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## **Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Water Resources Management**





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# Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Water Resources Management

Office of Research and Development  
US Environmental Protection Agency  
Washington, DC

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# Introduction

## The Hydraulic Fracturing Study

In its Fiscal Year 2010 budget report, the U.S. House of Representatives Appropriation Conference Committee identified the need for a study of the potential impacts of hydraulic fracturing (HF) on drinking water resources. The Committee directed EPA scientists to undertake a study of HF to better understand any potential impacts of hydraulic fracturing on drinking water and ground water. The EPA produced a draft study plan, which focuses on the key stages of the HF water lifecycle: water acquisition, chemical mixing, well injection, flowback and produced water, and wastewater treatment and waste disposal. This plan was submitted to the Science Advisory Board (SAB) in February 2011 and the peer review of the plan was held on March 7 and 8, 2011. At the time these technical workshop proceedings were developed, the SAB had not given its official review to EPA.

EPA has included stakeholder concerns in the planning process of the study from its inception, engaging stakeholders in a dialogue about the study through a series of webinars and facilitated public meetings held between May and September 2010. EPA also held four technical workshops in February and March 2011 to explore the following focus areas: Chemical & Analytical Methods (February 24-25), Well Construction & Operations (March 10-11), Fate & Transport (March 28-29) and Water Resource Management (March 29-30).

The technical workshops centered around three goals: (1) inform EPA of the current technology and practices being used in hydraulic fracturing, (2) identify research related to the potential impacts of hydraulic fracturing on drinking water resources, and (3) provide an opportunity for EPA scientists to interact with technical experts. EPA invited technical experts from the oil and natural gas industry, consulting firms, laboratories, state and federal agencies, and environmental organizations to participate in the workshops. EPA will use the information presented in this document to inform research that effectively evaluates the relationship between HF and drinking water.

An initial report of results from the EPA's study is expected by late 2012, with an additional report expected in 2014.

## About the Proceedings

These proceedings provide an overview of the twenty-two presentations and two posters given on water resources management at the Technical Workshop for the U.S. EPA Hydraulic Fracturing Study held on March 29 and 30, 2011. This workshop consisted of three themes: Theme 1– Water Use & Sustainability; Theme 2– Flowback Recovery & Water Reuse; and Theme 3– Disposal Practices. The proceedings include abstracts of the presentations and posters and a summary of the discussions that took place during the workshop. The

presentations from this workshop are not part of the proceedings document, but may be accessed at <http://epa.gov/hydraulicfracturing>.

This is the fourth of four technical workshops on topics relating to the EPA Hydraulic Fracturing Study. The other three workshops are: Chemical and Analytical Methods (Feb. 24–25), Well Construction and Operations (Mar. 10–11), and Fate and Transport (Mar. 28–29). Proceedings will be available separately for the other three workshops.

*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. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.*

### **Editorial Team for the Proceedings**

The attendees at the Water Resources Management workshop were selected based on information submitted to EPA during the attendee nomination process. Presenters, a workshop lead, and theme leads were selected from the pool of attendees based on the information submitted to EPA during the attendee nomination process. The workshop lead, John Veil of Veil Environmental, LLC, assisted EPA in finalizing details for the workshop and served as the lead editor of the proceedings document. The theme leads—Gary Hanson of Louisiana State University - Shreveport, Tom Hayes of the Gas Technology Institute, and Matthew Mantell of Chesapeake Energy Corporation —served as editors for Themes 1, 2, and 3, respectively.

## Workshop Participants

Name	Affiliation
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James	Arnold
Mike	Baker
Doug	Beak
Chrystal	Beasley
Amy	Bergdale
Matthew	Blauch
Jeanne	Briskin
Susan	Burden
Cal	Cooper
Jill	Cooper
Robin	Costas
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Robin	Danesi
Jill	Dean
Natenna	Dobson
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Jim	Weaver	US Environmental Protection Agency
James (Jim) H.	Welsh	Louisiana Office of Conservation
James	Werline	Devon Energy Corporation
Stevie	Wilding	US Environmental Protection Agency
Ron	Wilhelm	US Environmental Protection Agency
Nathan	Wiser	US Environmental Protection Agency
Brian	Woodard	Devon Energy
Mike	Worden	US Department of the Interior, Bureau of Land Management
David	Wunsch	National Ground Water Association
Pei	Xu	Colorado School of Mines
Paul	Ziemkiewicz	West Virginia University



## Agenda

### Technical Workshops for the Hydraulic Fracturing Study

*Water Resources Management · March 29-30, 2011*

*US EPA Conference Center  
One Potomac Yard (South Building)  
2777 S. Crystal Drive  
Arlington, VA 22202 Room S-4370 and 4380*

### March 29, 2011

**12:30 pm    Registration**

**1:00 pm    Welcome**

Fred Hauchman, Director of the Office of Science Policy, EPA Office of Research and Development

John Veil, Workshop Lead, Veil Environmental, LLC

Pat Field, Facilitator, Consensus Building Institute

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### ***Theme 1: Water Use & Sustainability***

**1:15 pm    Technical Presentation Session 1: Determinations of Appropriate Water Sources for Hydraulic Fracturing**

*How are Appropriate Water Sources for Hydraulic Fracturing Determined? Pre-development Conditions and Management of Development Phase Water Usage*, Gary Hanson, Louisiana State University – Shreveport

*Fresh, Brackish or Saline Water for Hydraulic Fracturing? What are the Options?*, Bill Godsey, Geo Logic Environmental Services, LLC

*Water Management Analysis of Hydraulic Fracturing using System Dynamic Models*, Carl Palmer, Idaho National Laboratory

*Water Requirements and Sustainable Sources in the Barnett Shale*, James Werline, Devon Energy Corporation

**2:45 pm    Break**

- 2:55 pm    Technical Presentation Session 2: Water Quantities used for Hydraulic Fracturing and Sharing of Water Resources**
- An Overview of Current and Projected Shale and Tight Gas Water Use in Texas: Implication for Local Water Resources*, JP Nicot, The University of Texas at Austin
- Water Demand and Supply in the Eagle Ford Shale*, Stephen Jester, ConocoPhillips
- Enabling Fracturing Operations with Zero Fresh Water Withdrawals*, Vikram Rao, Research Triangle Energy Consortium
- Sustaining Louisiana's Fresh Water Aquifers -- A Case Study in Bringing Community and Industry Together*, James Welsh, Louisiana Office of Conservation
- 4:25 pm    Revisit the Major Discussion Points of the Technical Presentation Sessions**
- John Veil, Workshop Lead, Veil Environmental, LLC
- Gary Hanson, Theme 1 Lead, Louisiana State University - Shreveport

**4:45 pm    Adjourn for the Day**

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## March 30, 2011

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### **Theme 2: Flowback Recovery & Water Reuse**

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- 8:00 am    Technical Presentation Session 3: Case Studies from Around the US**
- Produced Water Reuse and Recycling Challenges and Opportunities Across Major Shale Plays*, Matthew Mantell, Chesapeake Energy Corporation
- A Water Chemistry Perspective on Flowback Reuse with Several Case Studies*, Keith Minnich, Talisman Energy Inc.
- 9:15 am    Break**
- 9:25 am    Technical Presentation Session 4: Flowback Characteristics**
- Shale Frac Sequential Flowback Analyses and Reuse Implications*, Matthew Blauch, Superior Well Services
- Characterization of Marcellus Shale and Barnett Shale Flowback Waters and Technology Development for Water Reuse*, Tom Hayes, Gas Technology Institute
- 10:25 am    Break**

**10:35 am Technical Presentation Session 5: Reclamation Systems**

*Mid-Continent Water Management for Stimulation Operations*, D. Steven Tipton, Newfield Exploration Mid-Continent, Inc.

*Toolbox Available to Treat Flowback and Produced Waters*, Johanna Haggstrom, Halliburton Energy Services

*A Closed Loop System Using a Brine Reservoir to Replace Fresh Water as the Frac Fluid Source*, George King, Apache Corporation

*Williams Ford, Piceance Basin: Flowback Water Reuse – Quality and Quantity*, Jill Cooper, EnCana Oil & Gas (USA), Inc.

**12:05 pm Lunch**

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**Theme 3: Disposal Practices**

**1:00 pm Technical Presentation Session 6: Treatment Technologies and Processes Prior to Disposal**

*Treatment of Shale Gas Produced Water for Discharge*, David Alleman, ALL Consulting

*Novel and Emerging Technologies for Produced Water Treatment*, Pei Xu, Colorado School of Mines

**2:00 pm Break**

**2:10 pm Technical Presentation Session 7: Disposal Practices and Potential Impacts**

*Water Quality in the Development Area of the Marcellus Shale Gas in Pennsylvania and the Implications on Discerning Impacts from Hydraulic Fracturing*, Joseph Lee, Pennsylvania Department of Environmental Protection

*Simple Modeling of the Disposition of Fluids On-Site in a Pit*, Andrew Havics, pH2, LLC/QEPA

*Underground Injection Wells for Produced Water Disposal*, Rick McCurdy, Chesapeake Energy Corporation

*Wastewater from Gas Development: Chemical Signatures in the Monongahela Basin*, Paul Ziemkiewicz, West Virginia University

**3:25 pm Revisit the Major Discussion Points of the Technical Presentation Sessions**

John Veil, Workshop Lead, Veil Environmental, LLC

Tom Hayes, Theme 2 Lead, Gas Technology Institute

Matthew Mantell, Theme 3 Lead, Chesapeake Energy Corporation

**4:30 pm Closing Discussions**

John Veil, Workshop Lead, Veil Environmental, LLC

Jeanne Briskin, Hydraulic Fracturing Research Task Force Leader, EPA Office of Research and Development

## **Summary and Abstracts from Theme 1: Water Use & Sustainability**

## ***Summary of Presentations for Theme 1: Water Use & Sustainability***

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### **Technical Presentations**

The first set of technical presentations in this theme addressed determinations of appropriate water sources for HF.

**John Veil**, Veil Environmental, LLC, provided some opening remarks. He presented estimates of water requirements for shale gas activities in the Marcellus and Fayetteville Shales. Based on his calculations, water demand for wells in the Marcellus Shale could range from 2,255 million gallons per year (MG/year) to 11,275 MG/year, or 6.2–31 MGD per day (MGD). In the Fayetteville Shale, he approximated that water needs could be approximately 13.7 MGD. Mr. Veil noted that these estimates account for less than 1% of actual water withdrawals in these areas, and he thus concluded that, while local conditions may restrict water availability in some areas or in some parts of the year, sufficient water does exist to support natural gas development and other water use needs.

**Gary Hanson**, Louisiana State University -- Shreveport, discussed potential ground and surface water sources to be used to support HF operations. He described the history, mission, and accomplishments of the Red River Water Management Institute and other partnership groups with regard to HF water resources management in Louisiana. Mr. Hanson noted that the establishment of the Water Energy Working Group (WEWG) was critical in moving industry from ground water to surface water sources for HF. He noted that appropriate water sources for HF can change through time explaining that ground water had been a viable source until numerous Haynesville Shale wells were drilled and hydraulically fractured. He also pointed out one example of an operator who is currently using treated wastewater from a paper mill. Mr. Hanson also presented a set of preliminary water quality data from the Wilcox Aquifer in Louisiana and, from this data, concluded that there was no evidence of direct impact from HF or drilling, though there may be some impact from water withdrawals. Mr. Hanson also described an aquifer management initiative in the Sparta Aquifer in southern Arkansas, which he suggested as an excellent model for ground water resource sustainability.

**Bill Godsey**, Geo Logic Environmental Services, LLC, explored the potential benefits and negative impacts due to the use of fresh, brackish, saline, or blended waters for HF operations. He provided general information on aquifers in the Marcellus Shale area and the Potomac Aquifer in Maryland and Virginia, and then described differences in ground water quality as it relates to differences in aquifer depth and extent.

**Carl Palmer**, Idaho National Laboratory, described the use of system dynamic models to track HF water usage. He demonstrated how to build a model and presented an example of a system dynamics reservoir model that could be used within a geographic information system (GIS) framework. He explained that this type of modeling tool could relate to all three of the themes of this technical workshop, as it can integrate other modeling work and data collection initiatives while acting as a single predictive tool for water management decisions.

**James Werline**, Devon Energy Corporation, presented a case study of Devon's water requirements, sources, management, and use in the Barnett Shale in Texas. He described the different end uses of water in Texas and in the area underlain by the Barnett Shale as well as the proportions of ground water, surface water, and recycled water used by Devon for their HF operations in the Barnett. Mr. Werline also described Devon's water recycling processes using mechanical vapor recompression (MVR) units. He explained that MVR units vaporize saline fluids, allowing the operator to collect the resulting distilled water for reuse and dispose of the concentrated brine. Mr. Werline concluded by summarizing Devon's water reuse statistics to date.

The second set of technical presentations addressed water quantities used for HF and sharing of water resources.

**JP Nicot**, University of Texas at Austin, provided an overview of water use for shale gas and tight gas development in Texas. He presented water use data for several different types of oil and gas use, particularly for the main shale and tight gas formations in Texas and the horizontal and vertical wells in the Barnett. Dr. Nicot described historical and projected drawdown patterns for several aquifers in Texas. He noted that recycling can be a viable water management option, but that using alternative sources (collected rainwater, treated municipal wastewater, brackish water) or less water-intensive techniques may be more effective in areas with little produced water (where recycling opportunities are limited).

**Stephen Jester**, ConocoPhillips, addressed water demand and supply in the Eagle Ford Shale area in southern Texas. He presented estimated values for HF water demand in the Eagle Ford and compared them to water demand for other end uses. He also compared demand to supply volumes that were estimated using ground water availability models for the Gulf Coast and Carrizo-Wilcox Aquifers. Mr. Jester concluded that, on the large scale, evidence indicates that water demand for HF and other uses can be met by the available supply. However, he cautioned that local conditions should be monitored to avoid impacts such as methane migration.

**Vikram Rao**, Research Triangle Energy Consortium, discussed the possibility of HF with zero fresh water withdrawals and the associated benefits and challenges. Dr. Rao noted that industry has already responded to the challenge of recycling flowback water by using more saline water, and that, in some cases, use of saline water for HF has advantages over use of fresh water. However, Dr. Rao explained that increased use of saline water requires addressing issues such as scaling, chemical incompatibilities with additives, a need for better reservoir

characterization, and desalination and other treatment concerns. Dr. Rao also recommended further investigations and mapping of saline aquifers.

**James Welsh**, Louisiana Office of Conservation, presented a case study from Louisiana's Haynesville Shale area. Mr. Welsh explained that, initially, water for HF was withdrawn from the fresh water Carizzo-Wilcox Aquifer; however, increasing ground water withdrawals quickly began to conflict with other water use needs in the area. Working with operators, the state implemented policy changes and encouraged operators to use alternative water sources (e.g., surface water, non-potable ground water). Mr. Welsh noted that Louisiana continues to work with stakeholders on water management issues -- for example, Louisiana adopted regulations allowing the reuse of flowback water for HF. Mr. Welsh is of the opinion that state regulators are in the best position to implement solutions in their states and he cautioned against nationwide HF regulations.

### ***Summary of Discussions Following Theme 1: Water Use & Sustainability Presentations***

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*Clarification of items in the presentations.* Regarding the modeled aquifer depression and rebound in Dr. Nicot's presentation, a participant asked whether irrigation water use declined during the recovery period. The presenter clarified that water use for irrigation was highest in the 1940s and 1950s and has decreased since then, allowing the aquifer to recover; the presenter noted that these results suggest that the aquifer can recover from extensive pumping. However, Dr. Nicot emphasized that local impacts do need to be considered. He indicated that the water use figures in his presentation represented well completion information only, not necessarily total fresh water use. Dr. Nicot noted that operators are not required to report water use for other steps in the well construction and operation process. In response to Dr. Rao's presentation, a participant noted that some shallow aquifers do host bacteria; however, the presenter noted that more research is required in this area.

*Using high-TDS water for HF operations.* A participant asked if saline water can be used for both slickwater and gel fracture jobs. The presenters clarified that saline water can be used in gel systems, though compatibility tests are necessary and water handling is very important. A participant asked about corrosion effects from using high-TDS water. The presenters agreed that high salinity increases the amount of equipment loss and turnover. The presenters also noted that in some situations, matching the salinity of the injected fluids to the salinity of the reservoir improves production. Another participant asked for more information on using highly saline waters in fracturing fluids. One participant explained that using high-saline water can mitigate clay swelling issues in the shales. Participants agreed that industry has made significant

advances in the use of brines and that, in some situations, using highly saline waters could have a positive impact on production. Participants also emphasized the importance for operators to have choices for water sources and disposal options, and noted that potential local impacts and public opinions can play a large role in this process.

*Recycling and disposal.* A participant asked about the barium chloride content of produced water from operations using high-salinity water. The presenters agreed that barium could pose a problem and that characterizing the mineral content of the saline water is important, but noted that not much work has been done on adequately detailed characterizations of saline water resources in the United States. They mentioned, however, an ongoing USGS study that is currently working to map brackish aquifers. A participant stated that publicly-owned treatment works (POTWs) are not appropriate for the disposal of any kind of flowback fluids due to the high levels of strontium, barium, bromide, and other chemicals.

*MVR treatment units.* A participant asked about treating high-TDS water with MVR units. The presenter clarified that it is possible to treat water containing greater than 79,000 mg/L TDS, but these higher TDS levels decrease the efficiency of the units. The presenter added that deep well injection is the preferred disposal method for these types of fluids. The presenter indicated that the concentrate produced by the MVR units have TDS levels of approximately 140,000–150,000 mg/L. The presenter explained that this concentrate is injected into the Ellenburger Formation, where the native brines have TDS levels of approximately 180,000–190,000 mg/L. The presenter noted that, depending on transportation costs, MVR treatment costs approximately \$2.85–\$5.00 per barrel; in the Barnett Shale area, it costs approximately \$1.00–\$1.50 per barrel for deep well injection (including transportation costs). He explained that the MVR units are centrally located, and water is transported to and from the units by pipe. Finally, he noted that the Texas Railroad Commission (RRC) issues discharge permits for water treated by the MVR technique. Several participants emphasized that deep well injection is the preferred disposal method where it is available.

*Water withdrawals.* A participant asked if there are rate limitations for withdrawing ground water in Texas. A presenter responded that pumping rate is determined based on the aquifer and would be limited based on the permeability and conductivity of the formation. Tests conducted while drilling a water well would provide the relevant information. The presenters noted that water wells are registered with the county water districts, which monitor spacing, cones of influence, property setbacks, etc., to ensure that aquifer drawdown is not excessive. According to the presenters, operators also work with surface land owners when drilling water wells, and surface water withdrawals are regulated by the Texas Commission on Environmental Quality (TCEQ). The presenters explained that TCEQ permits one-time withdrawals of 10 acre-feet, after which a study must be conducted to investigate any impacts on upstream and downstream flows. These studies can take up to two years to complete. The presenters noted that availability is the primary concern when identifying water sources, and it is closely related to cost. One participant indicated that his company looks first for surface water sources; if these are not available, ground water sources are the second choice.

*Aquifer recharge rates and aquifer storage.* A participant asked about the recharge rates of aquifers used for HF. A presenter responded that, in Louisiana, the Wilcox Aquifer has a very low recharge rate and is exposed over a large uplift area with poor recharge characteristics including channelized sands with mineral precipitation. The presenter stated that the overlying terrace deposits also have low infiltration rates; however, the presenter indicated that the Red River can supply adequate water for HF operations in that area. A participant asked about aquifer storage of HF water. One presenter noted that he has experience with aquifer storage for drinking water, but not for other fluids. Another presenter described a situation in the Horn River Basin in British Columbia where brine is extracted, used, treated, and reinjected. A participant speculated that an injection well for produced water storage would likely be regulated as a Class V well.

*Storage and transportation issues.* One participant indicated that his company stores treated produced water in earthen ponds and that the low TDS levels (approximately 100 mg/L) of the water simplify storage concerns. Other operators stated that they do not discharge treated water but reuse it in their HF operations. A participant asked about on-site management of highly saline waters. One participant stores all waters with TDS levels above 2,000 mg/L in tanks, and other participants use lined pits with leak detection equipment. One participant avoids using pipe to transport brines due to the risk of ruptured pipelines.

*Water use terminology.* A participant asked for clarification on what “available” water means. A presenter responded that this generally refers to surplus water that is not being used for other purposes. Another participant noted that unused ground water might be considered “lost” due to rejected recharge, but other participants disagreed, arguing that all water is used by local industries and residents, though in some cases that use may be indirect.

*The importance of flexibility.* Participants noted that there are a variety of water source and disposal options, and individual options may not be appropriate or available for all situations. Participants indicated that in the Eagle Ford play, recycling options can be beneficial to industry and the environment are not always desired by landowners, who would prefer to sell water to operators instead of encouraging water reuse. One participant noted that Louisiana is an excellent example of cooperation between regulatory agencies and industry since the state has updated its regulations to include options for water reuse.

*Water management coordination groups.* A participant described a consortium of operators who coordinate water management issues in a basin in Utah. Similar consortia are forming in the Barnett (the Barnett Shale Water Conservation and Management Committee, or BSWCMC) and the Eagle Ford areas; in addition, a water-energy working group has been formed in Louisiana. The groups generally address water source issues and technology development for reclamation/reuse. Another participant noted that in the area of the Haynesville shale play, there is no formal consortium, but several operators are coordinating to develop a pipeline from the Toledo Bend Reservoir. One participant cautioned that water rights laws in Western states might complicate coordination efforts among operators.

