, and reduce truck traffic. By co-locating adjacent to a landfill and leveraging existing infrastructure, the CARES McKean Facility serves as a model for integrated and sustainable wastewater treatment, recycling, disposal and management in shale basins.

One of the sustainability attributes of this co-gen facility is its ability to convert methane gas produced from the landfill into usable energy required for the wastewater treatment and desalination circuit. Designed to beneficially use landfill gas ("LFG"), the CARES McKean Facility employs LFG fired boilers to generate steam for the AltelaRain® thermal distillation circuit. In this manner, the facility's energy operating costs are significantly reduced while also reducing certain air emissions from the LFG flare. The facility currently uses approximately 350 standard cubic feet per minute of landfill gas with an average methane content of approximately 52%. The methane gas is chilled prior to sending it in the transmission pipeline to the CARES facility using a multistage centrifugal blower. The landfill gas is regulated into either of two 9.8 million BTU low pressure steam boilers at roughly 2 psi. The boiler manifolds were modified to support beneficial use of the landfill gas.

By utilizing this landfill gas, the thermal distillation circuit becomes economically viable to allow for TDS and related salt removal of the wastewater to support an open-loop facility. Following desalinization, the treated water meets NPDES requirements for discharge into the PA Commonwealth's surface water bodies when recycling demand falls below supply. Without this open loop capability, out-bound water must be generally removed at the same rate as inbound wastewater in order to not reach storage constraints.

Facility Description

The CARES McKean Facility has approximately 13 full and part-time employees and operates 24/7 in varied shifts according to water acceptance demands. The 4-bay covered truck load-out area is designed for maximum receiving efficiency, convenience and ease of the driver. The facility has two 550,000 gallons storage tanks as well as three water storage impoundments. See site layout illustration below.

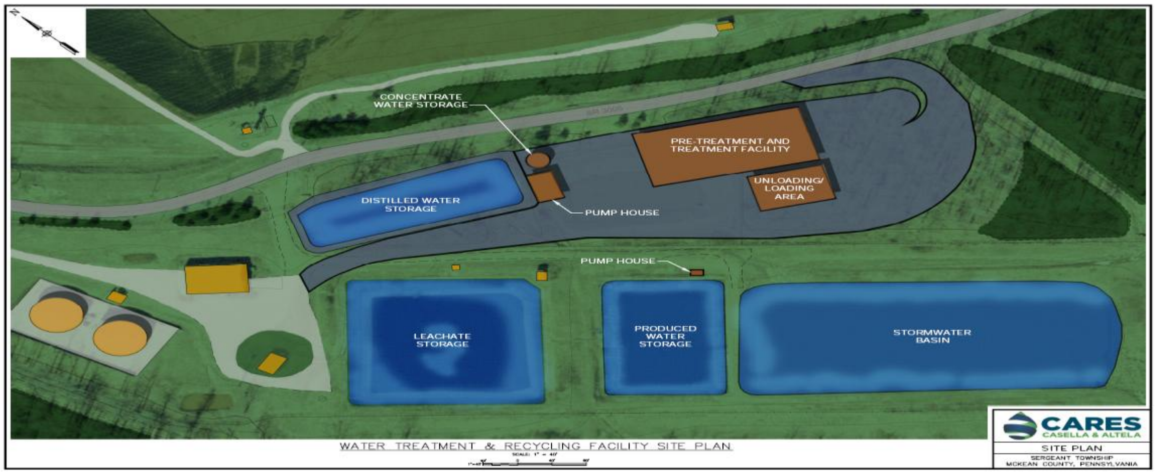

Figure 1. CARES McKean Site Plan

The wastewater entering the facility is processed through a variety of process systems, the first being a pre-treatment system that will yield Pretreated Frac Water ("PFW"). The PFW has two paths that it can take depending on the needs of the customer and the facility. The first path is to an outside storage facility where the PFW is mixed with Distilled Water ("DW") to produce Certified Frac Water ("CFW") for the customer to pick up for recycling. The second path for the PFW is to the AltelaRain® evaporation-condensation modules, which yields two liquid streams. The first stream which is the clean DW stream is as described above. The second steam which is the Concentrate Water ("CW") stream is the residual liquid solution remaining after approximately 80% of the pure H2O has been removed via the recycling process. This residual CW solution will contain nearly 100% of the salt products, by weight that was contained in the original volume of Produced Water ("PW") processed through the facility in a 24-hour period of time.

Similar to nature's process for making rain, the AltelaRain® technology operates at low temperatures and low-grade steam. Ambient air flows up through brackish water in an evaporation chamber to strip contaminants into a concentrate. The air is then combined with steam and pushed down through a condensation chamber creating a clean distilled water product. The AltelaRain® technology does not require pressure which translates into lower OpEx and CapEx costs. As noted above, the process can be driven by low-grade heat, waste heat or natural gas thereby making it suitable for "co-generation" applications to reduce energy costs.