*Surface and ground water regulations in Louisiana and Texas.* A participant stated that in Louisiana, the state owns the rights to running water (e.g., rivers, streams, lakes fed by streams) and has developed a protocol for pricing the water. Companies can buy the water outright, or they can provide a service to the state instead. The participant indicated that the state is considering a tiered pricing structure that would account for the greater value of some water sources (e.g., headwaters). Ground water is not priced and may be withdrawn as long as the use does not damage a neighboring property or well. Louisiana has a process for evaluating water wells with eight-inch or larger casings. According to the participant, a model is used to determine the zone of influence, cone of depression, and other factors. Another participant stated that Texas has 16 Ground Water Management Areas that are responsible for setting “desired future conditions” for their aquifers. Participants discussed whether withdrawals for drilling/production are exempt from the process of setting these “desired future conditions.”

*Ground water monitoring.* A participant asked about existing ground water monitoring programs. The presenter noted that some municipalities in Texas monitor ground water levels very closely. For example, in San Antonio ground water information is regularly published in a local newspaper. The presenters also stated that Texas has a statewide program at the state level to monitor ground water levels and quality, and it maintains a database with this information. The USGS also monitors ground water, but the presenter noted that some states have only a few participating monitoring wells. A participant noted that there is currently a movement to establish a more complete nationwide ground water monitoring network.

*Other comments.* Citing a review published in *Nature*, a participant noted that shale gas production is less water-intensive than several other types of energy production, including producing ethanol from corn. Another participant noted that water withdrawn during the three to four weeks required to drill a well can be used to fill water impoundments. Another participant noted that water withdrawals for HF are generally one-time withdrawals, compared to agricultural withdrawals that occur year after year.

### ***Abstracts for Theme 1: Water Use & Sustainability***

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# How are Appropriate Water Sources for Hydraulic Fracturing Determined? Pre-development Conditions and Management of Development Phase Water Usage

Gary Hanson  
Louisiana State University Shreveport

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Historically the determination of water sources for hydraulic fracturing has typically been left up to the oil or gas operator or their drilling contractor. Fresh water, although only one component of frac fluids in tight gas sand stimulation, was the source of choice and ease of access would determine whether surface or groundwater was used. Prior to multistage horizontal fracing of gas shales, use of ponds or nearby streams provided sufficient water to drill and frac a typical tight sand well in most areas of the country. However as the unconventional shale plays arrived on the scene using “slick-water” fracing technique and horizontally drilled wells that required multiple stages in order to effectively stimulate the reservoir, water demands increased dramatically. Groundwater, which had been only used periodically in the past, became the source of choice in many areas. Groundwater use for fracing increased in northwest Louisiana after the discovery of the massive Haynesville Shale. The public and rural water utilities saw this activity as a threat to “their” source of water, so from their perspective a water source (groundwater) that was previously considered an appropriate source for fracing, became an inappropriate source, as drilling and fracing continued.

Prior to the onset of the Haynesville Shale gas boom in northwest Louisiana, two critical actions were taken by local government and a university. First, a voluntary water committee called the Water Resources Committee of Northwest Louisiana (WRCNL) was formed and second, one of the member parishes (counties) worked with the local LSU Shreveport University to set up a groundwater monitoring system. Both actions were taken prior to the Haynesville Shale discovery and because there was a perceived need that groundwater and surface water resources were in jeopardy. In some cases, as operators moved into the area multiple Wilcox aquifer water wells were drilled to not only supply water for drilling, but also for fracing. Rig supply wells are considered exempt wells (no notification to Office of Conservation prior to developing) in Louisiana, but groundwater wells used for fracing are considered industrial wells and there is a 60-day pre-drilling notice required. Groundwater use for fracing is not specifically deemed unlawful. As stated earlier, operators have always used groundwater as an appropriate water source for fracing, but with the onset of the Haynesville high volume (5 million gallons), multistage, horizontal well development program, other groundwater users (district water systems, domestic & agriculture) became concerned. For them, groundwater was not an appropriate water source for fracing. The Office of Conservation stepped in and advised that surface water or non-potable aquifer alternatives should be used as a source of water.

In 2001, the Red River Watershed Management Institute (Institute) was formed at LSU Shreveport and the Red River Education & Research Park (RRERP) was developed adjacent to the campus in the floodplain of the Red River. Faculty and students developed monitoring wells in the Red River Alluvial Aquifer (RRAA), an aquifer that had been studied historically by the USGS and other agencies. The RRAA is considered non-potable, but exhibits high deliverability due to its' high porosity and high hydraulic conductivity and was a good candidate for alternative groundwater supply for fracing. The RRAA became an appropriate water source for fracing, and although there exists some competition from agriculture, it is deemed sustainable because it is sourced by the overlying Red River which has been impounded for navigation.

In the early stages of the Haynesville development, a sub-committee of the WRCNL was formed and met at the Institute. Co-chaired by the Director of the Institute and the Executive Director of the Red River Waterway Commission, the Water Energy Working Group (WEWG) was comprised of federal and state regulators, operators and water transfer specialists. Although many Haynesville Shale operators had become convinced that they needed to reduce their dependence on the Wilcox Aquifer, appropriate alternatives could not be used without some kind of approval process. The WEWG worked to establish USACE permits for access to the Red River. Following formal opinions by the Louisiana Attorney General and legislation that would allow for the states "running" surface water, including the Red River, to be withdrawn legally, operators were given surface water alternative. Private ponds became an easy and appropriate source of surface water in areas remote from large waterbodies. If landowners filled the ponds using groundwater wells, however, the pond is not considered an appropriate water source for fracing by the state.

Has the Wilcox aquifer been changed by Haynesville Shale drilling activity in northwest Louisiana? A study of up to 1000 domestic wells located in the areas of gas shale development, was undertaken by the Louisiana Geological Survey /LSU in cooperation with the watershed Institute at LSU Shreveport. Over one-third of the wells have been sampled and analyzed. About 75 domestic wells that were used in a previous study have been included (re-sampled and analyzed). No significant change in water quality has been observed at this point in the project.

A project in nearby south Arkansas has been challenged to develop a recovery plan for Sparta Aquifer, historically the main source of water for public and industrial use. This successful project, which funded the construction of a 20-mile pipeline to a large river in order to supply water for industrial needs, allowed industry to stop drawing water from the aquifer and should be a model for the nation. A potential unconventional gas play is in the early stages of development in South Arkansas/North Louisiana and the Union County Water Conservation Board has the potential to supply about 20 million gallons of surface water as an appropriate water source for fracing.

# Water Management Analysis of Hydraulic Fracturing using System Dynamic Models

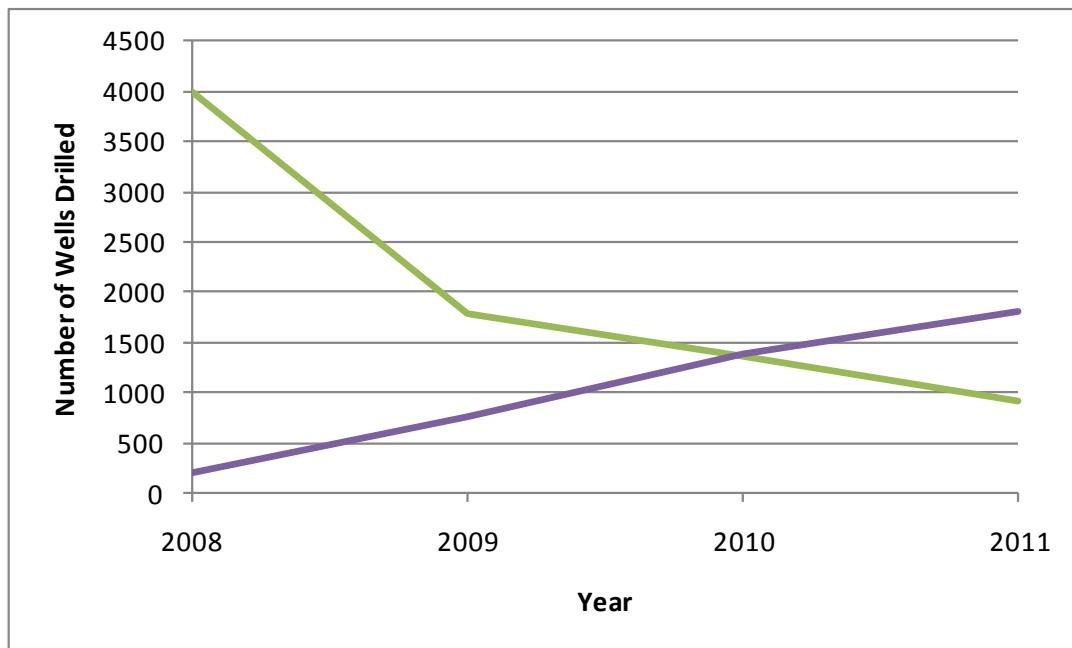
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## Introduction

The recent increased production of natural gas from tight gas reservoirs has lead to public concern of the protection and use of subsurface water resources. Although the water consumption to perform hydraulic fracturing of these tight reservoirs often accounts for a small percentage of the total water consumption of the region, the rate of water consumption is rising, leading towards potential conflicts of water availability even in the “water abundant” eastern states associated with the Marcellus Shale.

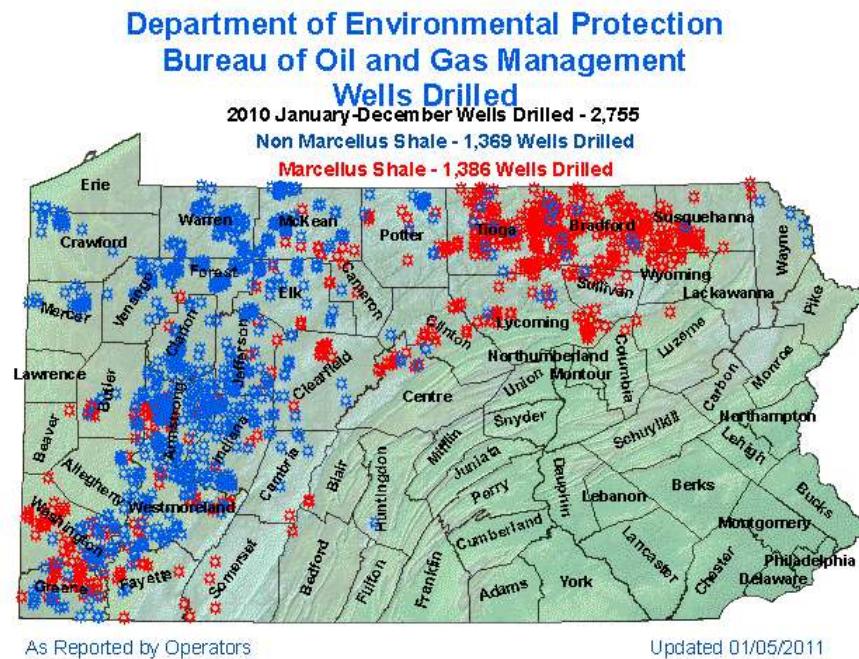
The amount of water needed is directly tied to the increase in the amount of natural gas production and hence to the number of wells that are hydraulically fractured. Hydraulic fracturing for the Marcellus requires approximately 4,000,000 gallons of water for each well that is fractured (GWPC, 2009). Drilling in Pennsylvania Marcellus Shale has been increasing by



*Figure 1. New oil and gas wells drilled in Pennsylvania by year. Green line is represents non-Marcellus Shale, Purple line represents Marcellus Shale wells. 2011 data is projected from January–February 2011 values.*

about 500 wells per year (Pennsylvania Department of Environmental Protection, 2011) (Figure 1). The resulting water demand for hydraulic fracturing of these wells requires approximately 6000 acre feet of water each year.

Furthermore, the location of the Marcellus gas drilling activity is not uniformly distributed. This drilling activity tends to be concentrated along available leasing, access to distribution pipelines, and overall profitability. Using Pennsylvania as an example, the most active areas tend to be near Bradford County in the north and Washington County in the Southwest, (e.g., Figure 2). These areas have been the focus of drilling in the Marcellus Shale since 2008, and will likely be the preferred areas for some time.



*Figure 2. Location map of oil and gas drilling activities in Pennsylvania in 2010 (from PA Dept of Environmental Protection web page).*

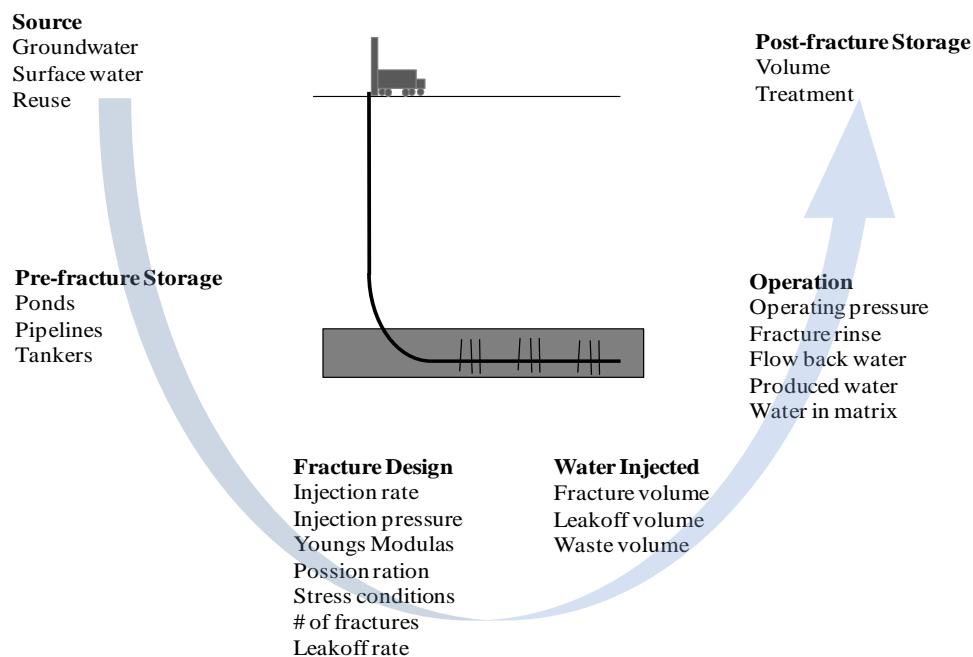
At some point in the future, the increase in hydraulic fracturing activity and the concentration of these activities in certain geographic locations could lead to over-allocation of the local water supply. The ability to understand, predict and minimize the impact of shale gas energy resource development on water supply within the local watersheds needs to be addressed.

System dynamic modeling is a potential tool that can provide a better understanding of the present and future water consumption for a diverse set of stakeholders (the multiple energy development operators, federal and state regulators, and the surrounding communities). This model is a dynamic non-linear simulation model with the capability to integrate “soft” and “hard” system components in a single tool. System dynamic modeling has been used to better

understand river basin models, fuel cycles, and population dynamics on resources. Although the connection of this set of information can be accomplished through the use of multiple software packages, one great advantage of system dynamic modeling package is that it provides a visual model of the system that allows non-technical stakeholders a better understanding of the complex system.

To develop a system dynamic model for hydraulic fracturing, the water cycle is first broken up into a number of sub-models that describe the potential water flows. Figure 3 illustrates a potential structure for a system dynamic model. The source water may be from surface water sources, shallow groundwater and other recycle/reuse sources. Due to the nature of hydraulic fracturing, this water is typically stored on-site in tankers, or storage lagoons. The fracture design module would either use data from the operators or from idealized fracture geometries (e.g. PKN planer fracture models) to determine water use for the fracture. Water distribution from the injection could be segregated into that contained in the fracture, leakoff volume, pre-treatment water use volumes. Finally, flowback and produced water could be accounted for via numerical approximations of physical phenomena or via operators' best judgment information on a specific location. Produced and flowback water returned to the surface can be examined for quantity (and potentially quality) allowing for decisions of treatment options and reuse.

Researchers at the Idaho National Laboratory are currently conducting an assessment for another unconventional fossil energy resource, oil shale. The following example describes how an *in-situ* oil shale retorting operation was modeled and used as input data for a GIS based groundwater consumption model of the Piceance Basin in Colorado.



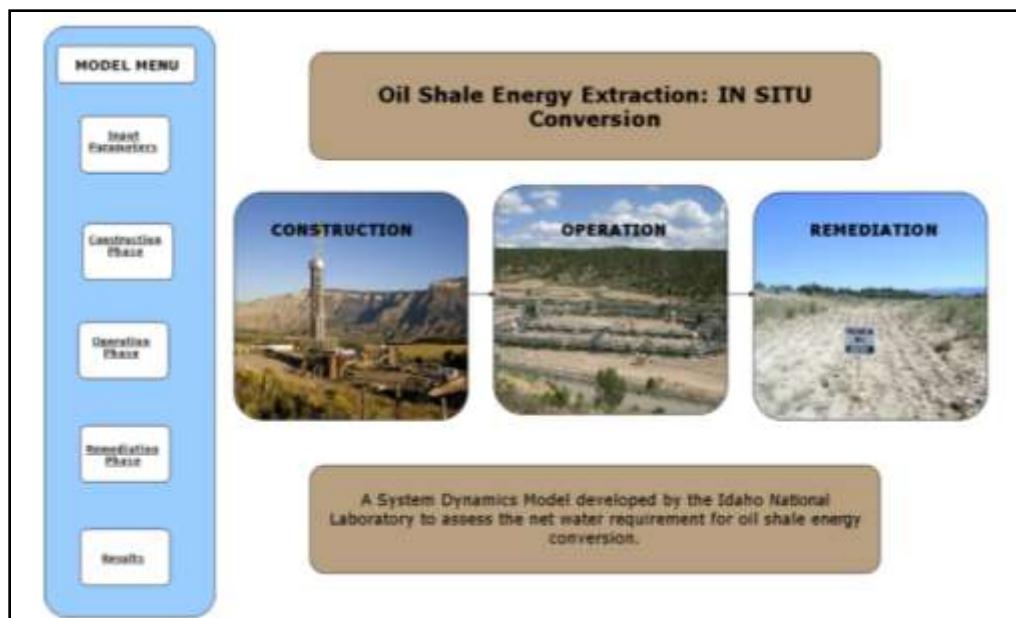
*Figure 3. Potential components of System Dynamic Model for Hydraulic Fracturing to better understand the water cycle.*

## **Oil Shale Water Model Example**

The use of oil shale as a supplemental energy source is rapidly emerging as an answer to increasing energy demand and cost. Oil shale is a sedimentary rock which contains a high content of kerogen. When subjected to high temperatures in an anoxic environment, oil shale decomposes into a mixture of liquid and gaseous substances similar to petroleum fuels (Brandt, 2007). Oil shale energy conversion is achieved by two basic methodologies: *ex-situ* retorting and *in-situ* retorting. *Ex-situ* processes involve mining oil shale in large open pits or subsurface mines, then applying heat in an above ground or surface retort. *In-situ* retorting process use subsurface heaters or steam to apply heat below ground. While still under development, an advantage of *in-situ* retorting is the reduction of environmental impacts caused by eliminating the mining process. Both processes are water intensive and consume large quantities of water for construction, operation, and remediation (Lee, 1991). Accurately modeling water requirements and consumption will greatly aid in the assessment of water availability and the potential to utilize oil shale deposits as a viable energy source in a region.

To assess the impact of water availability as a limiting factor for *in situ* oil shale conversion, a PowerSim™, system dynamic, model was developed. A pilot study conducted by Shell Oil Company, was used as a template for the theoretical model since *in situ* retorting is highly developmental. Patents, literature, and engineering principles were referenced where appropriate.

Model architecture for an *in situ* oil shale development was developed in three stages: construction, operation and remediation. Figure 4 illustrates the model interface and the three stage design architecture.



*Figure 4. Model Interface of an in situ-oil shale development*

Each oil shale stage has a system dynamic model that describes the water use during each stage. For example, the construction stage of the *in situ* retorting process was assumed to consist of any site preparation and development prior to oil production (Figure 5). An average well drilling rate of 8 ft/hr was estimated from average limestone and sandstone drilling rates. Drilling mud and seepage losses were estimated to be 30 barrels/hr and 1.5 barrels/hr (Devereux, 1999). Pilot study saturated porosities and effective porosities of 10.7% and 3.8% were assumed (Brandt, 2007).

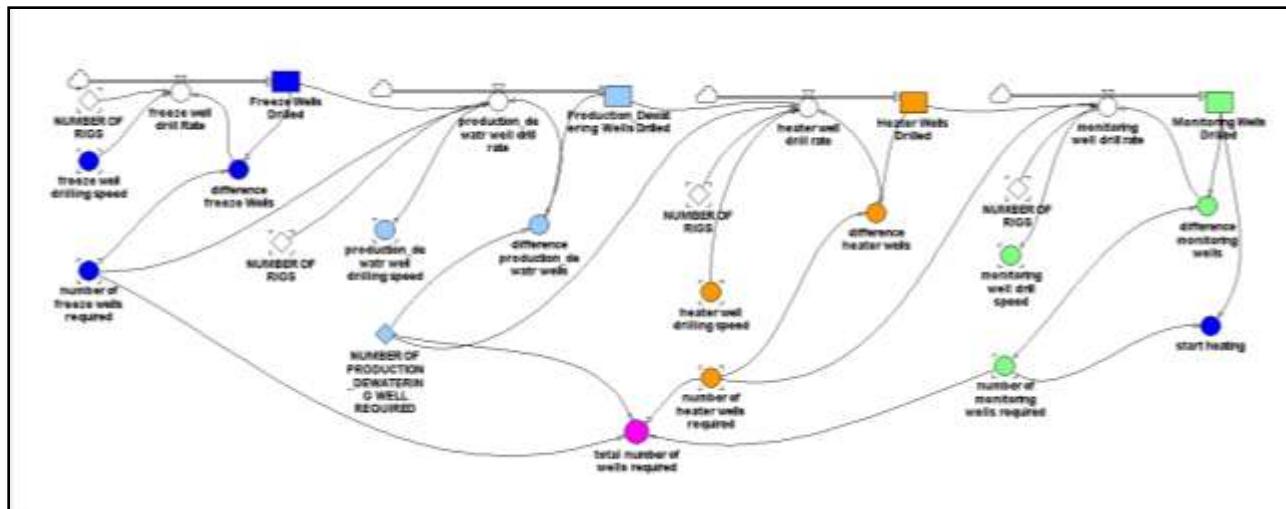


Figure 5. Construction phase model component of the *in-situ* oil shale example.