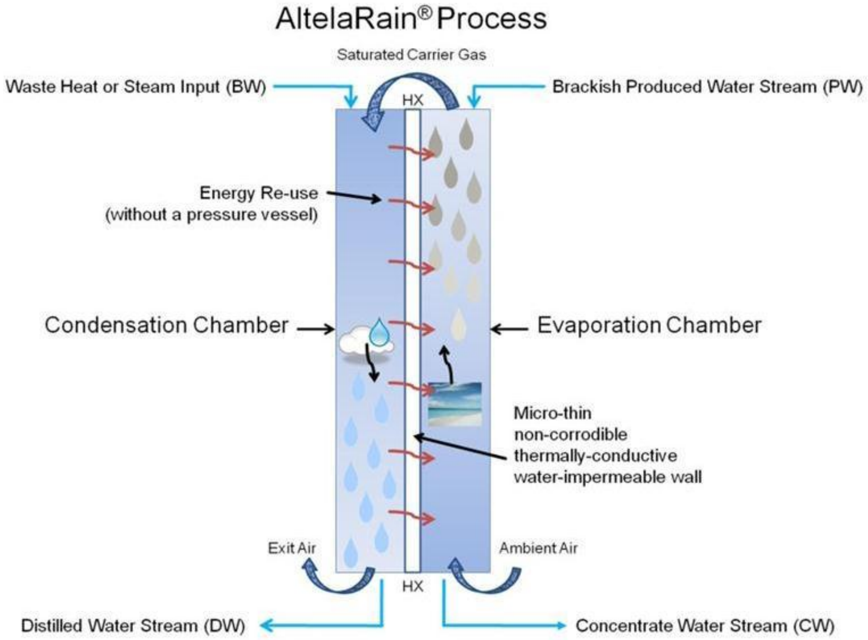

Figure 2. AltelaRain® Schematic

The clean DW produced during the recycling process is made available for beneficial re-use by oil and gas producers in on-going drilling operations, as make-up water for the boilers, or discharged, via the CARES McKean Facility's approved NPDES permit. The residual CW, is re-used as regulations permit (recycling, heavy brine water or road salt), can be solidified and disposed of as a solid waste in the landfill, or can be removed from the site and transferred to approved commercial produced water disposal facilities. Initial capacity of the facility is 500,000 gallons per day ("GPD") of PFW and 100,000 GPD of DW. See the general process schematic and floor plan figures below. The facility's recycled hydraulic fracturing water can be supplied with varying level of customer-defined limits of removal of TSS, iron, barium, calcium, chlorides, TDS, sulfates, friction reducers, surfactants, biocides, radionuclides, etc. In this manner, valuable recycled water-based products can be offered to industry including recycled hydraulic fracturing water for reuse in hydraulic fracturing, clean distilled water and heavy brine for winterization.

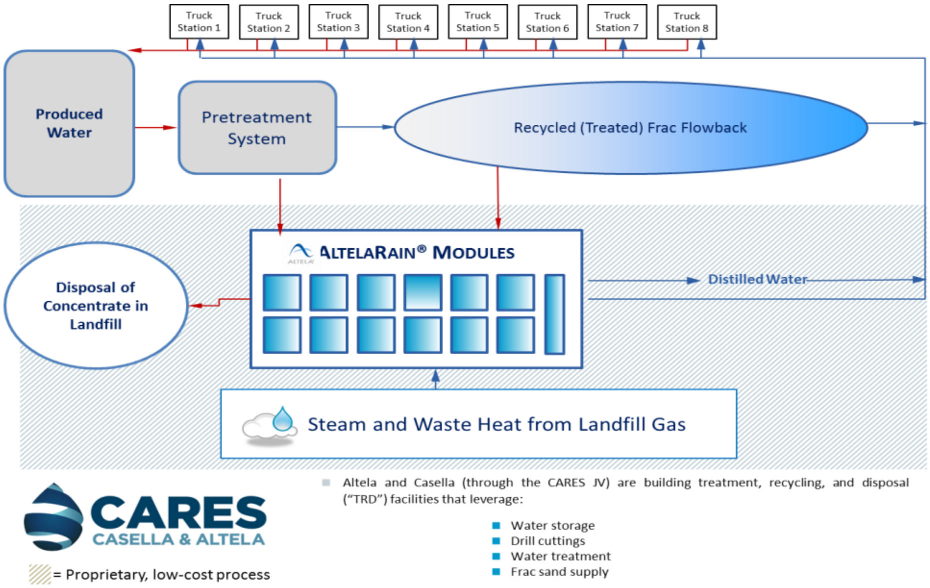

Figure 3. CARES McKean General Process Schematic Overview

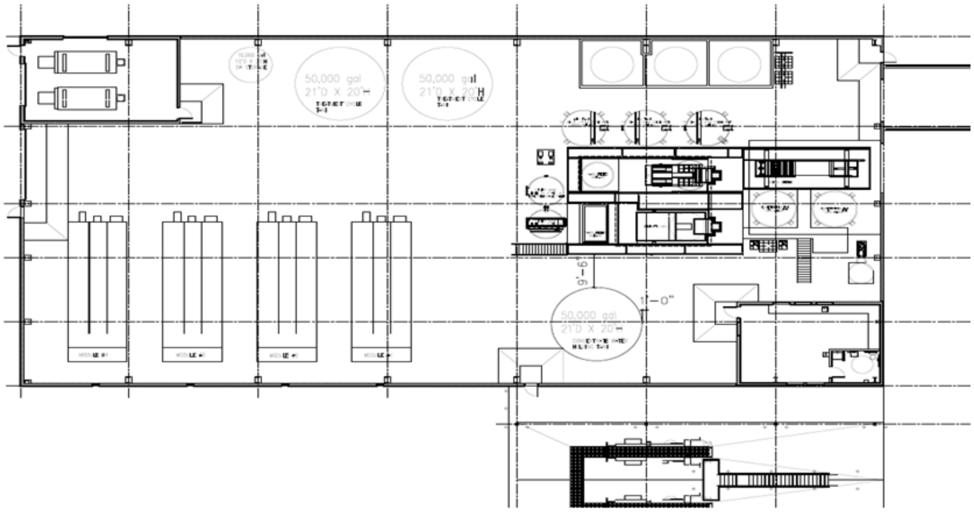

Figure 4. CARES McKean Floor Plan

Other capabilities of the facility include 1) separation and solidification services, 2) material sourcing including hydraulic fracturing sand supply, gravel for well-pad construction, and tanker cleaning and 3) storage and transportation services including interim water storage, centralized transportation network of rail and over-the-road trucking, and storage areas for lay-down yards.

Regulatory & Environmental Summary

The CARES McKean TRD Facility is a fully permitted centralized commercial wastewater treatment facility with the following primary permits: PA DEP WMGR123NW005 General Permit for the Processing and Beneficial use of oil and gas liquid waste, National Pollution Discharge Elimination System ("NPDES") discharge permit PA0102288 (as amended), including attendant Water Quality Management Plan Part II Permit, and related PA DEP air quality regulatory approvals. Following PA DEP's recent Chapter 95 regulatory changes, the CARES McKean TRD facility's technology is capable of meeting the required discharge requirements. These discharge requirements are summarized below:

Table 1. NPDES Discharge Requirements of Representative Outfall

NPDES CONSTIUENTS	**Final Outfall 001***	**UNIT**
CBOD (avg mo)	48.5	mg/L
AmoniaNitrogen (avg mo)		mg/L
" May 1-Oct 31 (avg mo)	2.1	
" Nov 1-Apr 30 (avg mo)	6.3	
Arsenic (avg mo)	0.0102	mg/L
Barium (avg mo)	10	mg/L
Bromide	Report	mg/L
Cadmium	0.0002	mg/L
Chloride (avg mo)	250	mg/L
Chromium (avg mo)	0.0522	mg/L
Copper (avg mo)	0.0092	mg/L
Gross Alpha	Report	pCi/L
Lead (avg mo)	0.0032	mg/L
Nickel (avg mo)	0.053	mg/L
Oil & Grease (avg mo)	15	mg/L
pH	9-Jun	SU
Radium-226 + 228	Report	pCi/L
Selenium (avg mo)	0.0051	mg/L
Silver (avg mo)	0.0024	mg/L
Strontium (avg mo)	10	mg/L
Tin (avg mo)	0.0367	mg/L
Titanium (avg mo)	0.00612	mg/L
TDS (avg mo)	818	mg/L
TSS (avg mo)	11.3	mg/L
Uranium	Report	ug/L
Vanadium (avg mo)	0.0518	mg/L
Acetophenone (avg mo)	0.0562	mg/L
2-Butanone (avg mo)	1.85	mg/L
Carbazole (avg mo)	0.276	mg/L
Fluoranthene (avg mo)	0.0268	mg/L
o-Cresol (avg mo)	0.561	mg/L
n-Decane (avg mo)	0.437	mg/L
n-Octadecane (avg mo)	0.302	mg/L
Phenol (avg mo)	1.08	mg/L
Pyridine (avg mo)	0.182	mg/L
Osmotic Pressure (avg mo)	51.3	mOs/kg
2,4,6-Trichlorophenol (avg mo)	0.0018	mg/L
Acetone (NPDES (avg mo)	3.5	mg/L
Total Antinomy (avg mo)	0.0057	mg/L
Bis(2-Ethylhexyl)Phthalate (avg mo)	0.0015	mg/L
Butyl Benzyl Phthalate (avg mo)	0.035	mg/L
Total Cobalt (avg mo)	0.0194	mg/L
Total Mercury (avg mo)	0.00005	mg/L
p-Cresol (avg mo)	0.164	mg/L
Zinc (avg mo)	0.078	mg/L

Numerous environmental controls are in place to ensure environmental protection and best business practice management including:

<u>Site Inspections</u>: PA DEP inspects the facility on a periodic basis. Regular visual inspections are carried out by CARES employees monitoring levels within the on-site impoundments

Groundwater: Due to the site proximity to the adjacent McKean County Landfill, there is an established groundwater monitoring system with protocols approved by PA DEP under the landfill solid waste permit.
Stormwater: The site has stormwater management controls in-place and approved by PA DEP.
Spill Control: The facility has an approved PA DEP Pollution Prevention Contingency Plan outlining the spill control and prevention measures.
Radiation Monitoring: The facility is equipped with stationary radiation monitors which screen each incoming truck to confirm that incoming loads do not exceed the facility's radiation thresholds. Trucks exceeding the minimum radiation thresholds are not accepted at the facility.

Conclusions

Safe, reliable and cost effective water treatment is a key requirement for natural gas drilling companies. Developing the CARES McKean Facility near the Marcellus drilling activity and providing a safe and reliable option for treating and recycling the water reduces long-hauls to deep well injection sites and enables a back-haul of clean distilled water for beneficial re-use. This co-generation facility utilizing landfill gas to economically purify wastewater to discharge standards can set an environmental sustainability example for hydraulic fracturing water treatment and recycling in other emerging shale basins.

Acknowledgements

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Feasibility of In Situ Sequesteration of Toxic Metals in Flowback Water from Hydraulic Fracturing.

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Synopsis

Hydraulic fracturing is playing a dramatically increased role in natural gas and oil production in the United States (1,2), but environmental issues are currently delaying its development, e.g., the moratorium on hydraulic fracturing in the state of New York. Dissolved barium is one of the most significant toxic contaminants in produced brines from oil and gas operations, including water recovered during hydraulic fracturing of shales and sandstones (3,4). Radium is the primary NORM (Naturally Occurring Radioactive Material) in these fluids (5,6). Barite ($BaSO_4$) 'scales' in wellhead and borehole equipment are radioactive due to radium incorporation (4) and above-ground barite precipitation has been employed as a treatment process for both contaminants (7). One possible method to significantly reduce the toxicity and radioactivity of produced waters and equipment could be to induce precipitation of contaminant as impurities in minerals directly in the subsurface geologic formations.

The focus of this poster is to discuss what would work would need to be done to evaluate the feasibility of in situ radium-containing barite. Specific issues include: **a)** the efficiency of impurity metal incorporation under subsurface conditions in the presence of hydraulic fracturing fluids; **b)** the effect of pore-confinement in geologic media on the rates and locations of barite precipitation and permeability of the formation; and **c)** the applicability of models for predicting the performance of in situ precipitation schemes.

Significance

Subsurface fluids produced as wastewater in hydraulic fracturing activities, particularly from shale formations, are resulting in significant amounts of produced toxic and radioactive metal contaminants (3-7). Some natural gas wells in the Marcellus shale (PA) are producing up to 18,000 pCi/L dissolved radium (Ra^{2+}) (8), whereas the U.S. EPA Safe Drinking Water Act Maximum Contaminant Limit (MCL) for this metal is 5 pCi/L. Barium (Ba^{2+}) is a toxic metal often present in produced oil and gas field waters at levels of several thousand mg/L (8,4), far exceeding the EPA MCL of 2 mg/L ($10^{-4.8}$ Molar).