While the construction phase of the *in-situ* retorting process is controlled by physical activities like well drilling and site preparation, the operation phase involves the complex interaction of heat transfer, chemical reactions, and material conversion (Figure 6). A non-uniform heat transfer rate assuming cylindrical geometries was used to model the *in-situ* heat transport (Hendersen, 1997). An initial oil shale temperature of 20 °C and a pyrolysis temperature of 400°C were used to calculate heat transfer rates (Brandt, 2007). Homogenous material properties were assumed to simplify calculations. Important oil shale material parameters include: thermal conductivity (1.2 W/m°C), density (1.75g/cm<sup>3</sup>), heat capacity (1.25J/g°C) (Lee, 1991).

The operation phase includes a process to describe the rate of oil production using kinetic factors for pyrolysis oil production published by Shell. Water synthesized during the pyrolytic conversion was modeled from chemical reactions, and kinetic factors published in patents and literature. An empirical formula for kerogen of C<sub>421</sub>H<sub>638</sub>O<sub>44</sub>S<sub>4</sub>NCl was assumed. Modification of the *in-situ* porosity was accounted for due to the retorting of the kerogen.

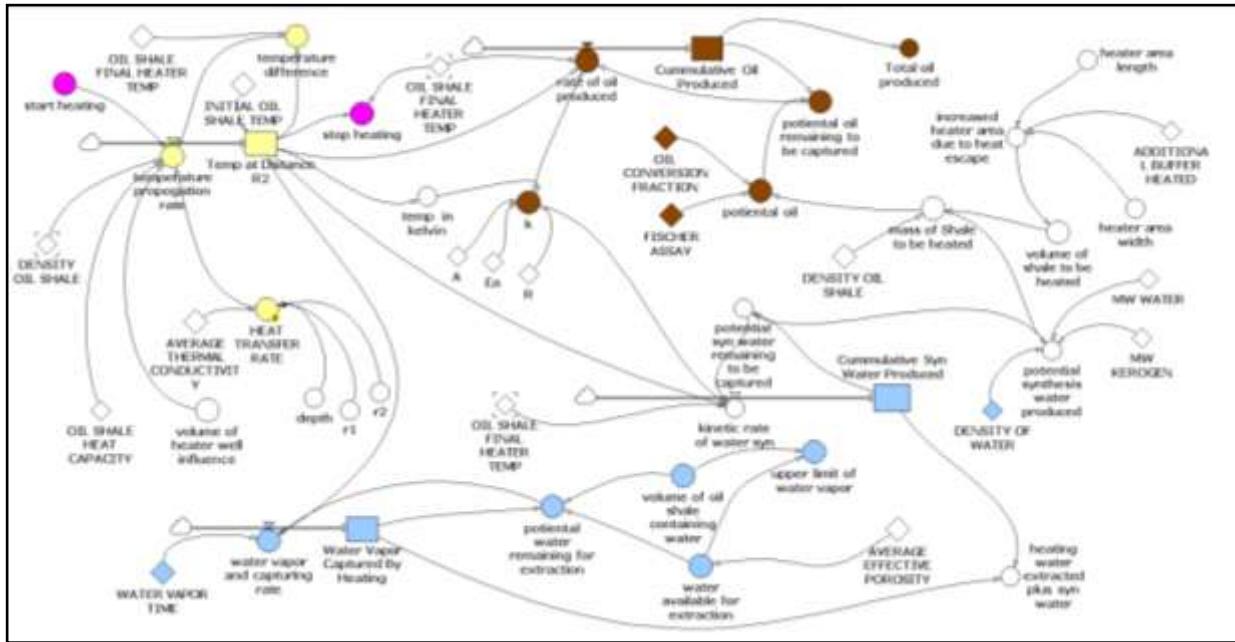


Figure 6. Operation phase model component of the in-situ oil shale example.

## Summary

In many areas of the country shale gas development is rapidly growing. Hydraulic fracturing of shale typically injects two to four million gallons of water per well into the subsurface. Of this water, 10 to 70 percent is returned to the surface via flowback and produced water mechanisms. A predictive method is needed to assess the impact of the projected shale gas development on the local water resources in both quantity needed for the fracturing process and to develop adequate treatment plans for water to the surface.

System dynamic models offer a potential tool to assess water needs of the shale gas industry and allow its development to coexist with communities needs. The model components can be as simple or as sophisticated as necessary and tailored to the complexities of the development region. Some components will be based on operators' judgment. Other components will be based from engineering standards, thermodynamics, pilot scale tests, and the results from other processes models. These components when combined together, can describe the water consumption, losses, and returns to the surface for each hydraulic fracture as a function of time and scale. The model should be designed with the intent to be able to connect to GIS databases and other state regulatory management tools. Connecting to a GIS database will allow the models to access regional spatial data to support the model and allow its output to be effectively used in other tools to make water management decisions.

## References

- Brandt, Adam R., Converting Oil Shale to Liquid Fuels: Energy Inputs and Greenhouse Gas Emissions of the Shell in Situ Conversion Process. *Environmental Science Technology* 2008, 42(7489-7495).
- Brandt, Adam R., Converting Green River Oil Shale to Liquid Fuels with the Shell in-situ Conversion Process: Energy Inputs and Greenhouse Gas Emissions. 2007. 2-31.
- Henderson, Perry, and Young. *Principles of Process Engineering*. ASAE. 1997. 150-201.
- Devereux, Steve. *Drilling Technology in Nontechnical Language*. Pennwell. 1999. 1(54-56).
- Ground Water Protection Council and All Consulting, 2009, Modern Shale Gas Development in the United States: A Primer, Report to the USDOE, April
- Oil Shale Test Project, Oil Shale Research and Development Project. Plan of operation. Submitted to Bureau of Land Management, Shell Frontier oil and Gas, Inc., 2006.
- Lee, Sunggyu, James G. Speight, Sudarshan K. Loyalka. *Handbook of Alternative Fuel Technologies*. CRC Press. 2007.
- Lee, Sunggyu, Robert Iredell, *Oil Shale Technology*. CRC Press 1991.
- Pennsylvania Department of Environmental Protection,  
[http://www.dep.state.pa.us/dep/deputate/minres/oilgas/new\\_forms/marcellus/marcelus.htm](http://www.dep.state.pa.us/dep/deputate/minres/oilgas/new_forms/marcellus/marcelus.htm), 2011

# Water Requirements and Sustainable Sources in the Barnett Shale

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This paper will focus on the water requirements and sustainable sources in the Barnett Shale. Devon Energy Corporation understands that water is a needed resource for its business as well as an essential part of the ecosystem. Water is vital to the health, social and economic well-being of communities in which we live and operate. Our success relies on executing a sustainable water management strategy that balances ecological, economic, operational and social criteria. Devon is committed to the principles of water conservation and reuse where feasible in its operations.

## Background

The Barnett Shale is located in the Fort Worth Basin in North Texas. This paper will focus on Devon's water requirements, water use and water sources in the Barnett Shale. This paper also will discuss Devon's water management and sustainability initiatives in the Barnett Shale. This paper focuses on an area covering six counties in North Texas. Devon operates more than 4,500 wells in the basin and produces approximately 1.2 billion cubic feet (Bcf) of natural gas per day. Devon is the largest producer of natural gas in the Barnett Shale and one of the largest producers of natural gas in Texas.

## Devon's Water Requirements in the Barnett Shale

Devon currently is drilling with 13 rigs in the Barnett Shale. Each well requires approximately 4.3 million gallons of water for the drilling and completion process. Ninety-six percent of the total water required for a Barnett Shale well is used for fracture stimulation. Generally, fracture stimulations in the Barnett Shale for horizontal wells are performed in six to 10 stages. Peak drilling activity for Devon was in 2008, when 584 wells were completed. The following table shows the number of wells completed in the Barnett Shale during the past four years by the industry and specific to Devon's operations (Table 1).

	2007	2008	2009	2010
<b>Industry wells</b>	2,536	3,084	1,627	1,876
<b>Devon wells</b>	469	584	298	420
<b>% Devon</b>	18.5%	18.4%	18.3%	22.4%

*Table 1. Number of wells completed in the Barnett Shale during the past four years by industry and specific to Devon's operations*

In 2010, Devon completed 420 horizontal wells requiring 41.3 million barrels of water and refractured 150 vertical wells requiring 4.5 million barrels of water. Of the water used, 11.5 million barrels were obtained from surface water sources, 32.3 million barrels were derived from groundwater sources and 2 million barrels came from Devon's recycling initiatives. As horizontal drilling technology has improved, Devon is drilling longer laterals in the Barnett Shale resulting in an increase in the number of fracture stimulation stages required to complete each well. The increase in stages requires additional water used on a per well basis; however, fewer wells will now be needed to develop equivalent gas reserves in the field. This should result in more efficient water use.

### **Water Use in Texas and the Barnett Shale**

Mining water use in Texas, in which oil and gas activity is included, represents only a small fraction of total water use in the state. Mining water use in the Texas Water Development Board (TWDB) annual 2008 water use compilation for the entire state resulted in only 0.5 percent relative to the total of the other water use categories including municipal, manufacturing, steam electric, irrigation and livestock. Overall, in 2008 the mining industry in Texas used approximately 139,000 acre-feet, including 35,800 acre-feet for fracture stimulating wells (mostly in the Barnett Shale/North Texas area). Water use in the Barnett Shale was approximately 25,000 acre-feet.<sup>1</sup> Figure 7 represents the water usage in the Barnett Shale in 2008 as per the TWDB.

The 2007 TWDB Water Plan that utilized water-demand surveys and projections estimated 0.27 million acre-feet as the demand for mining, compared to about 17.60 million acre-feet of total water use in 2010, equating to about 1.5 percent of the state water demand. Combining all water uses in the state, projections suggest that peak mining water use will occur in the 2020-2030 decade at approximately 250,000 acre-feet. Total mining use percentage is never expected to exceed 1.5 percent relative to total water use and oil and gas use is never expected to exceed 0.6 percent for any of the decades from 2010-2060.<sup>1</sup>

The basin-wide fraction of total fresh water resources used by Barnett natural gas producers in 2005 was estimated to be approximately 0.5 percent in comparison with all other users and uses. This was projected by TWDB to rise to approximately 2 percent during the year of peak Barnett drilling activity.<sup>2</sup>

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<sup>1</sup> TWDB, 2011, Current and Projected Water Use in the Texas Mining and Oil and Gas Industry, Draft

<sup>2</sup> Galusky, Jr. L.P. 2009. Fort Worth Basin/Barnett Shale Natural Gas Play: An Update and Prognosis on the Use of Fresh Water Resources in the Development of Fort Worth Basin Barnett Shale Natural Gas Reserves

## **Water Sources Available to Barnett Shale Operators**

### ***Groundwater Sources***

Devon produces groundwater from permitted water wells in the Trinity Aquifer. In many cases, these water wells are available for use by landowners. The Trinity ranges in depth from 600-1,400 feet. The Trinity Aquifer outcrops in the western part of the basin and the subcrop is from the west to east (Figure 8). The production volume from a single water well may range from 50-250 gallons per minute. Devon stores the groundwater in centralized earthen containments prior to fracturing a well. The basin-wide fraction of groundwater resources used by Barnett natural gas producers in 2005 was estimated to be approximately 2.5 percent in comparison with all other users and uses.

### ***Surface Water Sources***

Devon also utilizes surface waters for development of the Barnett Shale. These surface waters are obtained with surface-use agreements from local landowners, permitted withdrawals from river authorities, purchase agreements with municipal water suppliers and permitted withdrawals from local streams and impoundments regulated by the Texas Commission on Environmental Quality. The basin-wide fraction of surface water resources used by Barnett natural gas producers in 2005 was estimated to be approximately 0.2 percent in comparison with all other users and uses.

### ***Recycled Water***

Devon also utilizes recycled water processed with mechanical vapor recompression (MVR) units operated by Fountain Quail Water Management. Fountain Quail currently has four units operating for Devon with a capacity to process 8,000 to 10,000 barrels of water per day.

## **Water Management and Sustainability Initiatives in the Barnett Shale**

Devon recycles flowback water with a MVR evaporation process developed by Fountain Quail. MVR evaporation is an energy-efficient process that produces distilled water from flowback water that contains dissolved solids. The dissolved solids remain in solution and are removed from the system as a concentrate and disposed in permitted deep wells. The distillate recovery is based on the feed water's TDS (Total Dissolved Solids) (Figure 9).

This recycling initiative was implemented in the Barnett Shale in 2005. Fountain Quail currently has four units operating for Devon, with capacity to process approximately 8,000 to 10,000 barrels per day. Each MVR unit has a 2,500 barrel per day capacity. Devon utilized up to nine units during peak drilling activity in 2008, with the capability of processing 22,500 barrels per day. Devon has generated a total of 10.8 million barrels (454 million gallons) of distilled water, which is enough water to fracture stimulate more than 100 wells. With TDS removal, the water can be stored in centralized earthen containments and pumped via temporary piping to nearby fracture stimulation jobs with little environmental risk.

Flowback water composition dictates the volume an operator can economically recycle and what type of recycling methods may be technically feasible for use. Figure 10 illustrates how the TDS values change as a well is produced after fracture stimulation. As the TDS values

increase, the opportunities to efficiently recycle may decrease. Figure 10 also shows how flowback composition changes in different areas of a shale play. With the MVR process that Devon utilizes, the best efficiencies are realized when the TDS value is 70,000 parts per million or less.

There are several challenges in implementing a water sustainability and management program within a shale gas play. A few of these include technology limitations, maintaining an adequate supply of flowback water for treatment, sustained demand for recycled water, transportation, logistics and costs, construction of storage facilities, regulatory barriers in permitting and public education. Because the Barnett Shale area has several low-cost Class II saltwater disposal opportunities that allow operators to efficiently dispose of flowback and produced water, developing and implementing a cost-competitive sustainability program using recycling proves challenging.

Devon is constantly working at this challenge and researching new ideas to recycle water from natural gas shale development.

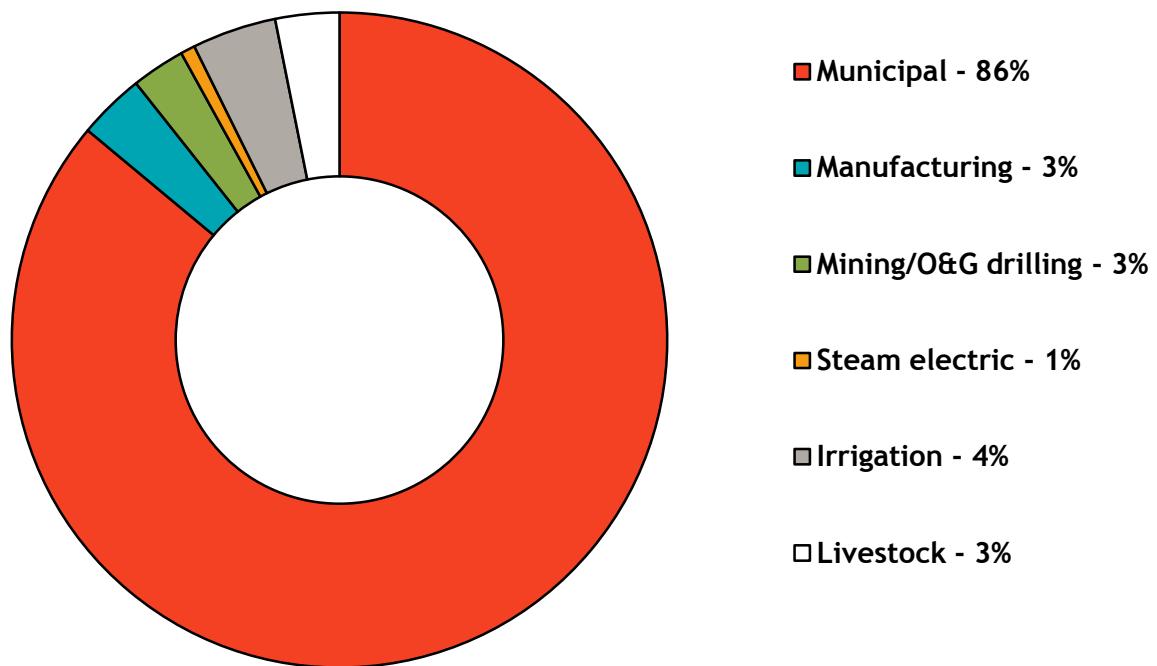


Figure 7. 2008 Barnett Shale Water Use Summary Estimates

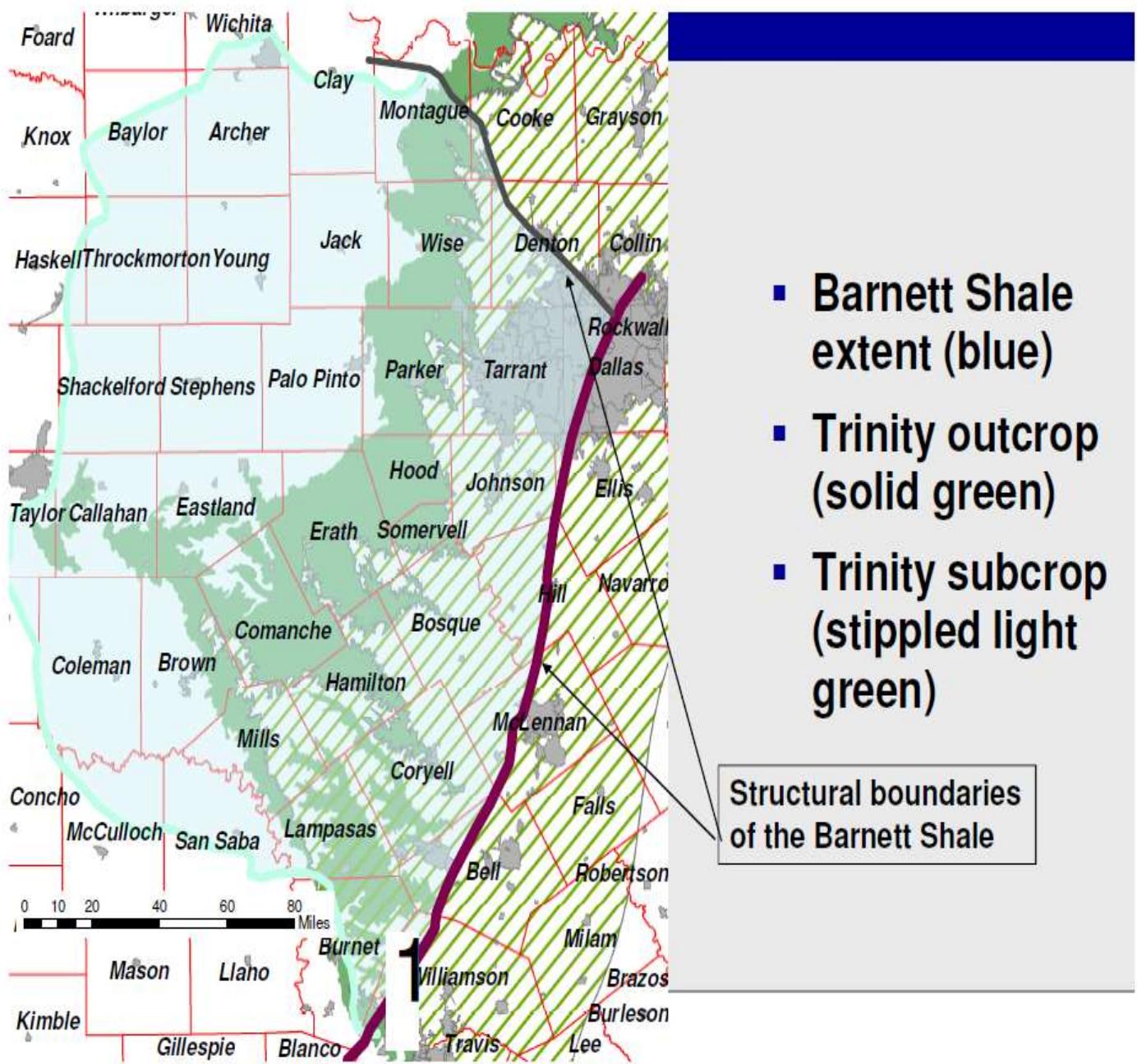


Figure 8. Trinity Aquifer

- **Barnett Shale extent (blue)**
- **Trinity outcrop (solid green)**
- **Trinity subcrop (stippled light green)**