A novel strategy to reduce the concentration of contaminants such as radium and barium in produced waters in oil and gas fields is to promote the precipitation of a mineral phase that contains the toxic and/or radioactive contaminants directly in the subsurface. This method has been proposed for other subsurface contaminants such as uranium (9,10) and strontium (11,12). Due to the very low solubility of barite, dissolved Ba^{2+} concentrations below the EPA MCL may be achieved if dissolved SO_4^{2-} concentrations above ~10 mg/L can be maintained in the pore waters during the period of water recovery. It has already been shown that incorporation of Ra^{2+} and Ba^{2+} as a major constituent or impurity in the highly-insoluble mineral barite ($BaSO_4$) may be an effective potential strategy for above-ground post treatment (7,13). A more desirable approach would be to induce the precipitation of barite in situ in the subsurface production zone prior to or during flowback water production, as this would avoid bringing contaminated water to the surface. However, there is a significant gap in our fundamental understanding of how to predict and control the precipitation of barite in rock pores. The size distribution of pores in which the precipitation reactions preferentially occur is particularly poorly understood. This is important because using in situ precipitation as a sequestration method requires engineering the precipitation to occlude pore spaces uniformly without immediately clogging the aquifer or screened intervals of production wells and blocking the flow of the fluids through the rock (14,15).

In order to better predict and control in situ barium and radium mineral trapping, one question to be dealt is how efficiently Ra^{2+} and Ba^{2+} can be co-precipitated, and how the sequestration conditions affect the rate of precipitation and the efficiency. Both Ra^{2+} and Ba^{2+} form sulfate salts that are orders of magnitude less soluble than other common sulfate minerals such as gypsum ($CaSO_4•nH_2O$) (16). Although $RaSO_4$ is only slightly less soluble than $BaSO_4$ at room temperature, the concentration of Ba^{2+} in produced waters is much higher than Ra^{2+}. Therefore it is reasonable to attempt to drive incorporation of Ra^{2+} into the barite crystal structure during its precipitation as a means of significantly reducing the concentrations of both species without precipitating other phases. Early free-drift studies (17-19) found that for the pure $Ba-Ra-SO_4$ system, the reduction of Ra^{2+} concentration in solution correlates with the reduction in Ba^{2+}. However, these studies did not yield a quantitative, predictive capability, nor did they account for competition by Ca^{2+}, Sr^{2+} and other dissolved ions (Na^+, Cl^-) or compounds abundant in typical flowback water. Electrolyte composition and concentration can affect the kinetics of barite precipitation (20) and substantial amounts of incorporating ions (e.g., Ca^{2+}, Sr^{2+} in barite) can inhibit the growth of a mineral (12,21). A field study of uranium mill tailings showed that the mobility of Ra^{2+} is entirely dominated by a disordered $(Ra,Ba)SO_4$ barite phase (19). The solubility of this phase will be slightly higher than either of the two ideal end-member sulfates but it is not likely to exceed more than approximately 1.3-1.6 orders of magnitude that of pure barite (22), so it still will be only sparingly-soluble relative to other common sulfate minerals. In the long term, sulfate-reducing bacteria present in the (reducing) shale subsurface environment may reduce sulfate in the precipitated barite to sulfide, but release of radium and barium has not been shown to be substantial in the short term as a result of this process (23). Lastly, the scale inhibitors that are added to the hydraulic fracturing fluid inhibit growth of a minerals. Since in the proposed in situ precipitation strategy requires precipitation in situ, scale inhibitors should likely not be used and scale formation by other compounds besides sulfates (e.g., $CaCO_3$) will need to be evaluated.

In addition to demonstrating that Ra^{2+} concentration can be efficiently reduced by co-precipitation in solutions containing much higher levels of Ba^{2+}, Sr^{2+} and Ca^{2+}, we need to develop an understanding of how pore size distribution, pore surface chemistry (e.g., shale mineralogy, surface coating by hydrocarbons, etc.) affects the sites and extent of barite precipitation in porous geologic media, while avoiding hindering or stopping fluid flow. The main constituents of shales are quartz, clays, and organics, although some shales also contain sizeable amounts of carbonates and other minerals. The distribution of barite between pores and exposed surfaces of these minerals is currently unknown but can be studied ex- and in-situ by X-ray and neutron scattering, using both synthetic model substrates as well as drill core samples from shale gas production sites. Finally, our ability to predict and control precipitation in the subsurface depends in part on applying a kinetics model measured in the laboratory under well-mixed conditions to a porous medium in the subsurface. Traditional geochemical kinetics models consider the rate of growth or dissolution of a mineral as a function of the saturation state of the system, but these models have been shown inadequate to describe reaction rates when the ratio of the aqueous form of the mineral's constituent ions deviates from that to which the model was calibrated (11,24). An alternative is a "process-based" model that is built from reactions thought to occur on the mineral surface itself (25-27). Our recent work on calcite ($CaCO_3$), has resulted in a process-based kinetics model that is suitable for direct inclusion into a reactive transport simulation used in porous media (28), which it may be possible to adapt to the Ra-Ba-SO_4 system.

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Wastewater Made Clear with Green Technology

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Electrocoagulation is the scientific discipline of utilizing electricity as the electromotive force to drive chemical reactions in a solution, suspension, or emulsion. A special form of direct current is introduced into the aqueous stream as it passes between predetermined electrodes in the electrocoagulation module. This energy from the electricity is the engine or driving force to shift the equilibrium of a reaction to less than equilibrium levels, thus providing a mechanism for removing dissolved, suspended or emulsified molecules, elements or ions to very minute levels in an aqueous stream.