Structural boundaries of the Barnett Shale

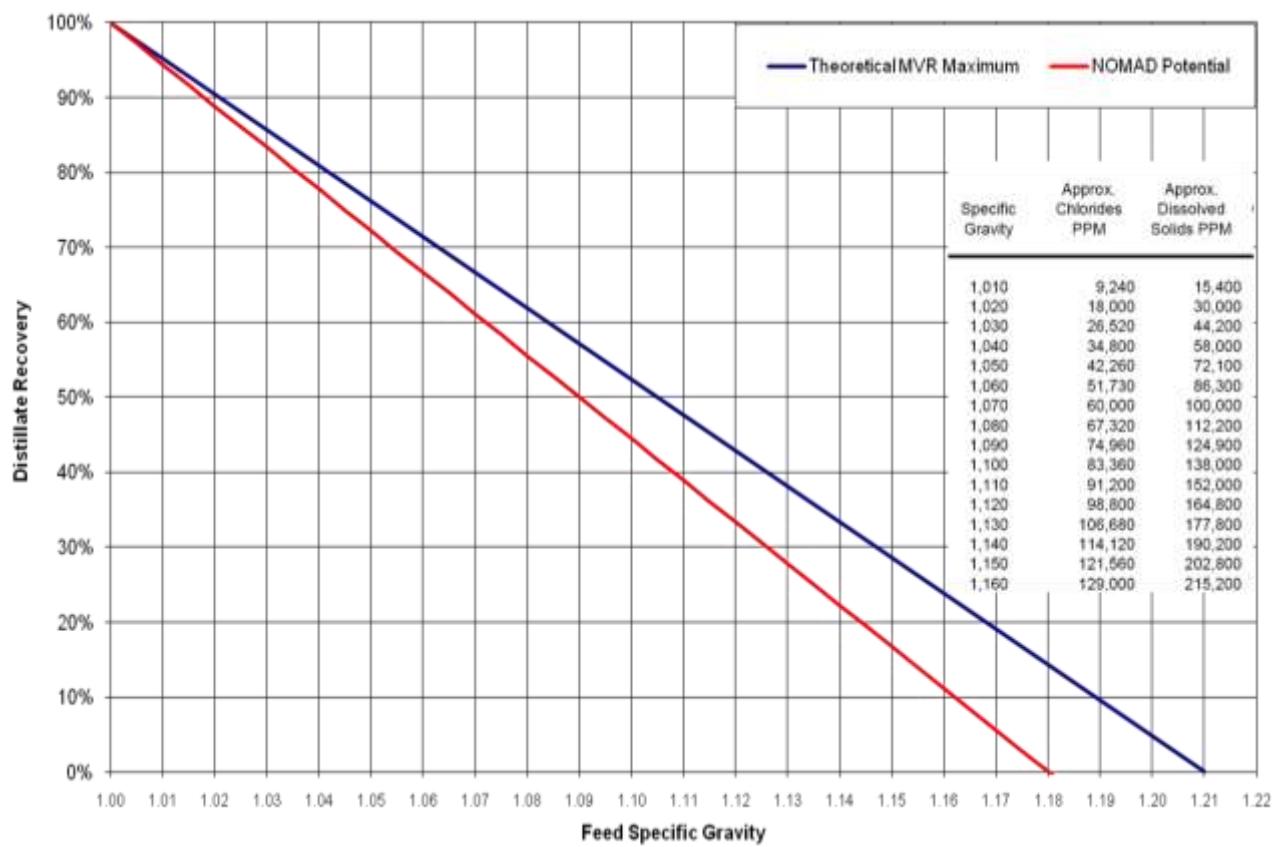


Figure 9. MVR Evaporator Recovery Based on Feed Gravity for NaCl Brine

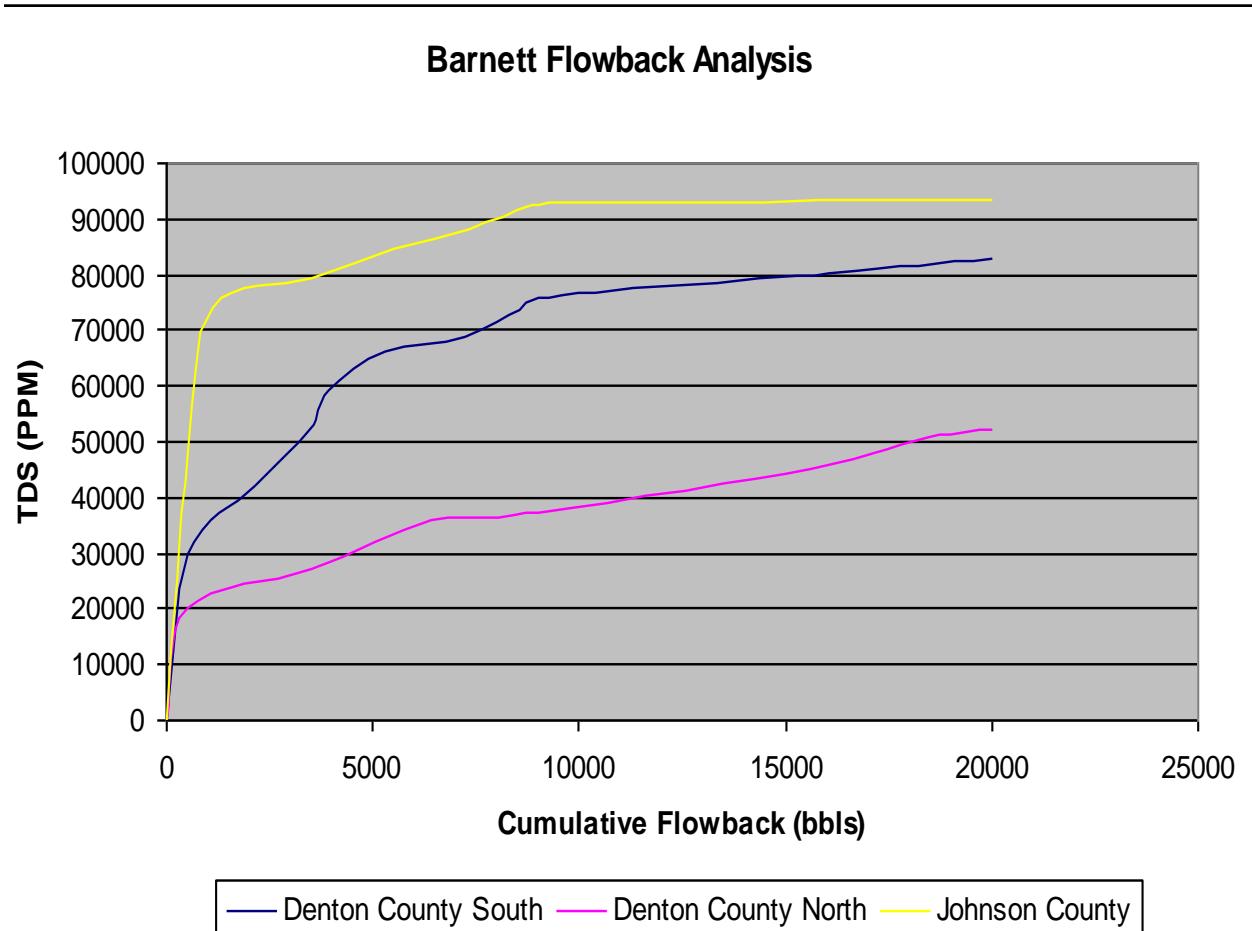


Figure 10. Barnett Flowback Analysis

# An Overview of Current and Projected Shale and Tight-Gas Water Use in Texas: Implication for Local Water Resources

Jean-Philippe Nicot

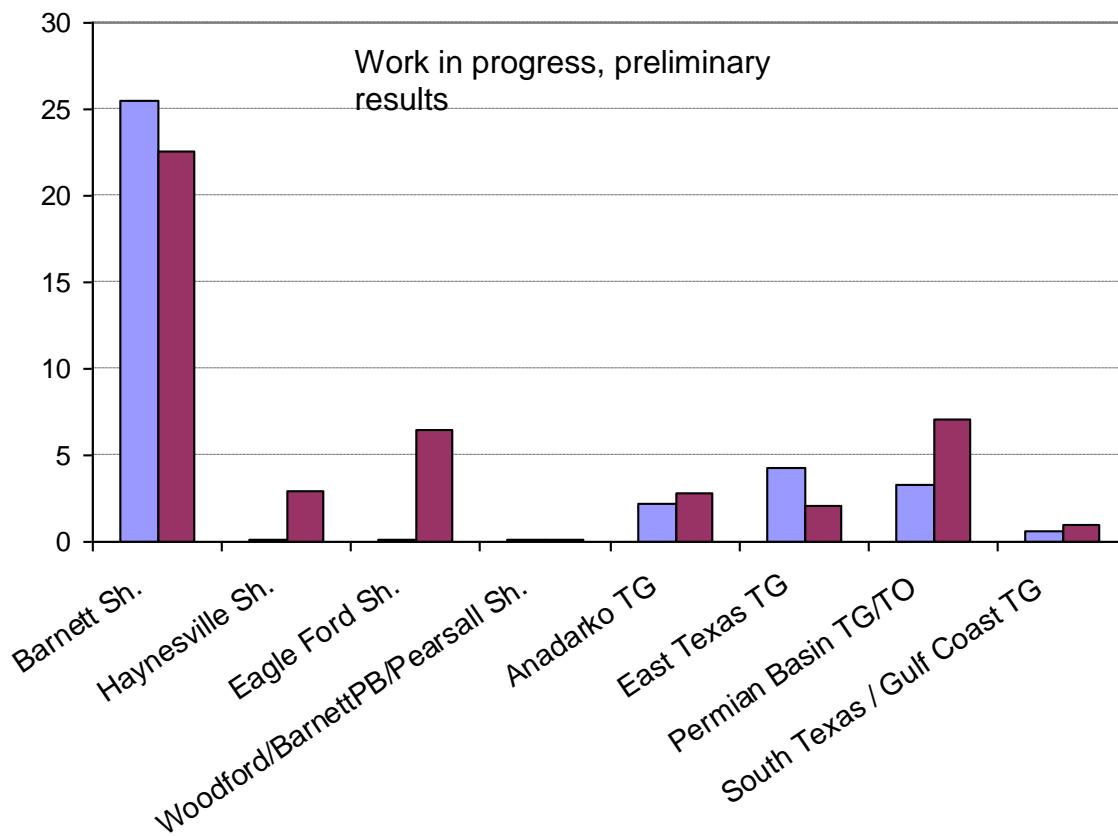
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In the middle of 2009, we undertook a study of water use in the state of Texas in the upstream segment of the oil and gas industry (that is, water used to extract the commodity until it leaves the wellhead), both current and projected for the next 50 years (Nicot et al., 2011). The objective of the study was to determine the amount of water used for different purposes (well drilling, completion, and secondary and tertiary recovery processes of conventional resources) across the state. With tens of thousands of wells having been hydraulically fractured in the past few years, the state water agency (TWDB) called for a study to assess hydraulic fracturing (HF) water use. Secondary objectives were (1) to collect information on the source of the water (groundwater, surface water, or another source) and the quality of the water (fresh or brackish) and (2) to understand the extent of recycling/reuse across the industry. We were able to gather relatively accurate data from the stimulation stage (HF), as a well is being readied for production. Operators have to report the amount of water used in the process, and tabulated data are available in a format easy to process from private vendors (IHS Energy). The data were not without typos, but they and other issues were resolved by ensuring consistency between amount of water, number of stages, and proppant loading. We assigned median values to those wells with no usable data. The split between surface water, groundwater, and other sources (waste water) was much harder to determine. It seems that neither groundwater nor surface water dominates in most plays, and both are used across the state. To the best of our knowledge, alternative water sources are still marginal in Texas. The amount of reuse/recycling was also difficult to discern. We estimated it at ~5% of the amount injected for shale-gas plays. We are more uncertain about water use for drilling wells and waterfloods, although it is clearly nonnegligible.

Overall, in 2010, we estimate that the oil and gas industry used (preliminary numbers) ~45,000 acre-feet (AF) for fracturing wells (Figure 11) and ~18,000 AF for other purposes more widespread across the state. These figures do not show a large departure from water volume used in previous decades, in which a similar amount of fresh/brackish water was used mostly for waterfloods in the western half of the state. Currently hydraulic fracturing is being used in many plays across the state, primarily in shale-gas plays, including the Barnett Shale play in the Fort Worth area, which is responsible for ~50% of the HF water use (22,500 AF). Other important shale plays include the Haynesville/Bossier play in East Texas straddling the Louisiana state line (~3,000 AF in Texas) and the Eagle Ford play in South Texas (6,500 AF). The Eagle Ford play also contains a significant oil section, which is the focus of current exploration and

production. The Permian Basin, a major oil-producing area, has also seen a recent revival, thanks to HF of long vertical wells (the “Wolfberry” play). In 2010, Permian Basin plays used ~7,000 AF for the hydraulic fracturing of many formations (including >3,500 AF in the “Wolfberry” play). Tight-gas plays, which, unlike shale plays, are conventional reservoirs or sections of conventional reservoirs with a very low permeability, have been receiving hydraulic fracturing treatment for decades in Texas. They too have seen a significant increase in interest, HF operations, and gas production. East Texas gas plays used ~2,000 AF for HF, whereas the Texas section of the Anadarko Basin in the Texas Panhandle used >25,000 AF. The south Gulf Coast gas province may be the only basin that has not seen an increase in the number of large HF jobs (~1,000 AF over a large area).



*Figure 11. Estimated hydraulic fracturing water use in 2008 and 2010 in the state of Texas.*

To put these figures in perspective, Texas has been projected to have consumed ~18.3 million AF of water in 2010, according the most recent 2007 state water plan, including >10 and ~4.8 million AF for irrigation and municipal use, respectively. HF water use composes a small fraction of the state water use (0.4%).

Projections for the oil and gas industry were made with the help of various sources by estimating the amount of oil and gas (including shale gas) to be produced in the state in the

next few decades and by distributing it through time (Figure 12). Given the volatility of the price of oil and gas, the figures provided clearly indicate only a possible future. We project that state overall water use in the oil and gas industry will peak in the 2020–2030 decade at ~<150,000 AF, thanks to the oil and gas unconventional resources that “will start” to decrease in terms of water use around that time.

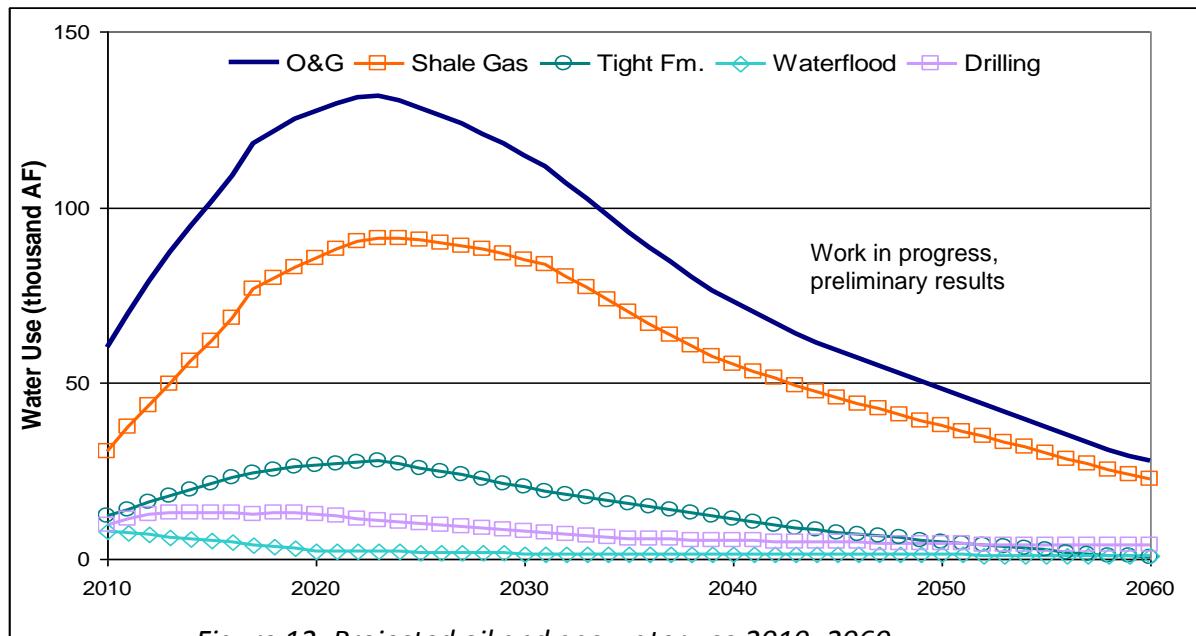


Figure 12. Projected oil and gas water use 2010–2060.

In Texas, only one thorough study (Bene et al., 2007) in the public domain and performed in 2007 addresses the regional impact of shale-gas water use on an aquifer (the Barnett Shale and the Trinity aquifer). The conclusion of the study was that the aquifer as a whole was not in danger of being depleted and that gas operators use only a relatively small fraction of the total demand. However, some rural counties, typically relying on groundwater for domestic use, are seeing a relatively large increase in groundwater pumping. A similar situation exists in the Carrizo aquifer overlying the Eagle Ford Shale in South Texas. Local recovery following the large decrease in irrigation-water demand could be slowed because of HF. In some other areas of the aquifer, HF water demand could increase stress to the aquifer. In both these aquifers, note that historical pumping stresses were much higher than could be generated by HF and that water levels rebounded relatively quickly. However, healthy aquifers do not necessarily mean an absence of local water-resource issues. If an HF water supply well is located close to a domestic well, pumps may have to be lowered and/or the well deepened, and pumping rates may be reduced.

## **Reference**

- Bene, P.G., B. Harden, S.W. Griffin, and J.-P. Nicot. 2007. Northern Trinity/Woodbine Aquifer Groundwater Availability Model: Assessment of Groundwater Use in the Northern Trinity Aquifer Due to Urban Growth and Barnett Shale Development. Texas Water Development Board. TWDB Contract No. 0604830613.
- Nicot, J.-P., A. K. Hebel, S. M. Ritter, S. Walden, R. Baier, P. Galusky, J. Beach, R. Kyle, L. Symank, and C. Breton. 2011. Current and Projected Water Use in the Texas Mining and Oil and Gas Industry, report prepared by the Bureau of Economic Geology. The University of Texas at Austin, in review for the Texas Water Development Board, Austin, TX.

# Enabling Fracturing Operations with Zero Fresh Water Withdrawals

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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.*

## Abstract

Water withdrawals represent an issue in some parts of the country where shale gas operations are active. Attempts to use surface water instead of ground water, and in some cases gray water, are worthwhile and should be pursued. However, the industry should be challenged to do without these. Industry has already responded to the challenge of recycling flowback water by becoming more salt tolerant. The ability to use saline waters of convenience should be seriously investigated. The primary candidates are sea water, saline aquifer water and produced water. Removal of some constituents such as solids, divalent ions and bacteria will likely be necessary.

## Principal Issues

Of the water issues facing shale gas operations, the two demanding the greatest attention are fresh water withdrawals and discharges of contaminated water. The latter can largely be addressed through re-use of flowback water, albeit with some treatment. But shale gas formations are such that only about a quarter to a third of the fracturing fluid returns. This causes a need for makeup water. The gel frac operations of the early Barnett are in the past except in some instances such as the Haynesville. These days most operations run slick that is with less than half of one percent of chemicals. This causes the volumes to go up, and up to 5 million gallons are used per well. Consequently, makeup water will run up to 3.5 million gallons.

To date makeup water has been sourced from ground water primarily, but also surface water. Schemes to use other sources with low utility, such as gray water, are also being executed. We suggest here a discourse on the proposition that all makeup water comprise produced water, saline aquifer water or sea water, whichever of these are the saline waters of convenience.

## Handling Salinity

Fracturing operations have become increasing salt tolerant. To some degree, this has been driven by the need to re-use flowback water with a minimum of processing, but once the industry approached the problem, it became obvious that in many instances the salinity had advantages. In the ternary diagram of carbonate, silica and clay, the preferred compositions are those with a higher proportion of the first two constituents. Nevertheless, there is enough clay to cause water absorption and swelling. This can be minimized at higher salinities. So a measure of salinity is actually a net benefit. In the limit one may want to match the salinity of the connate water in order to create a chemical potential balance.

Even if salinity is tolerable to about 80,000 ppm TDS, we know that flowback water can exceed that number. Table 2 shows some data for the Marcellus. In this particular study TDS topped out at around 220,000 ppm, but instances of 350,000 ppm are not completely uncommon in the Marcellus.

*Table 2. Typical Marcellus Salt Levels (ppm). Source: Blauch et al. SPE Paper 125740, 2009*

	Total Dissolved Solids (ppm)	Mg (ppm)	Ca (ppm)
Average	47,364	175	1750
Range	16,000 – 220,000	10-927	400-8600

It is possible that these are due to evaporite sequences or from accidentally allowing fractures to penetrate the highly saline Onandaga below the reservoirs. Assuming these are unavoidable in the main, one must be prepared to handle high numbers. This means that some level of desalination may be necessary although clearly not the levels dictated by the old paradigm of fresh water as base fluid. All desalination methods leave a residue that needs disposal, and in the case of reverse osmosis, the residue from sea water desalination has TDS of around 75,000 ppm. This may be usable, but in general one needs to be prepared to dispose of these residues. An option would be the saline aquifers, even if they were the source of water. Regulations allowing this would need to be studied. Produced water is currently being reinjected in some locations. This would not be that different.

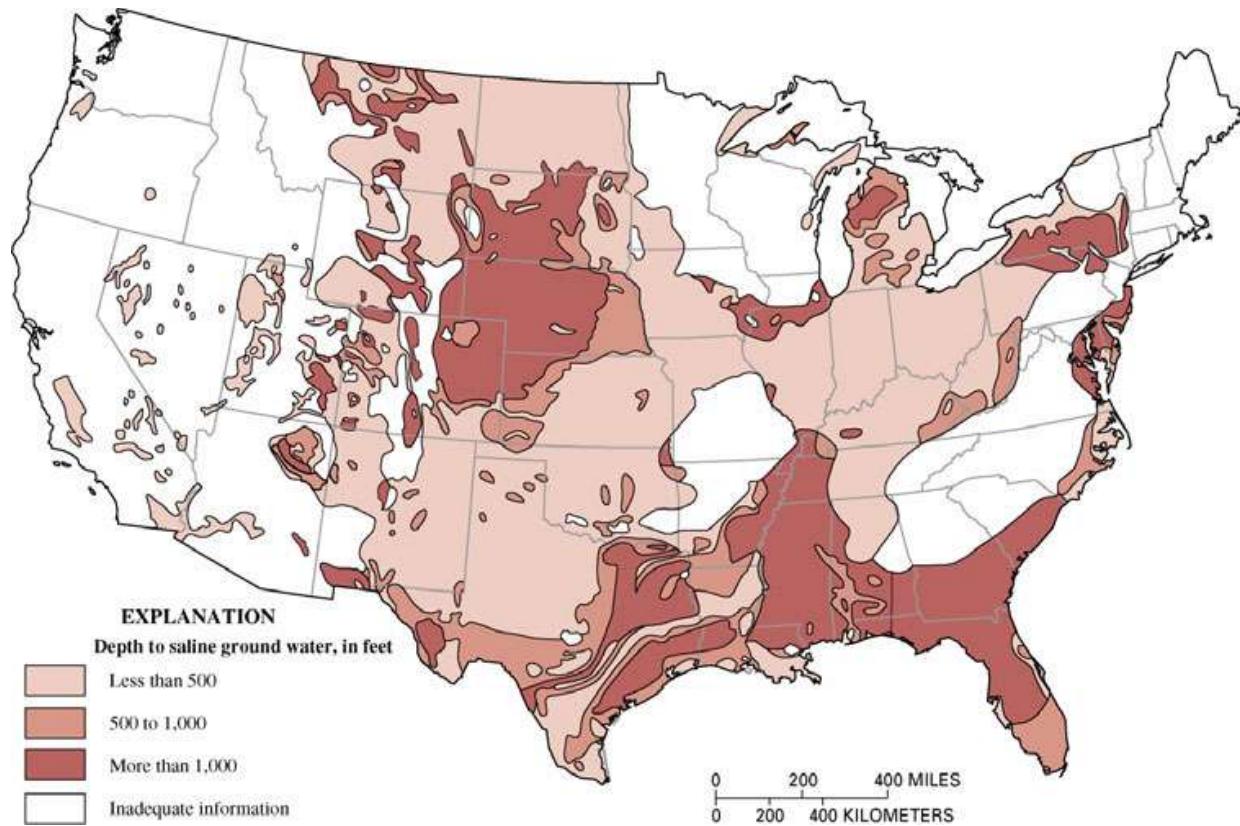
### Saline Aquifers

Since ground water tends to get saltier with depth, one can reasonably assume that saline aquifers are ubiquitous. Deep saline aquifers have been studied as repositories for captured carbon dioxide, and the Frio is the largest in the country. The last map was published around 1960 and one assumes the lack of updating is due to not enough importance being attached to these water bodies. (Figure 13 shows the available map of saline aquifers in the US.) Even this map demonstrates the existence of such water over much of the shale production areas. It also shows the depths to be low to moderate. This likely equates to modest salinity, which is good for hydraulic fracturing. The actual figures are almost certainly available in many instances. If the viability of use of this sort of water is confirmed, a mapping of location and composition would be of value.

### Divalent Ions

Divalent ions, in particular Mg and Ca, cause issues with some the ingredients of fracturing fluid. The affected chemicals include surfactants, breakers and friction reducers. All of this can be traversed through substitution. The worst actor is likely the formation of scale. In of itself it can be deleterious, but the propensity of scale to concentrate the very low concentration of radioactive elements sometimes present is a concern. Absent scaling, the divalent ions would

*Figure 13. Saline Aquifers in the US*



likely be returned to the formation through reuse of the flowback water therefore removal of these species is probably for the best. Technology for removal of divalent ions is very straightforward but the practicality of doing so at every site may be daunting. One fairly recent trend that could increase the use of treatment technology is the practice of pad drilling, which involves drilling up to 20 wells from a single location. This allows for aggregation of facilities of all types and has other environmental benefits.

### Bacteria

Bacteria are known to be bad actors in reservoirs because they cause the formation of various undesirables such as sulfates that plug pores and cause the formation of H<sub>2</sub>S. Therefore, any frac fluid must be free of bacteria. The bacterial content of saline aquifers is not known systematically. A 1975 study (Willis, et al., 1975) determined that three shallow unpolluted saline aquifers in the southeast contained various species, mostly anaerobic. Methanogenic bacteria were also found in each case. One can reasonably expect that biocidal treatment will be necessary.

### Discussion

The workshop participants should debate the advisability of using saline waters of convenience as makeup water. Saline aquifers are likely the most viable targets. These would need to be more completely mapped for the benefit of the industry. Economic considerations would

include the levels of processing required and the practicality of moving this water over distances.

### **Reference**

Willis, CJ, GH Elkan, E Horvath, and KR Dail. 1975. Bacterial flora of saline aquifers. *Ground Water* 13(5): 406-409.

## Sustaining Louisiana's Fresh Water Aquifers – A Case Study in Bringing Community and Industry Together

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The Haynesville Shale Natural Gas Play in Louisiana lies more than 10,000 feet below the surface. It is a consistent 500-foot thick layer underlying an area approximately 80 miles south to north by 60 miles east to west across the north Louisiana/east Texas border. In order to commercially produce the wells in the Haynesville Shale, operators use the technique known as "Hydraulic Fracturing". Fracking, as it is referred to, requires large volumes of water - up to 5 million gallons per well. Ground water had been the usual source for this drilling technique over the years, but as development in the Shale heightened, the potential for impacts on local domestic water use had become a real concern.

Recognizing that the extensive water demand could pose a stress on nearby fresh water aquifers, the Louisiana Office of Conservation (the state's regulatory authority) began to pursue alternatives to satisfy industry's need for water for this type of exploration and production (E&P) activity, while trying to avert impacts to the immediate source of water for area neighborhoods and the local community.

The Conservation Office wasted no time in researching and finding ample yield in several surface water sources. By combining this course of action with a few other water management procedures, and with amendments to the existing regulations, the office provided a successful and manageable solution. In this case, the outcome included appropriate use and protection of surface water, ground water and domestic water supply. Collectively, all stakeholders would share in the effort to conserve, protect, and sustain the state's fresh water aquifers.

## **Summary and Abstracts from Theme 2: Flowback Recovery & Water Reuse**

## ***Summary of Presentations for Theme 2: Flowback Recovery & Water Reuse***

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### **Technical Presentations**

The first set of technical presentations in this theme addressed case studies from around the United States.

**Matthew Mantell**, Chesapeake Energy Corporation, discussed the feasibility of produced water reuse in various shale formations. Mr. Mantell noted that this feasibility is influenced by initial and long-term produced water volumes as well as the quality of the produced water. He also described produced water management options, including disposal by deep well injection and simple and advanced methods for treatment and reuse. Mr. Mantell noted that natural gas combustion results in the release of water, replacing the water HF processes remove from the hydrologic cycle. He also emphasized that industry is working to improve the efficiency of fresh water use.

**Keith Minnich**, Talisman Energy Inc., provided information on produced water reuse from a water treatment and water chemistry perspective and presented case studies highlighting key water reuse issues. Mr. Minnich noted that, in some cases, produced water can be reused after simple settling of suspended solids and does not require other treatment techniques. In addition, he suggested that blending of produced water and fresh water might be effective for reducing the scaling potential of the HF water. He noted that the addition of barite “seed” crystals can be used to precipitate barite out of supersaturated waters. Mr. Minnich also discussed logistical considerations for water reuse and emphasized that treatment and reuse activities must be site specific.

The second set of technical presentations addressed flowback characteristics.

**Matthew Blauch**, Superior Well Services, described the results of sequential flowback analyses in the Marcellus and their implications for produced water reuse. He presented water chemistry results for TDS, chloride, hardness (calcium carbonate), and barium, as well as these components’ relationships to flowback volume and location. Mr. Blauch discussed evidence suggesting that salt content in produced water is due to primary dissolution of thin salt lenses within the Marcellus. Mr. Blauch concluded that formation water variations require ongoing chemical analysis of produced waters; however, these analyses can also provide a basis for predicting the chemical composition of produced waters in new development areas.

**Tom Hayes**, Gas Technology Institute, presented data on produced water chemistry from the Marcellus and the Barnett. The analyses included TDS levels in produced water over time and concentrations of chemicals of concern, including volatile and semi-volatile organics, pesticides, polychlorinated biphenyls (PCBs), metals, and radionuclides. Based on these results, Dr. Hayes identified possible treatment needs for reused water and described two broad treatment options (demineralization and conditioning without demineralization) that could achieve these objectives. Dr. Hayes also described examples of specific treatment methods currently in use in HF operations.

The third set of technical presentations in this theme addressed reclamation systems.

**Jill Cooper**, EnCana Oil & Gas (USA), described EnCana's water reclamation system in the Piceance basin of Colorado. Ms. Cooper explained that the target formations there have several properties that make the reuse of flowback water attractive, such as the presence of natural fractures and permeability. These properties allow EnCana to minimize use of proppant, reducing the amount of additives needed in fracturing fluid as well as the amount and cost of treatment necessary to prepare produced water for reuse. Ms. Cooper closed by recommending a regional approach to regulation because of the variation between different formations.

**D. Steven Tipton**, Newfield Exploration Mid-Continent, presented Newfield's flowback water recycling program. Mr. Tipton stated that water treatment, transport, and disposal are a huge cost for operators, and in the Granite Wash formation, Newfield can recycle up to 80% of produced water with no treatment. He explained that the water is transported to recycle pits via poly lines. He also explained that in the Woodford Shale, produced water has high chloride content and a small amount (6%) is reused as a brine source after treatment at a recycling facility, replacing the addition of potassium chloride (KCl) to the fracture fluid.

**Johanna Haggstrom**, Halliburton Energy Services, presented a "toolbox" of treatment options available for produced water recycling. Categories of treatment techniques she presented include clarification (removal of suspended solids and some metals and organics) and demineralization (removal of dissolved solids). Ms. Haggstrom emphasized that choosing a treatment option should be done on a case-by-case basis due to the unique makeup of produced waters from different formations and the different goals for the end-use of this water. Halliburton does not provide operators with specifications for final water quality of produced water on particular projects.

**George King**, Apache Corporation, described Apache's reuse of water in the Horn River play in British Columbia. Mr. King explained that the drilling operation is a closed-loop system that withdraws a 35,000 ppm brine from a nearby reservoir, uses it in the fracturing fluid, performs some minor treatment on the produced water, and then returns it to the original formation. He explained that the brine reservoir has other properties including high temperature and low

levels of solids and other suspended materials that make it an ideal component of the fracture fluid, require minimal additional chemicals, and facilitate reuse. The chemicals used in this system are commonly available in many household products. This closed-loop reuse system reduces the environmental impact of the drilling operation, freshwater use, and operator costs.

### ***Summary of Discussions Following Theme 2: Flowback Recovery and Water Reuse Presentations***

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*Clarification of items in the presentations.* A participant asked about the Marcellus Shale core shown in Mr. Blauch's presentation. The presenter clarified that both cuttings and standard core were taken; he noted that cuttings are easier to obtain, but cores allow a researcher to pinpoint the location of salt striations. A participant asked about the fluctuating produced water TDS levels shown on a graph in Dr. Hayes's presentation. The presenter explained that, generally, TDS levels steadily increase with time; however, individual cases may differ from this pattern. A participant asked about barium analysis in the second set of technical presentations. Both presenters indicated that the analyte was soluble barium, not total barium. A participant asked what kind of liner is used in Newfield's pits. The presenter clarified that Newfield uses a geo-membrane liner in their pits. For freshwater pits they use a 20 mil liner, and for flowback water, Newfield uses a 30 mil liner. The presenter explained that these liners are used because the water has a low TDS (17,000 mg/L) that meets Oklahoma agricultural use standards.

*Water treatment techniques.* A participant asked about testing recycled water before reuse. In the Marcellus Shale, one operator uses a centralized pad for filtration. According to this participant, water is analyzed on site for a few parameters, such as bacteria and scaling properties, and a titration method is used to analyze for chloride. A presenter asked if the settling tanks or effluent inlets are designed for swirling or other accelerated settling techniques. The presenter clarified that standard tanks have been used to date, with the inlets and outlets arranged in the optimum fashion. A participant noted that Amoco conducted research on settling tanks in the 1970s and 1980s. Another participant asked if on-site treatment techniques can be powered by the gas that is produced at the site. The presenters agreed that while this is possible, it is more economical to sell the gas. However, they noted that treatment techniques are sometimes powered by waste heat from the compressors.

*Use of surface water.* A participant asked if it is more economical to use surface water rather than recycled produced water in areas with sufficient supplies of surface water. The presenters indicated that this is generally the case, especially in the Haynesville where water chemistry is poorly suited to reuse. The presenters added that water quality in the Haynesville is generally

consistent across the shale play. However, they noted that the larger Marcellus Shale has variations in water quality from Pennsylvania to West Virginia.

*Biocides.* A participant asked about the use of biocides in recycled water. The presenters stated that they use standard biocides, such as glutaraldehyde or a glutaraldehyde quaternary amine blend, and that there are not special biocide treatments for recycled water. However, they noted that ongoing experiments are investigating the use of chlorine dioxide, similar to the techniques used by municipal water systems. The presenters of the third set of technical presentations indicated that use of biocides may not be necessary in some slickwater operations with high bottomhole temperature. However, they clarified that biocides are necessary if polymers for a gel are being mixed with surface waters.

*Economic drivers of water reuse.* A participant asked if reusing water is economical. The presenters indicated that reusing water is very cost-effective in the Marcellus because of the otherwise high disposal costs of produced water. They stated that operators try to reuse 100% of their water, including initial flowback and long-term flowback, especially in the northern parts of the Marcellus play. They noted that southern parts of the Marcellus are closer to disposal wells; according to the presenters, reuse is not as prevalent in these areas but it is increasing. The presenters noted that in the Fayetteville, recycling is also attractive because produced water does not have to be treated before it is reused. Some participants added that water reuse will likely become more economical as technologies develop and improve.

*On-site water management and multi-well pads.* A participant asked about environmental management and oversight at HF sites. Participants explained that once the well completion activities are set up, water managers ensure that the completions team is properly supported. A participant stated that a host of environmental and safety standards support these activities, and operators closely monitor the amounts of water and hydrocarbons produced. Another participant stated that large operators can dedicate staff to on-site water management activities. A participant pointed out that multi-well pads can reduce the risks and concerns associated with transporting produced water, since water may be able to be reused on site. Another participant noted that multi-well pads will likely become more prevalent once initial drilling is completed to maintain individual leases. A participant asked which party at a drill site is responsible for handling produced water. A presenter explained that the operator is ultimately responsible for the produced water (as well as for any individuals on the site). However, the presenter added that operators usually contract to a third party who specializes in flowback management.

*Removal of solids.* A participant asked about techniques for the removal of solids from produced water. The presenter clarified that there are two goals to this process: reducing the overall amount of solids in the water and reducing the particle size of the remaining solids. The presenter stated that, generally, nothing is added during this solids removal process. The resulting solids are inert compounds: a mix of sand, clay, rock cuttings, and some precipitated barite. The presenter noted that barium chloride is much more soluble and will not settle out.

The presenter commented that after settling, the material is removed from the tanks and a third party transports it to a licensed landfill. As far as the presenter is aware, the landfills have not encountered any issues with radioactive material in the removed solids. He also noted that naturally-occurring radioactive material (NORM) is generally present as soluble radium, which stays in the produced water and does not filter or settle out. A participant noted that in Colorado, data suggest that gross alpha/beta levels are high in produced pit liquids.

*Pipelines.* A participant asked about transporting fresh and produced water through pipes and how these used pipes are flushed and transported when they need to be moved. One participant transports flowback by truck but uses irrigation-based pipe for temporary fresh water pipeline. The participant noted that this irrigation pipe often allows water to seep out once it is pressurized. Another operator transports both fresh water and brine by pipe. The participant explained that the fresh water pipe is ten-inch aluminum irrigation pipe, while brines of high TDS levels can be conveyed with a pipeline of higher integrity of construction to eliminate leakage. The participant stated that pipes transporting flowback are “pigged” and flushed to ensure none of the water leaks out when the pipe is dismantled. Other participants do not use irrigation pipe for fresh water because of public perception issues. One participant avoids making 90 degree angles with the pipe and contracts a third party to conduct pressure tests to ensure the pipe’s integrity.

*Well pad reclamation.* A participant asked about the final steps for reclaiming a well pad, specifically whether reclamation is different when produced water is managed on site. A participant noted that on-site protocols for handling flowback are similar regardless if the water is destined for disposal or for reuse. However, a participant added that performing more extensive treatment on site can impact reclamation and this is one reason why operators might choose to treat water for recycling in a central location or to only treat water by settling. A participant noted that at the well pad, operators try to avoid any long-term remediation needs by installing liners, ensuring proper materials handling, etc.

*Research and development.* A participant asked if operators develop in-house methods to improve water quality for reuse. The presenters explained that operators both develop new methods and use established methods. They added that some operators are coordinating to evaluate different ways of managing chemical additives, especially in areas where fresh water aquifers underlie multiple leases. One participant noted that coordination happens best in the field, not on the management level. The participant suggested that, in the future, third-party firms might act as water brokers, treating and redistributing excess flowback. One participant noted that knowledge sharing is a key factor in water management. Another participant pointed attendees to the BSWMC’s Web site (<http://www.barnettshalewater.org/>) to find more information on coordinated water management efforts. The participant noted that there is an established structure for research, development, evaluation, and identification of best practices in this rapidly developing field.

*Chemical analyses of flowback.* A participant asked if the chemical components of flowback from the Marcellus and the Barnett are similar. The presenter explained that five-day flowback samples from both formations have similar general chemistries. In general, the Barnett seems to have a higher alkalinity. He noted that total organic carbon (TOC) is low and oil and grease levels are in the tens of mg/L for both formations. A participant asked about 2-butoxyethanol (2-BE) in flowback fluids. Dr. Hayes clarified that the study in his presentation analyzed for four alcohols. He explained that TOC levels indicate the order of magnitude of the alcohols and other organic compounds is low. In general, his study found that flowback fluids have very low TOC levels (tens of mg/L). A participant asked if future investigations of flowback fluid should include additional or different analytes. A presenter indicated that effective studies can include fewer analytes and that Dr. Hayes' study included a large list of the potential chemicals of concern, including some that are not used in HF. In addition, this study originally included radionuclides, but that analysis was postponed due to issues with salt interference. Participants added that data collection and analysis of flowback is very important and that other operators have been collecting similar data.

*Salt striations in the Marcellus Shale.* A participant asked about salt striations in Marcellus Shale core. The presenter explained that these salt deposits were analyzed by direct sampling and by leaching under surface/atmospheric conditions. A participant noted that the source of the salt deposits has not been extensively described in the geologic literature, but there is evidence showing that they may be evaporative. Another participant added that a presentation in Workshop 1 (Chemical and Analytical Methods) contained compelling evidence that the salt originates in evaporative sequences in the formation.<sup>3</sup>

*A water balance approach for monitoring.* A participant asked about using a water balance approach to determine whether fractures have grown into other zones: if long-term produced water volumes are greater than injected volumes, would that be evidence that fractures have broken into other formations? Another participant noted that this might be a useful approach, though long-term data on this subject are not available and it seems that the variability of subsurface properties would complicate any water balance approach. One participant noted that some shale plays have only been in production for a few years, limiting the availability of long-term flowback data. Multiple participants stated that, in general, the Barnett is the only shale play that will return more water than originally injected.

*Chemical partitioning.* A participant asked about the effect of condensate production on TOC levels in flowback. This would be relevant to the southwestern section of the Marcellus Shale. Other participants noted that samples from this area do not show elevated TOC levels, likely

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<sup>3</sup> EPA believes the presenter was referencing the presentation by Jennifer McIntosh (University of Arizona) on *Chemical and Isotopic Tracers of Natural Gas and Formation Waters in Fractured Shales*. The abstract that corresponds to the presentation is included in the *Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods* (EPA 600/R-11/066).

due to partitioning between the gas and the condensate. A participant described air quality results from condensate tanks in southwestern Pennsylvania, claiming that high levels of naphthalene, benzene, toluene, and xylene were present. The participant asked why these materials are not found in the water. Another participant suggested that this is likely also due to partitioning.

*Regulation and permitting.* In Colorado, drilling on federal lands is overseen by the Bureau of Land Management (BLM). BLM has a Memorandum of Understanding (MOU) with the Colorado Oil and Gas Conservation Commission (COGCC) regarding production activities on federal lands. A participant noted that obtaining a permit for produced water recycling in Texas requires the certification of a registered engineer, among other requirements. Oklahoma is in the process of permitting the first recycling pit. In Texas, one participant drains pits annually, inspects the liners, and makes repairs if necessary.

*Disclosure of fracture fluid additives.* Halliburton provides the composition of their fracture fluids in many of their areas of operation, available on their Web site. Apache and other operators have also made this information available and it will be included on the <http://fracfocus.org> Web site. Participants indicated that the main components of fracture fluid will be disclosed, although there will most likely always be some that remain confidential as trade secrets. Other participants added that some companies are developing more environmentally-friendly alternatives to fracture fluid components, dependent on demand for green alternatives from operators.

*Well siting.* The presenters of the third set of technical presentations clarified that a number of factors are taken into consideration when siting wells to minimize environmental impact, including, for example, proximity to drinking water system well fields. The presenters explained that directional drilling technology has advanced so that gas reserves can be reached by a well some distance away.

*Reusing other fluid types.* The presenters of the third set of technical presentations noted that while slickwater fracture fluids are generally the best candidates for reuse, linear gels have been reused in some regions. The presenters explained that the higher number of additives in gel systems generally makes them less attractive for reuse.