Background

Electrochemical treatment can precipitate dissolved heavy metals by a combination of oxidation reduction reaction that in many cases produces oxide crystals that are very stable. Hexavalent chromium is reduced to trivalent chromium and removed as a precipitate. Copper, Lead, Zinc, Nickel and other metals are oxidized into oxide crystal form and can sometimes be concentrated and removed from the sludge stream to be recycled. Some metals require an anion to be present to form a precipitate such as calcium, magnesium, molybdenum, and others. Many times this anion may already be present in the waste stream, but if not, it can generally be added very easily. These heavy metallic crystals can be a positive nucleus to attract the electron rich hydroxide floc and colloidal solids into a settle able precipitate. This precipitate can then be separated in a settling pond or in a clarifier after some of the heavy metals are classified and concentrated.

Electrocoagulation will break colloidal suspensions, which allows the precipitation and removal of suspended particles. The excess of electrons causes the colloidal particles to attract to a sacrificed metallic cation, which comes from the electrodes as the electric current passes through the electrode in accordance with Faraday's Law. This metallic cation acts as a nucleus to attract the electron laden colloidal particles together into a floc precipitate. This generates a larger heavier floc, which can then be separated by a secondary separation process such as settling, clarification or centrifugation.

Electrocoagulation will break oil emulsions and release the tied up emulsified oil to float to the surface where it can be skimmed off with a vacuum and recovered if viable. Oil becomes emulsified as shearing action from pumps or chemicals cause an open or broken bond in the hydrocarbon chain, which then attaches itself with a weak bond to the water molecule. Even though this is a weak bond, it is a protected bond and consequently very difficult to break by conventional means. As the electricity passes through the water being treated, electrons and energy are available as well as hydrogen ions or protons from the electrolysis of the water itself, and oxygen or hydroxide ions as a chemical feed stock for reaction completion. These subsequent reactions cause the weak bond to be broken and the oils to return to being a complete molecule and the emulsion is broken. At this point the oil again becomes hydrophobic and generally floats to the surface due to differences in specific gravity.

The Process

Electrochemical treatment is generally used on industrial waste streams to allow the reuse or discharge of an industrial waste stream. The process uses electricity rather than expensive, dangerous, and sometimes toxic chemicals to remove contaminants. Electrochemical treatment can be a pretreatment for other processes such as reverse osmosis, or a polish treatment for traditional treatment processes.

How Does Electrocoagulation Technology Work?

Electrocoagulation is the process of destabilizing suspended, emulsified or dissolved contaminants in aqueous medium by introducing a direct electrical current into the medium. The electrical current provides electromotive force to drive the chemical reactions.

When reactions are driven or forced, the elements or compounds will approach the most stable state. Generally, this state of stability produces a solid that is either less colloidal or less emulsified (or soluble) than the compound at equilibrium values. As this occurs, the contaminants form hydrophobic entities that precipitate and can easily be removed by a number of secondary separation techniques. Electrocoagulation neutralizes ions and particle charges, thereby allowing contaminants to precipitate. Colloids are then destabilized and aggregated and subsequently removed by sedimentation or filtration.

Under current wastewater treatment methods, a cocktail of chemicals is needed to treat large amounts of wastewater producing increased amounts of solids, which increase production costs and can create environmental problems when they are ultimately disposed. The negative impact on the environment is high using existing treatment methods.

Electrocoagulation can often neutralize ions and particle charges, thereby allowing contaminants to precipitate. Colloids can be destabilized and aggregated and subsequently be removed by sedimentation or filtration. The amount of solids is substantially much less and environmentally friendly.

This technology has been proven as one the most effective methods to treat large amounts of wastewater. The range of treatment is between 300 liters/hour to 600,000 liters/hour, depending on the site-specific requirements.

Electrocoagulation systems are part of a comprehensive treatment plan, as 75% of the water treatment is completed by this technology. For the remaining 25%, additional polishing systems would be added to meet the state and local discharge requirements.

For a range of wastewater treatment needs, electrocoagulation technology is a viable option. The technology itself has been successfully used for decades. The need for increased usage *now* is to help preserve and reuse our natural water resources. Droughts, natural disasters, municipal water needs and shale gas recovery will continue to put increased strain on our water resources and existing treatment facilities.

For states in the western United States, electrocoagulation technology has had positive environmental impact while solving many existing concerns of wastewater and hydraulic fracturing fluid treatment. States such as Texas, Wyoming and Colorado have successfully used electrocoagulation technology for the treatment of a wide-range of industrial wastewater – including hydraulic fracturing water.

Results

Analytical testing has been done on a wide range of waste streams including municipal water, animal/dairy waste, and drilling/hydraulic fracturing fluids. The following table reflects some results on raw and electrocoagulation treated water from a hydraulic fracturing site located in Texas.

Constituents	Units	Raw	Treated	% reduction
Calcium, Ca	mg/L	3,000	4.04	99.9
Magnesium, Mg	mg/L	637	0.78	99.9
Sodium, Na	mg/L	13,100	64.4	99.5
Potassium, K	mg/L	313	2.56	99.2
Iron, Fe (total)	mg/L	23	0.02	99.9
Bicarbonate, HCO3	mg/L	490	20	95.9
Chloride, Cl	mg/L	28,000	97	99.7
Sulfate, SO4	mg/L	141	0.404	99.7
Sulfide, S	mg/L	0.65	0.020	96.9
Boron, B	mg/L	19.8	1.91	90.4
Barium, Ba	mg/L	2.89	0.0032	99.9
Silica, SiO2	mg/L	65.6	0.546	99.2
Strontium, Sr	mg/L	249	0.261	99.9
Totals (Sum)		46,042	171.93	99.6
Total Dissolved Solids	mg/L	53,400	202	99.6
Calculated Hardness,CaCO3	mg/L	10,100	13.3	99.9
Total Alkalinity	mg/L	490	20	95.9
Sodium Chloride, (total)	mg/L	41,100	161.4	99.6
Sodium, Na (Calculated)	mg/L	13,100	64.4	99.5
pH		6.14	7.3	

Conclusions

Electrocoagulation is a technology that can be used in a variety of processes, is a “green” technology and may also produce beneficial by-products. Results indicate that water from a waste stream can be cleaned to most required discharge limits or reuse levels.