### ***Abstracts for Theme 2: Flowback Recovery & Water Reuse***

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# Produced Water Reuse and Recycling Challenges and Opportunities Across Major Shale Plays

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## Water Use in Shale Development

Water is an essential component of shale development. Operators use water for drilling, where a mixture of clay and water is used to carry rock cuttings to the surface, as well as to cool and lubricate the drillbit. Drilling a typical Chesapeake shale well requires between 65,000 and 600,000 gallons of water. Water is also used in hydraulic fracturing, where a mixture of water and sand is injected into the shale at high pressure to create small cracks in the rock and allows gas to freely flow to the surface. Hydraulically fracturing a typical Chesapeake shale well requires an average of 5 million gallons of water. The water supply requirements of shale oil and gas development are isolated in that the water needs for each well are limited to drilling and development, and the placement of shale wells are spread over the entire shale play. Subsequent fracturing treatments of wells to re-stimulate production are possible, but unlikely, and re-stimulation is dependent upon the particular characteristics of the producing formation and the spacing of wells within the field. A breakdown of approximate water use for drilling and fracturing by shale play is provided below:

Table 3. Water use in major shale plays

Shale Play	CHK <sup>1</sup> Average Drilling Water Use per Well (in gallons)	CHK <sup>1</sup> Average Hydraulic Fracturing Water Use per Well (in gallons)	Total Average Water Use Per Well *
Gas Shale Plays (primarily dry gas)			
Barnett	250,000	3,800,000	~ 4.0 Million Gallons Per Well
Fayetteville	65,000	4,900,000	~ 4.9 Million Gallons Per Well
Haynesville	600,000	5,000,000	~ 5.6 Million Gallons Per Well
Marcellus	85,000	5,500,000	~ 5.6 Million Gallons Per Well
Liquid Shale Plays (Gas, Oil, Condensate)			
Eagle Ford	125,000	6,000,000	~ 6.1 Million Gallons Per Well
Frontier / Niobrara	300,000	3,000,000	~ 3.3 Million Gallons Per Well

<sup>1</sup> CHK: Chesapeake; Source: Chesapeake Energy 2010b

## **Produced Water Management**

Produced water plays a key role in the environmental and economic viability of shale oil and gas development. Produced water is a byproduct of all oil and natural gas (energy) development. In order to successfully develop these resources, produced water has to be effectively managed.

For the purposes of this discussion, *produced water* is all water that is returned to the surface through a well borehole and is made up of water injected during the fracture stimulation process, as well as natural formation water. Produced water is typically produced for the lifespan of a well, although quantities may vary significantly by play. Produced water quality can also vary tremendously from brackish (not fresh, but less saline than seawater) to saline (similar salinity to seawater) to brine (which can have salinity levels multiple times higher than seawater). Furthermore, the term *flowback* refers to the process of excess fluids and sand returning through the borehole to the surface. For this discussion, the water produced during flowback operations is considered produced water.

The feasibility of produced water reuse is dependent on three major factors. First is the quantity of the produced water generated, including the initial volume of produced water generated (typically during the first few weeks after stimulation). The second factor is the duration in time of produced water generation, including the rate at which water is generated and how it declines over time. Wells that produce significant volumes of produced water during the initial time period are preferred for reuse due to the logistics involved in storing and transporting the water for reuse. A continuous volume can keep tanks and trucks moving, increasing the economic efficiency of reusing the produced water from one wellsite to another. The Barnett, Fayetteville, and Marcellus Shales all produce a significant volume of initial produced water enabling the effectiveness of reuse. These three major shale plays produce approximately 500,000 to 600,000 gallons of water per well in the first 10 days after completion. This volume is sufficient to provide approximately 10% to 15% of the total water needed to fracture a new well (see Table 3 above). The Haynesville Shale produces less water, approximately 250,000 gallons per well in the first 10 days after completion. This is approximately 5% of the total water needed to fracture a new well.

Long-term produced water production is also important because wells that produce large volumes of produced water for long periods of time will require a disposal or reuse option that is located in close proximity to the wellsite in order to retain the economic viability of the operation. The unit of measurement used for comparison of long term produced water is gallons of water per million cubic feet (MMCF) of gas or hydrocarbon liquid equivalent. This unit of measurement for comparing volumes is exclusive to shales because there appears to be a direct correlation between hydrocarbon production and long term produced water generation in the major shale plays. Barnett Shale wells generate by far the largest volume of produced water of any major shale play at greater than 1,000 gallons per MMCF. The Barnett Shale is believed to contain larger volumes of natural formation water present in, and in close proximity to the shale. The Eagle Ford, Haynesville, and Fayetteville Shale are moderate produced water generating plays at approximately 200 to 1,000 gallons per MMCF. These shale formations are relatively desiccated and allow less fluid production per MMCF. The lowest long term produced

water volumes come from the Marcellus Shale. The Marcellus is a highly desiccated formation that tends to trap fluids in the shale through physical / chemical interactions. Water production is less than 200 gallons per MMCF in the southern portion of the play in West Virginia, and closer to 25 gallons per MMCF in northern portion of Pennsylvania.

The third major factor in produced water reuse is the quality of the produced water. Total dissolved solids (TDS), also known as the salinity, total suspended solids (TSS), the larger suspended particulates in water, scale-causing compounds (calcium, magnesium, barium, sulfate) and bacteria growth all have a major effect on the feasibility of reusing produced water. TDS can be managed in the reuse process by blending with freshwater to reduce the TDS. Blending is necessary because high TDS can increase friction in the fluid which is problematic in the hydraulic fracturing process. TSS can be managed with relatively inexpensive filtration systems. Filtration of TSS is necessary because elevated solids can cause well plugging and also decreases biocide effectiveness. Scale and bacteria causing compounds can be managed with chemical treatments or advanced filtration, but each additional treatment step reduces the economic efficiency of the process. The ideal produced water for reuse has low TDS, low TSS and little to no scale or bacteria-causing compounds. (Chesapeake Energy 2010d)

### **Produced Water Management Options**

While produced water is generated with the production of oil and gas (energy) as stated above, energy also plays a key role in determining the best way to manage produced water. Most produced water is of very poor quality and may contain very high levels of natural salts and minerals that have dissociated from the target hydrocarbon reservoir.

Two classifications of treatment technologies are available for treatment and reuse of produced water: conventional treatment and advanced treatment technology. Both classifications have energy, environmental, and economic impacts that are directly impacted by produced water quality. Conventional treatment includes flocculation, coagulation, sedimentation, filtration, and lime softening water treatment processes. These treatment processes are generally effective in removing water quality parameters such as suspended solids, oil and grease, hardness compounds, and other nondissolved parameters. These conventional water treatment processes can be energy intensive, but are typically *much less* energy intensive than the salt separation treatments listed below. Conventional processes such as flocculation, coagulation, and lime softening utilize chemicals (sometimes in large volumes) which may have a significant energy input in the development of these chemicals used in the treatment process. However, simple filtration methods with little to no chemical inputs have a much lower energy, environmental, and economic impact.

Advanced treatment technology includes reverse osmosis membranes, thermal distillation, evaporation and/or crystallization processes. These technologies are used to treat dissolved solids, primarily consisting of chlorides and salts, but also including dissolved barium, strontium and some dissolved radionuclides. These dissolved parameters are much more difficult and energy intensive to treat and can only be separated with these advanced membrane and thermal technologies. Treating dissolved solids is a very energy intensive process. These

processes are the “second level” or more advanced form of treatment because similar conventional processes listed above are typically needed upfront to ensure that most of the non-dissolved parameters listed above are removed prior to the dissolved solids treatment process.

Outside of treatment for reuse, disposal is the other produced water management option. Outside of the Marcellus Shale, salt water disposal wells are by far the most common method of disposing of produced fluids from shale operations. Surface discharge via wastewater treatment plants has historically been a common treatment technique in the northeast United States, but has been generally phased out due to stricter discharge regulations and natural evolution of the industry due to the Marcellus Shale development. As a note, Chesapeake Energy does not currently discharge any produced water either directly, or via wastewater treatment plants in any shale play.

Energy, environmental and economic considerations must be carefully considered when discussing possible reuse and disposal options for produced water. Much discussion and technology development has focused on treatment technologies that can treat produced water so it is suitable for some form of reuse. These options include reuse in oil and gas operations, municipal, agricultural, and/or industrial operations. Lower dissolved solids produced water (<30,000 ppm TDS) may be feasible for treatment to reuse outside of oil and gas operations. Higher dissolved solid produced waters (> 30,000 ppm TDS) should only be reused where the high salt/salinity content can be kept in solution (to avoid the intense energy input to separate salts). Operators have successfully demonstrated this ability by using conventional treatment processes on high TDS waters, then managing the TDS by blending the fluids in hydraulic fracturing operations. The feasibility of relying on high TDS produced waters for potential municipal or agricultural water supply doesn’t make sense from an energy, economic, or environmental perspective due to the availability of alternative low quality water resources that could be treated to acceptable standards with far lower energy inputs. This includes municipal wastewater, brackish groundwater, and even seawater when logistically feasible. Based on this same logic, environmental and economic benefits may directly correlate when evaluating reuse versus disposal. For example, in areas with extensive salt water disposal well infrastructure like the Barnett Shale, salt water disposal wells are in close proximity to operations, and are a low cost, low energy, safe, and effective alternative to advanced reuse.

The energy requirements needed to treat Barnett Shale produced water (outside of direct filtration and blending) is significant. Since all energy sources result in some form of air emissions, water use, and/or waste generation; reusing produced water in this area using an advanced treatment technology may have greater negative environmental impacts than salt water disposal. Furthermore, oil and gas operations that keep dissolved solids in solution and use the fluid in completion operations for subsequent wells can effectively reduce the volume of fresh water needed for future operations by significant amounts. The onshore shale oil and gas industry has recently been very successful in utilizing conventional, low energy treatment systems to remove suspended solids from produced water and in using this water in hydraulic

fracturing operations. From an energy efficiency standpoint, this is a much more efficient use of energy and water than treating produced water to drinking water standards.

### **Produced Water Reuse and Recycling: The Chesapeake Energy Experience**

Over the past three years, Chesapeake has developed and implemented a highly successful produced water reuse program in its Marcellus Shale operating area, and has extended this program to all its shale operating areas. Chesapeake is not alone as many other onshore shale oil and gas companies have also been working to continue to reduce the volume of freshwater utilized in operations and thereby reducing the need to compete with other traditional users of freshwater.

#### ***Barnett Shale Reuse***

Reuse of produced water in the Barnett Shale is limited by the high volumes of water produced and the corresponding availability of Class II saltwater disposal wells (SWDs) in close proximity to well sites. Barnett Shale produced water generally has higher levels of TDS, low TSS and moderate scaling tendency. Chesapeake is currently treating and reusing approximately 6% of the total water needed to drill and fracture Barnett Shale wells in the southern portion of the play. Currently, logistics and economics are the main limiting factors in preventing higher levels of reuse in this area. These factors (logistics and economics) as well as urban curfew limitations (limited 24 hour operations in urban Ft Worth areas) currently prevent the feasibility of reuse in Chesapeake's northern Barnett Shale operational areas. However, in the northern (urban) portion of the Barnett Shale, Chesapeake is pioneering the use of evaporative technologies that utilize waste heat from gas compressors to reduce the volume of water injected into salt water disposal wells. The benefit of this technology is the prolonged lifespan of the salt water disposal well (heavier concentrated brines may actually be better for disposal wells) and also the ability to manage fluids with fewer disposal wells.

#### ***Fayetteville Shale Reuse***

Fayetteville Shale produced water is generally of excellent quality for reuse and the volumes of water generated are typically sufficient. Fayetteville Shale produced water has very low TDS, low TSS and low scaling tendency. Chesapeake is currently meeting approximately 6% of drilling and fracturing needs in the Fayetteville Shale with produced water reuse with a target goal of 20% reuse in the play. Since TSS levels are low, very limited treatment (filtration) is needed prior to reuse. As with the Barnett Shale, logistics and economics are currently the main limiting factor in preventing higher levels of reuse in the Fayetteville Shale.

#### ***Haynesville Shale Reuse***

The Haynesville Shale produces a smaller volume of produced water initially (compared to the other major plays) and has very poor quality produced water. TDS levels are high immediately, TSS is high and the produced water has high scaling tendency. The quality and volume factors combined with an adequate SWD infrastructure make produced water reuse in the Haynesville very challenging. Chesapeake has looked into produced water reuse in the Haynesville, but low produced water volumes, poor produced water quality and the resulting economics have prevented successful reuse of produced water in the Haynesville Shale to date. However, due to the large volumes of higher quality drilling wastewater generated during the drilling process,

Chesapeake is actively exploring options to reuse this wastewater in subsequent drilling and fracturing operations.

### ***Marcellus Shale Reuse***

In terms of produced water generation, the Marcellus Shale is ideal in that it produces a significant volume of produced water within the first few weeks and then the water production generally falls off very quickly. The quality of Marcellus Shale produced water is good with moderate to high TDS, low TSS and moderate scaling tendency. The TDS is managed with precise blending of produced water with freshwater during a subsequent fracture treatment and the TSS is managed with a simple particle filtration system consisting of a 100-micron filter followed by a 20-micron filter. Scaling and bacteria are managed through a very precise monitoring and testing program to ensure the compatibility of the produced water with the freshwater when blended for use during fracture stimulation.

Chesapeake's Marcellus Shale reuse program has been tremendously successful. In Chesapeake's core operating area of the northern Marcellus in north-central Pennsylvania, Chesapeake is reusing nearly 100% of all produced water and drilling wastewater. This reuse can reduce the volume of freshwater needed to drill and hydraulically fracture subsequent Marcellus Shale wells by 10% to 30%. Resulting benefits include the need for less fresh water for hydraulic fracturing operations (which reduces the impact on local supplies) and also reduces truck traffic on public roads because less fresh water is hauled (resulting in less wear and tear on roads, reduced noise and air quality impacts). From an operational perspective, the reuse program is attractive because it helps reduce the cost of operations including wastewater disposal costs, water supply costs, and transportation costs. Note that only a fraction of the water utilized in the drilling and fracturing process is returned to the surface as produced water (Chesapeake Energy 2010b). Furthermore, Chesapeake has moved to a closed loop synthetic oil based mud system for drilling operations, which significantly reduces wastewater generated from the drilling process.

### **Criticisms of Shale Gas Water Use: Removal of Water from the Effective Hydrologic Cycle**

One of the major criticisms to the use of water in the development of oil and natural gas supplies, particularly in the hydraulic fracturing of shale plays, is the so-called "permanent removal" of water from the surface and near sub-surface (effective) hydrologic cycle. While the focus of this abstract and presentation is on produced water management, it is important to address this criticism about the loss of water as it directly relates to salt water disposal well practices, produced water generation volumes, and shale water management in general. Regardless of the shale play, since the majority of produced water either remains in the formation or is disposed of in another suitable geologic formation (via Class II SWDs), this water is indeed removed from the effective hydrologic cycle. This may lead some to criticize and treat oil and natural gas water use differently than other major water users like power plants who *consume* water during the cooling process. The argument is the power plant type of *consumption* is *evaporation* and the volume of water evaporated is simply released to the atmosphere as water vapor and is still in the effective hydrologic cycle. These concerns about

the permanent loss of water from the effective hydrologic cycle can easily be addressed with a simple explanation of natural gas combustion. When natural gas is combusted with oxygen (air) it forms two by-products, carbon dioxide and water vapor. The balanced combustion reaction is shown below:

It is the generation of water vapor that ultimately offsets the removal of water from the effective hydrologic cycle. Based on some common assumptions about natural gas and natural gas combustion, approximately 10,675 gallons of water vapor are produced with the combustion of one MMCF of natural gas. (These calculations are shown in detail along with all assumptions in Appendix A.) This volume of water vapor generation was applied to determine approximately how much natural gas needs to be generated and combusted to offset the volume of water used in the development of a typical shale well in each major shale play. The results are calculated and shown in Table 4 including the average amount of time needed for a typical Chesapeake well to produce the volume of natural gas needed to offset the water used to develop (drill and fracture) the well.

*Table 4. Water vapor combustion and hydrologic cycle volume recovery by major shale play*

Shale Play	Average Water Use Per Well (in gallons)*	CHK Estimated Average Natural Gas Production Over the Life of Well (in cubic feet **)	Cubic Feet of Natural Gas Needed for Combustion to Offset Shale Gas Water Use (Based on 10,675 gal/MMCF Natural Gas Combusted)	Time for an Average CHK Well to Produce Needed Natural Gas to Offset Water Used in Well
Haynesville	5,600,000	6,500,000,000	525,000,000	< 6 Months
Marcellus	5,600,000	5,200,000,000	525,000,000	< 6 Months
Barnett	4,000,000	3,000,000,000	375,000,000	< 6 Months
Fayetteville	4,300,000	2,600,000,000	403,000,000	< 9 Months

Source: \*Chesapeake Energy 2010b, \*\*Chesapeake Energy 2010c

As shown above, a well in any of the four major shale plays produces enough natural gas in less than nine months, that when combusted, offsets the entire volume of water used in the development of that well with wells in the Barnett, Marcellus and Haynesville generally producing enough gas in less than six months of production. Please note that these wells are anticipated to produce natural gas for more than 20 years. (Chesapeake Energy 2010b)

## Major Conclusions

1. The U.S. Onshore Oil and Natural Gas Industry is reducing the volume of freshwater utilized in operations, thereby reducing the need to compete with other traditional users of freshwater
2. Feasibility of produced water reuse is dependent on three major factors: quantity, duration, and quality of produced water generated

3. Produced water quantity, duration, and quality can all vary considerably between shale plays and can even vary geographically within the same play
4. Environmental and economic benefits may directly correlate when evaluating reuse versus disposal options
5. The volume of water “removed” from the effective hydrologic cycle during hydraulic fracturing OR produced water disposal via salt water disposal wells is more than offset during the combustion of the hydrocarbon fuels produced

## Appendix A: Water Vapor from the Combustion of Natural Gas Calculations

### **Assumptions**

- Typical natural gas makeup assumptions:

Methane (CH4) ~ 95%

Ethane (C2H6)	}	~5% combined
Propane (C3H8)		
n-Butane (C4H10)		
Carbon Dioxide (CO2)		
Nitrogen (N)		

Sulfur (S)

- Due to variations in natural gas makeup (above), take conservative approach and only use
- methane to calculate water vapor production, although ethane (C2H6), propane (C3H8) and nbutane
- (C4H10) when combusted will also produce water vapor.
- Balanced Equation for Methane Combustion: **CH4 + 2O2 → CO2 + 2H2O**
- Assume normal temperature and pressure (68°F and 1 atm)
- Volume of 1 mole of CH4 at 68°F is 0.0026 lb mole/ft<sup>3</sup>
- Molecular weight of water is 18 lb/lb mole
- Liquid water density at 68°F is 8.33 lbs/gallon

### **Calculations**

**Step One:** Determine how much methane is in one million cubic feet (MMCF) of natural gas:

$$1,000,000 \text{ cu-ft of natural gas} \times 0.95 \text{ (methane component)} = 950,000 \text{ cu-ft of CH4}$$

**Step Two:** Determine the number of pound mol of CH4 using the assumption above for the volume of one mole of CH4.

$$2. 950,000 \text{ cu-ft of CH4} \times (0.0026 \text{ lb mol CH4 / ft}^3 \text{ of CH4}) = 2,470 \text{ lb mol CH4}$$

**Step Three:** Using the balanced equation above, determine how many pounds of mols of water vapor are produced in the combustion process.

$$3. 2,470 \text{ lb mol CH4} \times (2 \text{ lb mol H2O / 1 lb mol CH4}) = 4,940 \text{ lb mol H2O}$$

**Step Four:** Using the molecular weight of water, determine how many pounds of water vapor are reproduced in the combustion process.

$$4. 4,940 \text{ lb mol H}_2\text{O} \times (18 \text{ lb H}_2\text{O}/1 \text{ lb mol H}_2\text{O}) = 88,920 \text{ lb H}_2\text{O}$$

**Step Five:** Using the liquid water density, determine the volume of water vapor produced.

$$5. 88,920 \text{ lb H}_2\text{O} \times (1 \text{ gal H}_2\text{O}/8.33 \text{ lb H}_2\text{O}) = \mathbf{10,675 \text{ gals H}_2\text{O (as vapor) per MMCF}}$$

*Note: Not all natural gas that is consumed is combusted. According to a 1995 DOE Topical Report on "Economic Evaluation and Market Analysis for Natural Gas Utilization," approximately 3.5% (relatively negligible) of natural gas is used as feedstock for ammonia, methanol, ethylene and hydrogen production.*

## References

Chesapeake Energy. 2010b. Operational Data.

Chesapeake Energy. 2010c. Investor Presentation.

<http://www.chk.com/Investors/Pages/Presentation.aspx>

Chesapeake Energy. 2010d. Operational Experience.

USDOE, 1995. U.S. Department of Energy: Economic Evaluation and Market Analysis for Natural Gas Utilization – Topical Report – 1995.

<http://www.osti.gov/bridge/purl.cover.jsp?purl=/211345-iEUh0M/webviewable/>

# A Water Chemistry Perspective on Flowback Reuse with Several Case Studies

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## Summary

Operators have tested the feasibility of using frac flowback water that has received only a minimum level of treatment. Successful fracture operations have been reported using frac solutions with total dissolved solids (TDS) in excess of 50,000 mg/l.

Any discussion on reuse must emphasize the differences between the North American (Western Canada, Eastern Canada, Eastern USA, and Southern USA) shale gas formations and differences between locations in the same formation make reuse decisions and logistics site specific. Operations must be conducted in compliance with applicable local laws and regulations.