Oil and Gas Water Purification using Switchable Polarity Solvent Forward Osmosis (SPS-FO)

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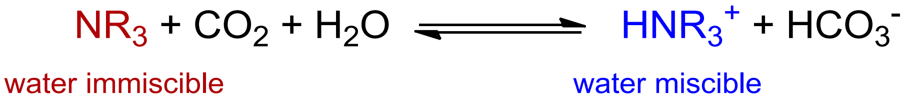
Introduction

Oil and gas waters are very challenging feed solutions which vary greatly depended on source but often contain high total dissolved solid (TDS) in the form of salts and organics, suspended oils and solids, and feature a non-neutral pH. To apply reverse osmosis (RO) to oil and gas water feed solutions usually requires substantial pretreatment to prevent fouling and is only applicable to feed solution with a TDS below 47,000 ppm given RO practical limit of 70,000 ppm for it concentrate output.[1] Electrochemical methods such as reverse electrodialysis (RED) do not remove uncharged organics and are historically limited to brackish water (<8,000 ppm TDS) because of their relationship between processing cost and salinity.[1] Distillation can treat high TDS but it is a mature field and has substantial cost; distillation is generally double the cost of RO for seawater desalination. An alternative is forward osmosis (FO) which moves water from a feed solution across a semi-permeable membrane to a draw solution based on an osmotic pressure differential.[2] A forward osmosis (FO) process in which the osmotic draw solute is removed by means other than RO has the potential to address high TDS feed solutions. Such a next generation FO system would require a minimal amount of pretreatment when compared to competing methods and could have a significantly lower cost than distillation and RO.

A number of next generation draw solutes have been explored including dissolved gases, hydroscopic organics, nanoparticles, inorganic salts, thermosensitive solutes, and thermolytic solutes. Each of these can each be removed by distillation or precipitation with the addition of salt mixtures, pH adjustments, temperature adjustments, or application of a magnetic field.[3–18] Each of these systems has serious drawbacks, such as limited osmotic pressure and flux rate, limited recyclability, loss of the draw solute through diffusion through the FO membrane, and overall systems cost that have hindered their implementation.

Switchable polarity solvents (SPS)[19–22], mixtures of carbon dioxide, water, and tertiary amines (Figure 1), are presented as viable forward osmosis (FO) draw solutes allowing a novel SPS-FO process.[23] In this study substantial osmotic strengths of SPS are measured with freezing point osmometry and were demonstrated to induce competitive fluxes at high salt concentrations on a laboratory-scale FO unit utilizing a flat sheet cellulose triacetate (CTA) membrane. Under the experimental conditions the SPS degrades the CTA membrane; however SPS experiments with polyamide reverse osmosis (RO) membranes display greater stability towards SPS. Once the draw is diluted the major fraction of the switchable polarity solvent can be mechanically separated from the purified water after polar to nonpolar phase shift induced by introduction of 1 atm carbon dioxide to 1 atm of air or nitrogen with mild heating. Trace amounts of SPS can be removed from the separated water with RO in a process that avoids solution concentration polarization. The separated nonpolar phase can be regenerated to a full strength draw and recycled with the re-addition of 1 atm of carbon dioxide.



$$NR_3 + CO_2 + H_2O \rightleftharpoons HNR_3^+ + HCO_3^-$$

Figure 1. A general example of an SPS from its nonpolar water immiscible form to its polar water miscible form.

An advantage of SPS-FO is the potentially low cost of operation, as compared to competing technologies that are reliant on expensive energy inputs from electricity, such as RO. SPS-FO functions at a fraction of the cost of other methods through a thermolytic cycle that avoids the distillation of water but still uses heat energy which costs a fraction of electrical energy. SPS-FO technology has the potential to address the water challenges presented by the most challenging produced water and flowback water feed solutions.

In addition a series of tertiary amines have been screened for their function as switchable polarity solvents (SPS). The relative ratios of tertiary amine and carbonate species as well as maximum possible concentration were determined through quantitative ^1H and ^{13}C NMR spectroscopy. The viscosities of the polar SPS solutions were measured and ranged from near water in the dilute systems through to the formation of a gel in specific systems at high concentrations. The van‘t Hoff indices for SPS solution were measured through freezing point depression studies as a proxy for the solutions osmotic strengths. A new form of SPS with an amine:carbonate ratio significantly greater than unity has been identified. Tertiary amines that function as SPS at ambient pressures appear to be limited to molecules with fewer than 12 carbons.

RESULTS AND DISCUSSION

Initial SPS-FO Process Study

In their polar forms, many switchable polarity solvents (SPSs) form highly concentrated ionic solutions with substantial osmotic pressures that are well suited to act as a draw solute. For example, a 18.0 mol/kg (77 wt%) dimethylcyclohexylammonium bicarbonate $[HN(Me)_2Cy\ HCO_3]$ solution is too concentrated to measure its osmolality through freezing point depression; however, diluted solutions can be measured as illustrated in Figure 2. Extrapolation from this dilute data predicts a fully concentrated 18.0 mol/kg $[HN(Me)_2Cy\ HCO_3]$ solution has an osmotic strength of ~800 atm. This study used a 7.6 mol/kg $[HN(Me)_2Cy\ HCO_3]$ draw solution with a projected osmotic pressure of ~335 atm, which at the time of the study was believed to be the maximum concentration of the $[HN(Me)_2Cy\ HCO_3]$ solution.

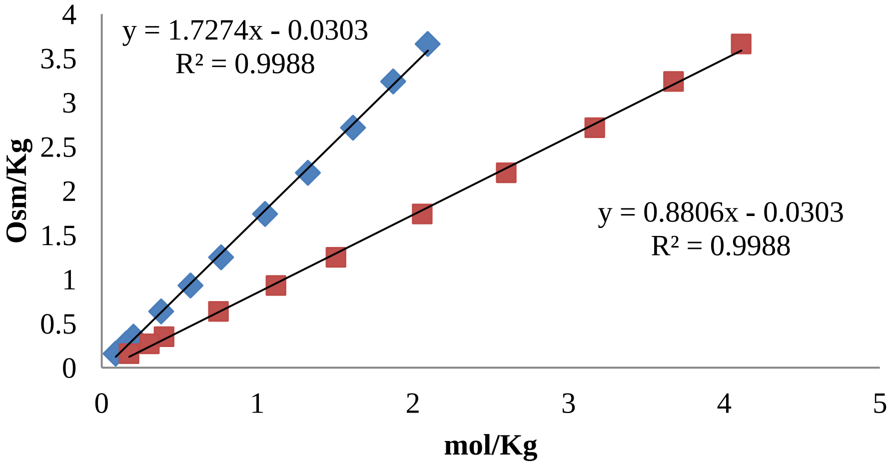


Figure 2. Osmotic pressure measured through freezing point depression experiments based on (red squares) amine concentration and (blue diamonds) total solute amine and bicarbonate.

FO flux experiments were conducted to verify the osmotic pressure measured for the polar SPS with freezing point depression was accessible to drive osotic flux. Feed solutions of varying NaCl concentrations exposed to a 7.6 mol/kg [$HN(Me)_2Cy$ HCO_3] draw solution across an HTI cellulose triacetate (CTA) FO membrane. Figure 3 presents the initial flux measured at each concentration. These initial results are promising with favorable flux observed through a 5.0 mol/kg NaCl feed solution. A 5.0 mol/Kg NaCl feed solution is 10-times the concentration of 35 salinity seawater with a 226,000 ppm TDS and an osmotic pressure of ~275 atm. Flux against a feed solution with a known ~275 atm osmotic pressure supports the projected ~335 atm for our 7.6 mol/Kg draw solution and suggests that the full strength 18.0 mol/Kg draw solution (~800 atm) should be able to pull water out of a fully concentrated sodium chloride solution (6.1 mol/kg) which has an osmotic strength of ~340 atm.[24]

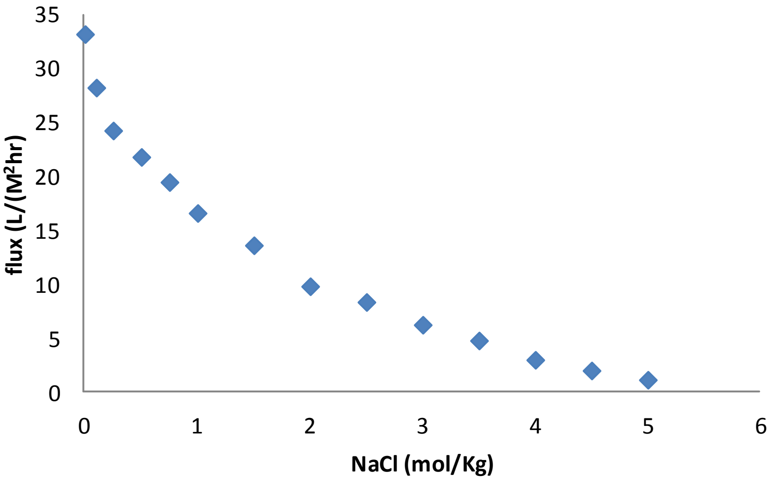


Figure 3. Water flux using 7.6 mol/Kg [HN(Me)2Cy HCO_3] draw solution against different concentrations of sodium chloride at 30°C, HTI CTA membrane in PRO mode (active layer draw solution).

Conventional FO systems act primarily as pretreatment methods, homogenizing a water stream for ultimate purification through RO, or they must include their solute in the final product. An SPS-FO system is significantly different; FO is the primary water purification method in which a miscibility shift liberates the majority of the water from the draw. Once a draw solution is saturated with water or reaches a desired dilution, the carbon dioxide is removed from the solution driving a shift in the SPS to its nonpolar immiscible form, which phase separates from the water. The two phases then can be mechanically separated, resulting in water purified to greater than 98 wt% in a system using $N(Me)_2Cy$ (solubility 18 g/L). This switching process was demonstrated in Jessop's initial report with the best result found using low grade heat of 60°C and a nitrogen purge.[21]

Trace amounts of SPS draw solute can be removed from the separated water through an RO process. This RO step is very different than the RO process involving a solution containing conventional solutes. During conventional salt RO, the volume of the feed solution is reduced as pure water is forced through the membrane, the reduction of volume corresponds to concentration polarization, which ultimately limits how much water can be obtained from the feed despite the application of pressures between 50 and 70 atm.[25] At its 18 g/L solubility limit, $N(Me)_2Cy$ has a maximum osmotic pressure of 3.4 atm which it never exceeds. Thus, low osmotic pressure aids RO by minimizing required energy and pressure. An RO experiment conducted on a 16.7 g/L solution of $N(Me)_2Cy$ with a polyamide thin-film composite membrane achieved a stable 99.65% rejection of the organic over a 4-hour period to produce a solution with 0.06 g/L $N(Me)_2Cy$ concentration.

A 0.06 g/L $N(Me)_2Cy$ concentration may be acceptable for some beneficial uses such as agriculture, microbial (algae) growth, solution mining, hydraulic fracturing water, and thermoelectric makeup water. There is no immediate toxicity concern from a 0.06 g/L solution at the oral LD_{50} rate of 425 mg/Kg, but it is likely still too high for human consumption over the long term. The RO treated water will need to be purified through an additional inline polishing step using an absorbent such as activated carbon.