This abstract discusses the reuse of frac flowback from a water chemistry perspective. Two examples of flowback reuse, where a minimal water treatment has been used, describe the rationale for why the practice is considered acceptable. Associated logistics considerations are also presented.

## Introduction

Hydraulic fracturing is essential to the production of natural gas from tight shale. Fracture fluids are predominantly a water and sand mixture with a small percentage of other chemicals with specific functions. Fracturing requires high pressure. Friction reducers are used to decrease the frictional force in the pumped water allowing the pumping pressure to reach the formation. A mild acid prepares the stimulated area to accept the fracture treatment, biocide kills any bacteria collected in the water prior to pumping, scale inhibitors prevent mineral buildup from the water produced from the well, and corrosion inhibitors are added to protect equipment. Breakers to reduce the viscosity of friction reducers, clay stabilizers, and surfactants might also be used.

Approximately 10% to 50% of the water used for hydraulic fracturing may be returned quickly to the surface as frac flowback. Reuse of frac flowback has multiple benefits:

- Reduces demand for fresh water
- Reduces water disposed
- Reduces truck hauling to offsite disposal

### **Frac Flowback Reuse by Creating Near Fresh Water Quality**

Until recently it was believed that near fresh quality water, or water with most metals and hardness removed, was required for use in fracturing fluid. Historically, most shale gas fracture flowback was disposed of by deep well injection. Deep injection wells are not always available and offsite disposal costs can be quite large relative to other water related costs.

Various technologies have been proposed to achieve near fresh quality standards by removing suspended solids, heavy metals, hardness, organics, and dissolved solids. In some cases, a relaxed requirement of specifying only the removal of heavy metals and hardness was considered acceptable.

These technologies are usually expensive, add operational complexity, increase environmental and safety risks, and generate by-products which require disposal in compliance with applicable laws and regulations.

There are clear advantages to reuse of frac flowback which requires only a minimum amount of treatment for removing suspended or dissolved solids. Several operators, including Talisman Energy, are routinely using frac flowback which has had a minimum amount of treatment.

### **Talisman Energy USA Goals for Flowback Reuse**

Data collected from recent drilling in the Marcellus shale formations by Talisman Energy indicates initial flowback ranging between 10% and 25% of the injected volume. The initial flowback has lower dissolved solids than later flowback. The maximum concentration of Total Dissolved Solids (TDS) in the blended flowback is less than 200,000 mg/l. To consistently reuse virtually all of the flowback by blending with fresh water, frac fluids need to function effectively with a maximum TDS of 50,000 mg/l.

### **Water Chemistry Perspective on the Water Quality Requirements for Frac Flowback Reuse**

The typical constituents in shale gas frac flowback water have been identified through various sampling programs. While the relative proportions of these constituents vary depending on the formation, there are some consistencies in the types of constituents present. Typically, the range of Total Dissolved Solids (TDS) is between 25,000 mg/l to 250,000 mg/l. The constituents which might impact the performance of the chemical additives to a frac fluid or impact the formation include:

- Suspended Solids – fine clay (could also include biosolids)
- Organics – both added and naturally occurring
- Scaling ions – barium, strontium, calcium, and magnesium along with alkalinity and sulfates
- Chlorides and oxygen – accelerate corrosion
- Residual friction reducers – interfere with constituents in the frac fluid
- Microbes – souring of the formation and microbiologically enhanced corrosion

The recommended functional performance considerations for reuse are:

- Friction reducer effectiveness
- Scale formation
- Microbiology control
- Corrosion
- Breaker
- Clay stabilization
- Long term impact on formation

Friction reducers with salinity tolerance of 90,000 mg/l or more have been advertised by several companies. Friction loop tests were performed for Talisman Energy and the acceptability of using a blend of flowback and fresh water with a TDS of 50,000 mg/l was demonstrated. Talisman's service providers were confident that the other functions could also be addressed. The two functional performance considerations which generated the most discussion were suspended solids and scale control.

Two case studies -- one for suspended solids and one for scale control -- are discussed below.

### **Water Chemistry Perspective; Case Study 1 - Suspended Solids**

The recommendation for water used to prepare frac fluids is that it should be substantially free of suspended solids. There are various specifications to define what total amount of suspended solids and what particle size range meet the expectation of substantially free.

Talisman Energy conducted filtration of flowback tests for removing suspended solids but commonly experienced filter plugging. Thus the requirement to filter the flowback created an obstacle to reuse.

All of Talisman Energy's fracture operations include flowback storage. Application of Stoke's law to the various storage configurations suggested that under ideal conditions all particles greater than 30 micron in diameter would be removed from the frac flowback.

Samples were collected from several frac operations to determine the effectiveness of unaided gravity settling in flowback tanks whose primary purpose is surge control and storage.

- Slide 7 shows the sampling arrangement and the location of the filter recommended by water treatment companies.
- An investigation was made to compare a Stoke's law prediction to actual removal. The prediction indicated that under ideal conditions solids > 30 microns would be removed. It was understood that particle size and inlet/outlet configuration of the tanks were not ideal.
- Slides 8 and 9 show the particle size distribution of suspended solids before and after flowback holding tanks. The inlet and outlet of the surge and holding tanks were arranged to facilitate site set-up, not suspended solids removal, and the configuration was not ideal for settling. As a result, suspended solids removal was less than predicted. Side 10 summarizes the solids distribution before and after the holding tanks.

- Slide 11 show that most of the sand and clays are removed by settling, leaving primarily barite.
- Slide 12 shows the configuration of tanks to achieve performance which is closer to what is predicted by Stoke's law.
- The reuse of flowback with 50 mg/l or less of suspended solids, with a particle size range of greater than 30 microns and less than 100 microns, has not had a noticeable effect on well performance. No long term studies have been made.
- Talisman Energy has not observed interference from biomass.

Settled solids are periodically removed from the tanks by vacuum trucks and disposed in licensed landfills in compliance with applicable laws and regulations.

### **Water Chemistry Perspective Case; Study 2 – Scale Control**

The scaling potential of barium, calcium, and iron with sulfate and carbonate ions has been discussed at length in the literature and there are both ongoing and new studies. There are many public and proprietary computer programs available to calculate scaling potential.

For the purpose of this case study a flowback chemistry for Northeast Central Pennsylvania chemistry is presented in Slide 14.

Slide 15 highlights that the chemistry is a high ionic strength, chloride based system with very high concentrations of the scale forming cations and very low concentrations of sulfate and carbonate.

When the ions are matched with each other the extent to which the salts are chloride based becomes more clear (refer to Slide 16).

Slide 17 shows the extent to which ionic strength has an impact on the total and relative solubility of salts.

It was recommended to Talisman Energy that metals and hardness be removed from the flowback before reuse. The open literature has examples of similar recommendations. Due to the high concentration of barium, strontium, calcium, and magnesium large amounts of sodium sulfate, soda ash, and lime are required.

In many cases the source of sulfate and carbonate alkalinity is the fresh make-up water. Since the high concentration of scaling cations are in the formation, it is best to remove the sulfate and carbonate alkalinity from the frac fluid before injection.

An alternative is to settle out the gross suspended solids, as described in Case 1 and then take advantage of the remaining barium sulfate “seeds” to quickly de-supersaturate sulfate. The chemistry of this approach is well established (refer to Slide 20). There are also literature references to co-precipitation of other scaling salts on seed crystals.

Talisman has reused flowback with only settling and no chemical addition for metals and hardness reduction for blend TDS of approximately 50,000 mg/l with no apparent negative impact on the formation or gas production.

Several hypotheses have been put forth for why blending of flowback and fresh water might be effective at reduced scaling potential of the blend:

- Iron is likely oxidized and precipitated as Fe(OH)<sub>3</sub> in surface tanks
- Reduction in ionic strength reduces BaSO<sub>4</sub> solubility by 50%. SO<sub>4</sub> from surface water reacts with excess Ba and likely precipitates on seeds
- Some CaCO<sub>3</sub> and SrCO<sub>3</sub> precipitation will occur. However, at this time scale control is indicated because of inverse solubility with respect to temperature and lack of definite information on co-precipitation

There are questions about the impact of flowback reuse on the formation:

- The presence of barite “seeds” should reduce down hole and formation scaling due to preferential precipitation on the seeds
- Caution is recommended for formations with soluble sulfate. However, barite “seeds” might be useful in such situations
- In principle, fewer salts should be solubilized from the formation with higher TDS frac fluid
- The impact of increased frac fluid density has not been investigated

### **Logistics Considerations for Frac Flowback Reuse**

There are differences between the North American (Western Canada, Eastern Canada, Eastern USA, and Southern USA) shale gas formations and differences between locations in the same formation. Reuse decisions and logistics will be site specific. Operations must be conducted in compliance with applicable local laws and regulations.

The logistics of transporting and handling flowback to minimize environmental and public health risks must take the following into consideration:

- Number of wells per pad - flowback reuse on multi-well (refer to Slide 24) pads reduces movement of flowback off the pad
- Timing - storage required to deal with when flowback is available and when it is required
- Variations in the amount of flowback – flowback ranges from 10% to 50% of the injected frac fluid, which impacts the choice and style of storage (refer to Slides 25 and 26)
- Location of fresh makeup
- Contiguity of leases

In general, reusing flowback on site with Multi-Well pads will reduce the amount of fresh water required at the pads and significantly reduce the movement of flowback from the pad.

# Shale Frac Sequential Flowback Analysis and Reuse Implications

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Water re-use challenges and solutions have direct and indirect influences in the design of hydraulic fracturing fluid systems and products used in High Volume, High Rate (HVHR) hydraulic fracturing of shale wells (1,2). In general, effectively engineered water reuse solutions should: provide effective fracture development, allow practical application and economic performance, be non-damaging to well production, extend microbiological control, minimize environmental impact and reduce environmental risk.

Until relatively recently, HVHR fracturing required the use of fresh water as the base fluid due to the sensitivity of polymeric friction reducers to high TDS waters and concerns that the interaction of the frac fluid constituents with the formation would result in adverse precipitation of geochemical mineral species often referred to as “scale”(3).

Significant lessons learned from early HVHR fracturing and flowback analysis from the Marcellus shale has led to the development of products that have a higher degree of compatibility with the inorganic constituents in flowback waters as well as better understanding of the impacts of recycled flowback water on well performance (1). In general, much higher salinity fluids are now used than during initial development. However, much still remains to be learned from geospatial variations both within the Marcellus and other shale plays (2).

Exploration into the geochemical variations and implications of high TDS flowback fluids for recycling and re-use in closed system fracturing applications is provided through ongoing flowback water analysis. To date, over 500 flowback samples obtained following HVHR fracturing operations have been catalogued. Sequential flowback studies involve time and volume dependent analysis of the flowback samples. The study presented includes results obtained from 25 sequential flowback studies representing discrete well site locations throughout the Marcellus shale play.

In this case study, flowback analysis locations trend from the northeast to the southwest. A number of significant trends are observed.

## TDS and Chloride Content

There is an exceptionally good correlation between chlorides and total dissolved solids (TDS) (i.e.,  $R^2 = 0.995$ ). This would be expected since chlorides are the predominant anion in flowback waters. TDS levels range from approximately 200 mg/L to nearly 145,000 mg/L and concentration increases with time and flowback volume. Regional distribution of the TDS levels

appear to vary significantly. Well sites representing a cross section of Marcellus region were from the following counties; 1) Susquehanna; 2) Jefferson; 3) Armstrong and 4) Fayette. The highest salinity (TDS) content appears in the Jefferson data with TDS approaching 145,000 mg/L. The lowest TDS levels were observed in Armstrong County with values reaching approximately 30,000 mg/L.

### **Hardness vs. Marcellus Flowback Volume by Region**

Total hardness, represented as  $\text{CaCO}_3$  shows a similar trend to the TDS on a distribution basis for each of the four regions. The significance of total hardness relates to both compatibility of the fracturing fluid chemical package and the geochemical propensity to precipitate potential production impairing minerals (3). The highest level of total hardness is represented in the Jefferson data set with values exceeding 30,000 mg/L in the late stage flowback.

### **Barium Content vs. Marcellus Flowback Volume by Region**

Barium content is of particular interest during reuse due to the susceptibility of barium to form barium scales such as barium sulfate. Barium trends in the sequential flowback data show three primary geospatial signatures. In the Fayette and Armstrong signatures, very little barium is observed. In the Jefferson trend, barium levels are relatively low (approximately 50 to 400 mg/L) up to approximately 7,000 bbls recovered after which the levels rise to approximately 1,700 mg/L. The Susquehanna trend curve shows a relatively constant linear trend showing higher early uptake.

### **Geospatial Variation of Flowback Geochemistry**

Correlation of water geochemistry to physical location (both latitude and longitude) provides insight into the potential to predict key water chemistry values for geochemical simulation purposes. One example is illustrated in the calcium trend versus longitude and latitude. With the exception of one anomalous point, when compared on a fixed volume basis, it appears that calcium content increases from west to east. However, there appears to be some very high brine content wells in the mid-state region. Such information can be utilized as a predictive tool in planning development of future well sites, with improved water management strategies, better scale prediction and more convergent reuse strategy.

### **Post-Frac Water Load Recovery**

Load recovery following fracturing operations is a key aspect of any water reuse program since the load recovery volumes may vary across operating locations and the amount of water that can be recycled is dependent upon the final water chemistry. In many cases, significant dilution of flowback water with fresh water is applied to new completions. However, reuse consisting of 100% flowback water with no fresh water dilution is possible when augmented with treatment<sup>4</sup> to remove all or a portion of the detrimental constituents. The load recovery from selected well sites indicates a range from less than 10% to nearly 60%. The dataset includes both vertical and horizontal wells. Geospatial variation shows weak, but positive correlation to latitude and longitude with the higher load recovery percentages occurring in the southern operating regions.

## **Geochemistry and Source of Salts**

Interaction between shale and fracturing fluids has been the subject of a number of studies (1, 3, 5, 6). Providing both a predictive method and preventative measure to controlling geochemical precipitates, scale, microbially induced deposits and other rock/fluid interactions is important for enabling sustained reuse of flowback waters and for optimization of production performance. A geochemical simulation method has been developed to help predict potential mineral species that have a tendency to form insitu based on inputs from flowback water analyses<sup>3</sup>. Based on a study conducted to address the question of the origin of salts observed in the Marcellus shale flowbacks, the authors present hypotheses regarding the origin of dissolved salts observed in the flowback waters (1). Geologic interpretation of the genesis of shale basins such as the Marcellus provides insights into the origin of the salts. Potential mechanisms for the observed salinity in the flowbacks include:

1. Primary dissolution of Autochthonous salt
2. Primary dissolution of Allochthonous salt
3. Encroachment of Basinal brines
4. Mobilization of Hypersaline connate fluids
5. A combination of the above

Experiments using drilled cuttings and cores show some evidence for the Autochthonous origin. In summary, it cannot be assumed that observed flowback geochemistry is simply due to “fracturing” into brine water within subjacent wet formations, as previously assumed. Piper analysis appears to be a potentially useful tool for characterizing the water “genetics” and determining pathways for mixing with various compositions of water types. Additional work is suggested in this area including “water fingerprinting”.

Comparison of Marcellus flowback geochemical results with limited studies from other shale plays such as the Haynesville appears to show similar trends regarding soluble salts. In one study, Haynesville flowback waters show higher levels of TDS than observed in the Marcellus study with values exceeding 120,000 mg/L after 7,500 bbls flowback volume. These flowback waters also show higher initial salt uptake.

## **Reuse Implications**

Water reuse has been enabled and is now a reality for HVHR shale fracturing operations in a wide range of geologic settings. Insights obtained from analysis of flowback waters provide a basis for chemical additive package design, treatment options, geochemical implication and environmental risk assessment. Inherent variations in downhole geochemistry and the equilibration of injected frac water with the subsurface rock environment provide a technical need for continued analysis of flowback waters. Analysis and interpretation of the geospatial variation of inorganic dissolved species can provide a basis for future prediction of geochemical composition anticipated in new development areas. Such prediction could enable better planning, development of water management strategies and hydraulic fracturing fluid design.

## References

1. Blauch, et. Al., 2009. Marcellus Shale Post-frac Flowback Waters – Where is All the Salt Coming from and What are the Implications?. Presented at the SPE Eastern Regional Meeting held in Charleston, West Virginia, USA, 23-25 September, 2009.
2. Houston, et. Al., “Fracture-stimulation in the Marcellus Shale: Lessons learned in fluid selection and execution,” SPE 125987 presented at the SPE Eastern Regional Meeting, Charleston, W.V., Sept. 23-25, 2009.
3. Blauch, 2010. Geochemical fixes boost shale completion efficiency. World Oil, July 2010, pp. D121-D124.
4. Papso, J., et. Al., 2010. Gas Well Treated with 100% reused Frac Fluid. August 2010, Harts E&P.
5. Lash, Gary G. 2009. Overview of the Tectonic and Eustatic Framework of Yager, Kappel, and Plummer. Devonian Black Shale, Appalachian Basin. Presented at the SPE Cooperstown Applied Technology Workshop, Cooperstown, New York.
6. Dresel, P.E. 1985. The Geochemistry of Oilfield Brines From Western Pennsylvania. MS Thesis, The Pennsylvania State University Department of Geochemistry and Mineralogy.

# Characterization of Marcellus Shale and Barnett Shale Flowback Waters and Technology Development for Water Reuse

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The Barnett and Appalachian Shales are among the largest and most active natural gas plays in the U.S. that geographically covers all or part of 20 counties in North Texas and large areas of Pennsylvania and West Virginia. The Barnett area is proven to have approximately 2.5 trillion cubic feet ( $59 \text{ km}^3$ ) of natural gas reserves and is widely estimated to contain up to 27 trillion cubic feet ( $700 \text{ km}^3$ ) of technically recoverable natural gas (USGS, 2004; Clouser, 2006). The Marcellus Play of the Appalachian Shale Region is considered to be larger in size and capacity in comparison to the Barnett. Both shale plays are considered to be unconventional gas formations; each of these plays depend upon the economical utilization and environmentally-responsible management of large volumes of water for continued sustainable development.

Hydraulic fracturing (fracing) is a necessary step for initiating economical well performance, requiring between 1 and 4 million gallons of water for successful well completion. Vertical wells require approximately 1 million gallons and horizontal wells require 3-4 million gallons according to Barnett Shale Producers. These per-well levels of water production also apply to the wells installed and completed in the Marcellus Shale. In both plays, horizontal wells comprise more than 90% of the total wells that are constructed. Of the total water used by the industry, completions using hydraulic fracturing represent more than 94% and drilling represents 5% as seen in Slide 6 (Galusky, 2007). During years when more than 2,000 wells are constructed in a shale gas play, approximately 2 billion gallons will be used for new completions. This level of water demand poses a number of challenges for industry in the course of developing the Barnett and Appalachian Shales for natural gas production. In recognition of this need, the natural gas industry has supported efforts to characterize flowback water and evaluate water reuse approaches that significantly reduce freshwater demand while providing environmentally acceptable options for flowback water management.

## Flowback Water Characteristics

Effective management of flowback water requires some level of knowledge of the characteristics of the water; a breakdown of categories of constituents found in many flowback and produced waters is depicted in Slide 8. Flowback water contains salts, metals and organic compounds from the formation as well as many of the compounds that were introduced as additives to the influent stream. Discussions between the industry and regulatory agencies of Pennsylvania and West Virginia have pointed to the need for an information base on the composition and properties of flowback water and on the influent water streams that are used

to perform frac jobs. The objective of this effort was to conduct the initial sampling and analysis of water streams associated with shale gas development in the Marcellus Shale.

In recognition of the importance of this effort, 17 member companies of the Marcellus Shale Coalition (MSC) volunteered 19 locations where shale gas wells were scheduled to be hydraulically fractured. The Field Sampling and Analysis Plan and the Quality Assurance Project Plan were developed, reviewed, and finalized for the effort by the companies of the Appalachian Shale Water Conservation and Management Committee (ASWCMC), PA-DEP and WV-DEP. At each of the host sites, samples of influent water streams at Day 0 and the flowback water streams at 1, 5, 14, and 90 days following the frac job event were collected by a single engineering subcontractor, URS. All samples were sent to Test America (a PA-DEP certified environmental testing laboratory) for analysis. The list of constituents recommended for the characterization study was developed from comments received from the PADEP, the WVDEP and members of the Appalachian Shale Water Conservation and Management Committee (ASWCMC). Categories of determinations that were conducted included: 1) General Chemistry, 2) Organic Compounds, and, 3) Metals. Once reviewed and qualified, data from these analyses were organized and tabulated in a source blind manner into an Excel spreadsheet that currently represents the information base.

Results from this effort indicate that values for pH, alkalinity, total dissolved solids, total organic carbon, oils and greases and other parameters from general water characterization are within the normal ranges reported for conventional produced waters by the USGS. General characteristics of Marcellus Shale waters (influent and 5-day flowback) are shown in Slide 13. Comparisons of characteristics of 14-day flowback waters with conventional produced waters are shown in Slide 14. Flowback water concentrations of total dissolved solids ranged from 3,000 to 260,000 mg/l; typical profiles show an increase in total dissolved solids in flowback water with time following a frac job event (as shown in Slides 16-18). Anions and cations of influent and 5-day flowback water are shown in Slide 15; as with conventional produced water, shale gas flowback water cations are dominated by sodium and calcium; the main anion is chloride.

Metals normally seen in conventional produced waters, such as iron, calcium, magnesium, and boron, are at levels in flowback waters that are well within known ranges for normal produced waters. Heavy metals that are of concern in urban industrial wastewaters and POTW sludges --- such as chromium, copper, nickel, zinc, cadmium, lead, arsenic and mercury --- are at very low levels in flowback and produced waters (as shown in Slide 34).