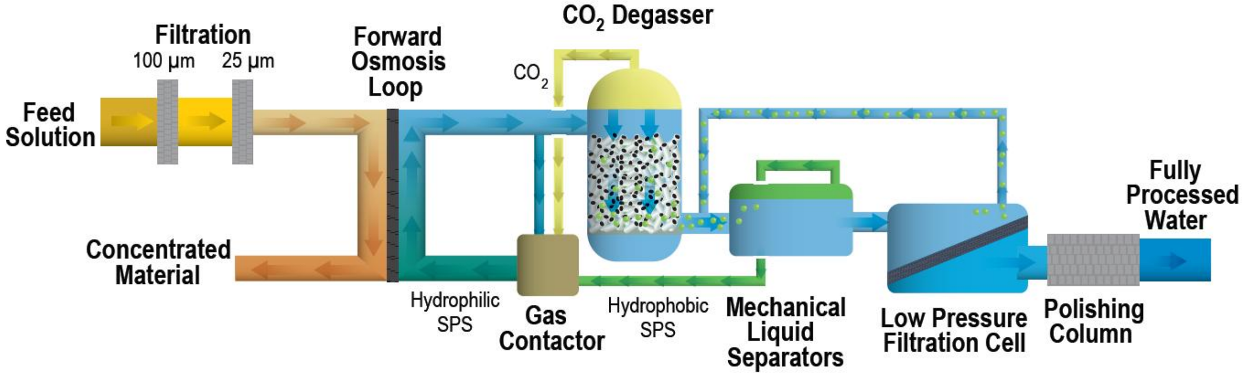


Figure 4. Proposed SPS-FO water purification process.

The complete SPS-FO system illustrated in Figure 4 featuring six major components: an FO loop, carbon dioxide degasser, mechanical liquid separator, low pressure filtration cell (RO like), a finishing step such as a polishing column, and a gas contactor to recycle the SPS. In addition to these major items, there will be various pumps, heat exchangers, and holding tanks. The capital cost of this system is expected to be comparable to a double pass seawater reverse osmosis

(SWRO) system. Based on current costs of heat ($3.00 MMBtu) and electricity ($0.10 kWh) and the capital cost the SPS FO system could cost half of SWRO per unit of water product while recovering a greater fraction of the water in a seawater feed >75% and economically treat higher concentration feeds.

SPS-FO Comparison to Ammonia-CO_2 Draw Solutions

There are other thermolytic draw solutes similar to the function of SPS most notably the ammonia-CO_2 system actively developed since 2005.[11–14] Fundamental theoretical energy requirements for the SPS-FO are expected to be less than the ammonia-CO_2 system (Table 1), however the real advantage is practical energy requirements. To sufficiently remove ammonia form water the ammonia-CO_2 system must bring the aqueous solution near reflux regardless of the pressure.[15] In contrast preliminary experiment indicate that tertiary amines used in SPS effectively separate from water at much lower temperatures. Furthermore, both the draw and the feed solutions need to be heat stripped to remove ammonia in the ammonia-CO_2 system due to the diffusion of ammonia from the draw solution into the feed solution.[16] The tertiary amines used in SPS-FO are not expected to penetrate the FO membrane due to their greater molecular volume.

Table 1. Thermolytic draw solute energy requirements comparison.

	Ammonia-CO_2 kJ/mol	SPS-FO kJ/mol
Carbamate decomposition $NR_3HCO_2NH_2 \rightarrow 2NH_{3(aq)} + CO_{2(g)}$	72.3(X) X = 0.1-0.8	0
Bicarbonate decomposition $NR_3H_2CO_3 \rightarrow NR_{3(aq)} + CO_{2(g)} + H_2O$	64.3(1-X) 1-X = 0.9-0.2	64.3*
NH_3 heat of dissolution	30.5(1+X)	~0
Total	98.7 to 125.6	64.3

*X is the stoichiometric excess of NH_3 used to maintain solute solubility.

Structure Function of Tertiary Amines for SPS-FO

A series of tertiary amines have been screened for their function as switchable polarity solvents (SPS).[26] The relative ratios of tertiary amine and carbonate species as well as maximum possible concentration were determined through quantitative ^{1}H and ^{13}C NMR spectroscopy. A number of limitation on tertiary amines capacity to function as SPS have been identified. This includes a carbon:nitrogen ratio of 12:1 when working at ambient pressures. A non-osmotic form of SPS was also indentified, whose primary compositional feature is an amine to carbonate ratio greater than unity. These non-osmotic SPS systems dominate tertiary amines with a C:N ratio of 10:1 through 12:1. The SPS that do function as osmotic SPS (C:N ratio of 6:1 through 8:1) have been demonstrated to be aggressive solvents that attack membranes as well as common polymers used in constructing water treatment systems.

This chemical aggressiveness combined with the amines toxicities adds cost to any system designed around such tertiary amines. If the chemical aggressiveness the SPS can be addressed with existing membranes and materials then SPS-FO process is at a technological readiness level where the next step is an integrated lab-scale system followed by a pilot system. If the chemical aggressiveness cannot be overcome there are two promising research fronts for the selection of an optimal SPS for SPS-FO: 1) explore conditions that allow the tertiary amines with elevated C:N ratios to function as osmotic SPS and 2) exploration of SPS other than mono tertiary amines that are less toxic (nontoxic) and less chemically aggressive while still providing high osmotic pressures, low viscosity, and good phase transition behaviors at a reasonable cost. Based on our structure function study the SPS-FO process it should be possible to identify an optimal SPS and associated conditions for an effective SPS-FO process.

CONCLUSION

SPS draw solutes have been found to enable an entirely new SPS-FO process for purifying water and concentrating solutions. The osmotic pressure and FO water flux properties of SPS reported here are substantial; suggesting that high osmotic pressure feeds produced water may be dewatered using this method. The novel phase switching from a high osmotic pressure aqueous solution to purified water and a nonpolar liquid, which can be physically separated, is a potentially revolutionary advance.

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