Among volatile organic constituents, more than 93% of all constituent determinations were at non-detectable levels and less than 1% of the determinations (mainly volatile constituents that are a natural part of formation waters) were above 1 ppm (as shown in Slide 23). Virtually all man-made halogenated solvents were at non-detect levels; volatile constituents that are measureable, are those that are normally found in conventional produced waters.

Regarding semivolatile organic constituents, more than 96% of all determinations were at nondetectable levels and less than 0.1% of all constituents were above 1 ppm; the remainder of

constituents were at low trace levels – usually below 10 ppb (as seen in Slide 27). All chlorinated pesticides, organophosphorus pesticides and polychlorinated biphenyls in all samples were determined to be at non-detect levels. The results of this shale gas water characterization effort indicate that all pesticides, PCBs, and a large fraction of the volatile and semivolatile constituents should be considered to be unnecessary for the sampling and analysis of flowback waters in the future.

Recently, characterization of shale gas waters has been completed for five locations in the Barnett using the same procedures employed in the Marcellus Shale Project; general characteristics of the 5-day flowback waters are compared between the two plays. For the limited number of sites sampled, the Barnett Shale waters appear to be significantly lower in total dissolved solids -- about half of the TDS levels of the Marcellus Shale waters that range from 38,000 to 238,000 mg/l TDS. Alkalinites of the Barnett waters at 238 to 1630 mg/l (as CaCO<sub>3</sub>) are relatively higher than the Marcellus waters -- perhaps four times higher -- due to the greater presence of bicarbonate concentrations in the Barnett waters. Marcellus shale water, however, showed significantly higher levels of TOC than Barnett waters though most samples from both plays had TOC levels below 70 mg/l (modest TOC levels).

### **Water Reuse Technology Evaluations and Development**

Information on water flows in the shale gas industry indicate that although each well completion represents a potential significant flowback water output equivalent to 5-35% of the influent water, it is also true that future hydraulic fractures represent substantial opportunities for the reuse of these waters, especially during the growth phase of each shale gas development area. The median flowback water volume collected from 19 locations in the Marcellus Shale was approximately 24 percent of the influent water volumes used for each completion operation.

Predominantly, the industry prefers to dispose of flowback and produced waters using Class II deep well injection if such disposal capacity is locally available and economically accessible. In areas of the U.S. where Class II wells are sparse (the Marcellus Shale has only 7 Class II wells which represents a very low capacity to accept produced waters and flowback), water reuse has been a logical alternative to pursue as is done in the Pennsylvania portion of the Marcellus Shale. In areas of the U.S. where severe limitations of water availability can arise from frequent occurrences of drought, shale gas developers have considered water reuse as a means of significantly reducing demands on sources of fresh water that compete with community water supplies.

Where flowback and produced water reuse are being pursued aggressively, there are mainly two schools of thought that exist in the shale gas industry. Approach A is comprised of conditioning the brines for the removal of suspended solids, oils and greases, bacteria, and scale forming ions (i.e. constituents that potentially interfere with equipment and infrastructure maintenance) with no demineralization (desalination) prior to reuse. Currently, this approach is being used within the Marcellus Shale as the predominant shale gas water management practice. A more rigorous treatment ("Approach B") is comprised of treating shale gas water all

the way to the recovery of distilled or demineralized water with the concomitant generation of a small volume of concentrated brine; this rigorous treatment approach is usually capable of recovering demineralized water equivalent to 70-80% of the original flowback/produced water stream. A general flowsheet that encompasses water reuse options available to the industry are shown in Slides 40-42.

Since 2005, the shale gas developers have evaluated a number of processes capable of demineralization and brine volume reductions. The most capable demineralization approach that has been demonstrated in the treatment of shale gas waters -- in terms of reliability and performance -- is the mechanical vapor recompression thermal distillation (MVR) process. This process is capable of handling a very wide range of brines (from less than 10,000 mg/l to more than 120,000 mg/l TDS) while achieving over 70 percent efficiencies in water recovery. This process is commercially applied to shale gas water stream management in the Barnett and in some shale gas fields of the Western U.S. Another demineralization process that has been tested on shale gas waters in the field is reverse osmosis (RO), though to a much lesser extent than the MVR process. Tests with RO on shale gas waters have verified the ability of the process to recover about 60% of highly demineralized water as long as the influent water did not exceed 40,000 mg/l of TDS. Photos of MVR and RO field demonstration units (located in the Barnett Shale) are shown in Slides 43 and 44. Demineralization with either process comes with a significant cost that must be evaluated and understood to achieve effective deployment. In the shale gas industry, demonstrations involving both processes are continuing.

# Mid-Continent Water Management for Stimulation Operations

## *The Case for Recycling Frac Water*

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### **Introduction**

Water use and management is critical to the petroleum industry. It is the most common and heavily used fluid in our 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 gas reservoirs of the Woodford Shale in the Arkoma 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.

### **The Life of a Barrel of Frac Water**

Source	Ground water for the Granite Wash Surface ponds built to store run off from rain for the Woodford Shale
Storage	Fresh water is stored in ponds or large pits Recycled water is stored in lined pits or frac tanks
Transfer to well for stimulation	Fresh water is pumped through aluminum irrigation or poly pipe to the well site Recycled water is either trucked to the well site or pumped through poly pipe Water is transferred from the storage facilities to the well being completed at up to 100 BPM
Fracturing operation	Halliburton, Schlumberger, BJ or other companies mix the water with proppant and other chemicals and pump it into the well
Flow back water	The flow back water is separated from any hydrocarbons at the well's test or production facilities and then pumped to a recycle pit for reuse or trucked to a processing facility for

clean up and 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 which is a conventional reservoir. Since 2001, Newfield has drilled over 150 vertical Granite Wash tight gas wells. Initially, frac pits were built at each well site. It soon became apparent that having central water supply pits was more economical and as the amount of water being used increased it made sense to begin recycling it. 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.

Fresh water is generally transported from the pits to the well being completed through 10" aluminum irrigation pipe. The recycled water is transported through 8" HDPE (high density polyethylene) pipe. Newfield owns 38 miles of 8" poly and 10 miles of 4" poly to move water from pit to pit and from the pits to the wells being stimulated. Generally three or four lines are used to deliver water from the frac pits to the well being completed. Once the completion is finished and the well is being flowed back one poly line is left in place to pump the water back to the pit. The company 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 17,000 mg/l) and is relatively clean. Any solids produced with the water drop out in the flow back pits. By reusing the water Newfield saves over \$8 million per year in reduced requirement for potassium chloride and another \$1 million a year in 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 flow back water so once the entire load is recovered the produced water must be trucked 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.

Each of the recycle pits is permitted by the Texas Railroad Commission. They 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 frac 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 produced 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 with the average initial production of 17 MMCFD with much lower decline rates than the vertical wells. As can be seen with these numbers, horizontal wells have substantially improved both the initial productivity and 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 frac 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 frac to recover the reserves efficiently. Based on the frac mapping, we have not been able to achieve the frac height desired. (As an aside, these attempts to intentionally increase the frac height have proven to us that in most cases getting more than 250 feet of height growth is very difficult. So if the probability of fracturing into a USDW zone more than 10,000 feet above the reservoirs we are stimulating is very low.)

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 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. It is also being copied by other operators in the area.

### **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 six years the lateral lengths have 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.

Fracturing volumes on the vertical wells was generally small (less than 10,000 bbl) and could be done from frac 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.

As the horizontal play developed Newfield build over 60 fresh water ponds to collect run off from rain water. The ponds ranged in size from 50,000 to over 750,000 bbls with a total capacity of over 8 million barrels. Fresh water is transferred from the pond to the well sites through 10" aluminum irrigation pipe. In cases where there is not enough fresh water in one pond they may 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 frac operations. Recycled high chloride water is trucked from our Ecosphere water treatment facility to the well site where it is stored in frac tanks. Fresh water is then mixed with the recycled water through the frac blender to make an equivalent of 1 percent chloride water.

Ecosphere is a technology Newfield uses to clean up its recycled high chloride water for use as a potassium chloride substitute. The technology is provided by Ecosphere Energy Services LLC which uses ozone to oxidize hydrocarbons, residual chemicals and heavy metals. 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 saves over \$13 million per year in reduced chemical usage by using Ecosphere to clean up its recycled water.

Once the completion is finished and the well is flowing back, the produced water is 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 is stored in in frac tanks until it is needed. At this time only six percent of the frac water is recycled.

Newfield is working on locating a place for recycle pits and being able to use higher chloride water as a frac fluid so that more water can be recycled.

## **Conclusion**

Newfield's Granite Wash operation is a prime example of where recycling frac water is environmentally responsible and makes the company money at the same time. This is a win-win for the landowners, the community, and the company.

## Toolbox Available to Treat Flowback and Produced Waters

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Increased demands on freshwater sources, stricter local legislation on the use of municipal waters in industry, and the unpredictability of drought conditions all conspire to make the use of non-freshwater-based stimulation technologies, as well as the ability to recycle flowback and produced waters an important objective in today's oilfield. The advantages of using these non-freshwater sources include the reduction or elimination of disposal costs and the environmental benefit gained by recycling non-freshwater sources (as opposed to the large-scale consumption of freshwater required by current technologies). Water produced from the formation (produced water), as well as treatment flowback water, is becoming more costly for disposal due to increasing trucking costs and disposal fees and hence, the demands for water conditioning and reuse have increased dramatically this past decade. Furthermore, the complexity of global water management is significantly magnified when contemplating the local challenges concerned with government regulations, water volumes, water quality, and the like.

Conventional means of waste water regeneration include, for example, water softening, distillation, ion exchange, reverse osmosis (RO), ozonation, and a wide range of filtration technologies. Flowback and produced water vary in composition tremendously depending on several factors, including location of the formation, chemicals used during stimulation, and age of the well. Total Dissolved Solids (TDS) vary tremendously and can reach up to saturation levels (around 300,000 mg/L). In addition, the water can contain a variety of different salts, making one field's water very different from the next. This variability makes no "one-treatment method" suitable for all waters. For example, during distillation of salt water, the amount of distilled water generated depends on how much salt is in the water; in other words, the overall throughput decreases with increasing salt content. The cost effectiveness decreases with increased salt concentration and is hence not cost effective for produced waters very high in salt.

When deciding between water treatment methods to treat flowback and produced waters, it is important to consider the end use and its specific requirements, as well as composition of the water. With water treatment processes, the cost of treatment chemicals, type of equipment, and maintenance of the equipment, ease of process mobility, personnel, and disposal of treatment waste should all be considered, and as the end use and incoming water quality will vary, the treatment processes have to be selected accordingly.

# A Closed Loop System Using a Brine Reservoir to Replace Fresh Water as the Frac Fluid Source

*Minimization of Fresh Water Use: The Use and Reuse of 35,000 ppm Brine from a Dedicated Deep Reservoir as a Fracture Fluid for Shale*

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A non-fresh water source has been proposed and tested in the laboratory and field for application as a fracturing fluid in shale gas formations, with potential to replace a very high percentage of the fresh water used in the Encana and Apache area of the Horn River Basin in British Columbia, Canada (Pond, 2010; DeMong, 2011). The water source is the Debolt formation, which overlies the Horn River Play gas zones by several thousand feet. The Debolt formation in the EnCana/Apache area of the Horn River Basin contains a moderately saline water (35,000 ppm TDS), in a high strength, high permeability rock matrix capable of supplying thousands of barrels of water per hour. The intent of the project is to sharply reduce the amount of fresh water used in fracturing and to form a closed loop system that will reduce storage of water at the surface. Additional benefits include reduction of air emissions (pumps and heaters), reduction in chemicals (oxygen scavengers and biocides) and overall reduction in surface pipe lines and truck traffic. The project equipment involves dedicated water supply wells, large electric submersible pumps (ESP), a stand-alone water treating plant (to remove hydrogen sulfide gas ( $H_2S$ )), and equipment to recover the after-frac produced water from the wells and reinject the fluids into the Debolt formation.

Shale gas developments in North America have centered on using fresh water as a fracturing base fluid since about year 2000, when the C.W. Slay well in the Barnett shale was refractured after foam fracture treatment and gelled fracture treatments were found to be expensive and created substandard well performance (Steinsberger, 2009; Grieser, 2003; Palisch, 2008; Schein, 2004; Arthur, 2009). The slick water re-fracture on this well (slick water contains 0.25 gallons of polyacrylamide polymer friction reducer per 1000 gallons of water, plus smaller amounts of scale inhibitor, biocide and oxygen scavenger (Authur, 2009)) provided gas rates above even the initial rates from the well when it was first stimulated in 1983. The ability of slick water fracturing to enhance the productivity of shale well from the unfractured initial flows of 0 to less than 100 scf/d, to fracture stimulated average initial flows of 1,000,000 to 10,000,000+ scf/d, has been shown to be controlled by penetration of the low viscosity water (water at 0.6 to 1.0 centipoises) into the natural fractures of the shales, providing ability for the increasing pressure to widen the natural fractures, opening up flow paths to the natural gas trapped within the shale. Previous fracture fluids were less effective in the shales due to higher viscosity preventing fluids from invading and opening the natural fracture systems and the high

cost of gelled and foam fracturing fluids with accompanying large amounts of expensive additives. Well performance has been directly linked to larger amounts of water, larger amounts of proppant and higher injection rates (Coulter, 2004; 2006, King 2008, 2010).

Objections to fresh water use for hydraulic fracturing have risen in several places and, while the quantity of fresh water is lower in these shale developments than many local industries, agriculture and municipal uses, the returning water is often highly saline, making water recovery to the fresh water supply more technologically difficult (Gaudlip, 2008; Blauch, 2009).

This presentation focuses on a joint project by EnCana and Apache to use the moderately saline water from the Debolt formation as a primary source for fracturing fluid for the Horn River Basin (HRB) Shales in the northern British Columbia (BC) Province of Canada. The pilot projects and initial fracturing operations from multi-well pads in the HRB area was accomplished with fresh water from municipal water sources and finally from the local lakes within the guidelines set up by the BC Oil and Gas Commission (OGC). For larger scale operations, the companies sought a source of water that was more stable and less environmentally intrusive, settling on the Debolt formation brine.

Laboratory testing (Pond, 2010) identified the water treatment necessary to address H<sub>2</sub>S (60 to 80 ppm in water phase and up to a few thousand in the water vapor phase) and several other considerations. The following chart from SPE 138222 summarizes the EnCana work.

*Table 5. Source: SPE 138222*

Method	Justification
Maintain high pH	Safety - potential release of H <sub>2</sub> S if pH is lowered
pH buffering	Required for H <sub>2</sub> S equilibrium
Downhole separation	Compatibility with wellbore
Stimulation of nitrate-reducing bacteria	Questionable effectiveness - source of H <sub>2</sub> S not known
Biocides to kill sulfate-reducing bacteria	Questionable effectiveness - source of H <sub>2</sub> S not known
Precipitation, coagulant, flocculent	Solids production - removal/disposal versus introduction into Horn River
Steam stripping	High energy requirement
Mechanical stripping	Option to scale up
CO <sub>2</sub> stripping	Cost - CO <sub>2</sub> not readily available
Gas stripping	Required to strip H <sub>2</sub> S from water
H <sub>2</sub> S scavenging chemicals	Required for final polishing

General water treating steps and rational behind the operation was as follows:

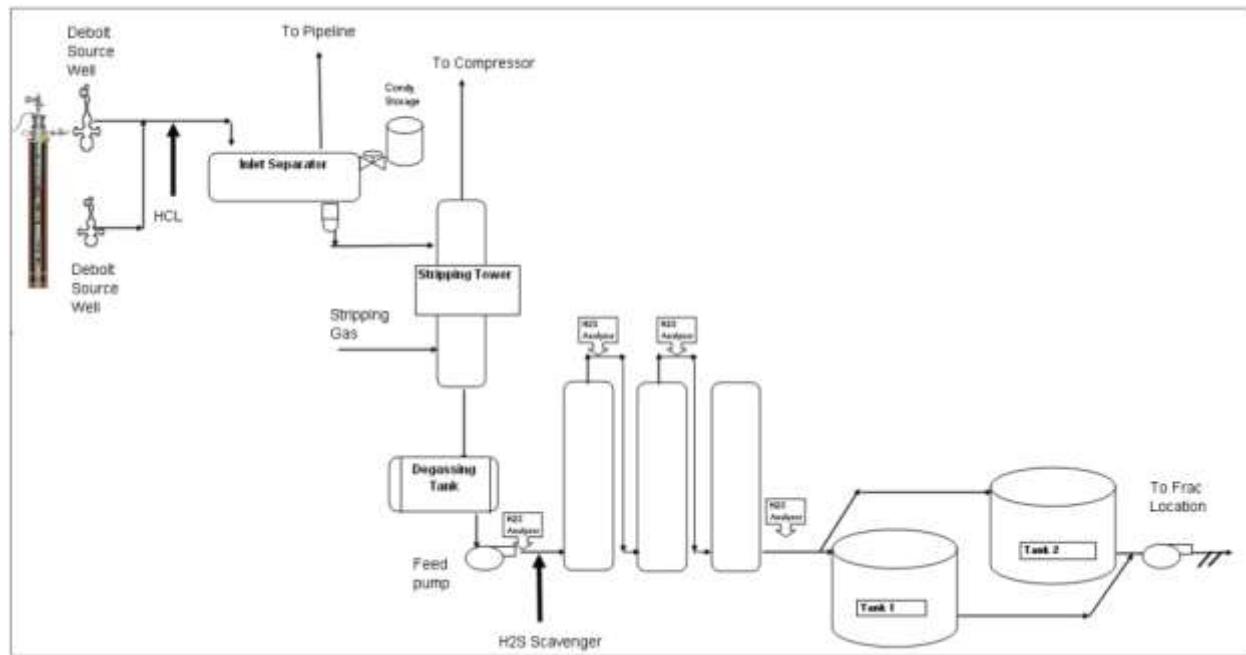
- Dilute HCl with corrosion inhibitor injected downstream of supply wellhead to lower pH and prevent scaling.
- Inject high pressure natural gas to strip H<sub>2</sub>S and CO<sub>2</sub>. Second step was low pressure gas stripping of water.

- Collect water in a tank and flash off gas and vapor for treatment and recovery or incineration.
- Monitoring water flow rate accomplished by inline measurement.
- Small storage of water was accomplished in positive pressure tanks with a propane atmosphere.
- Final “polishing” step with a chemical scavenger reduced H<sub>2</sub>S in the frac water to zero.

The process was brought to a commercial, high rate level with twenty-one total potential steps and optional steps (Table 6). The testing met objectives of 0 ppm H<sub>2</sub>S with no unfavorable by-products. Detailed water monitoring checked on bicarbonate concentrations, scale potential, barium concentration and iron sulfide content. Other testing on biocides, scale inhibitors and general shale impact of the Debolt water showed minimum impact. The salinity of the water did require re-engineering of some additives.

The Debolt water source is provided by two ESP pumped wells. Each ESP has an operating envelope in the range of 31,250 to 50,000 barrels per day (5000 to 8000 m<sup>3</sup>/d). The water treatment plant is designed for 100,000 barrels per day (16,000 m<sup>3</sup>/d), which is sufficient for 3 to 4 fracs per day.

*Table 6. The Debolt Process Flow Diagram (SPE 138222)*



There are two tanks, each with a volume of 9375 bbls (1500 m<sup>3</sup>) for storage of processed water (sweet). A frac spread may only draw from a full tank, eliminating the possibility of an upset in the treating system supplying out-of-spec water to the pumping equipment.

Post-frac produced water flow from the wells will be processed with a minimum of treatment except to remove solids and gas, and then re-injected into the Debolt formation. On-going studies will monitor both the supply and the disposal.

## Conclusions

- The Debolt water source is a regional sour aquifer with a TDS level unsuitable for either agriculture or drinking water.
- Use of the Debolt water required a series of tests focused on water treatment, formation interaction and disposal potential.
- Environmental impact improvements are seen in a number of areas:
  - Minimization of water heater emissions by using the hot water from the Debolt (approximately 140 °F/60 °C) instead of heating lake water to prevent freezing in the -20C operations.
  - Minimization of fresh water usage. Fresh water still used for surface drilling and cementing.
  - Possible reduction of biocides and elimination of several other chemicals by keeping oxygen out of the water.
  - Reduction of surface frac water storage to less than 5% of total needed
  - Reduction of surface pipe from lakes.
  - Reduction of truck traffic and roads by using the closed-loop system.

## References

- Arthur, J.D., Bohm, B., Coughlin, B.J., Layne, M.: "Evaluating Implications of Hydraulic Fracturing in Shale Gas Reservoirs," Paper SPE 121038, presented at the 2009 SPE Americas Environmental and Safety Conference, San Antonio, TX USA, 23-25 March.
- Arthur, J.D., Bohm, B, Cornue, D.: "Environmental Considerations of Modern Shale Developments," Paper SPE 122931, presented at 2009 SPE Annual Technical Meeting, New Orleans, LA, USA, 4-7 October.
- Blauch, M.E., Myers, R.R., Moore, T.R., Houston, N.A.: "Marcellus Shale Post-Frac Flowback Waters – Where is All the Salt Coming From and What are the Implications?," Paper SPE 125740, presented at the 2009 SPE Regional Meeting, Charleston, WVA, USA, 23-25 September.
- Coulter, G.R., Benton, E.G., Thomson, C.L.: "Water Fracs and Sand Quality: A Barnett Shale Example," Paper SPE 90891, presented at the 2004 SPE Annual Technical Conference and Exhibition, Houston, Sept 26-29.
- Coulter, G.R., Gross, B.C., Benton, E.G., Thomson, C.L.: "Barnett Shale Hybrid Fracs – One Operator's Design, Application and Results," Paper SPE 102063, presented at 2006 SPE Annual Technical Conference and Exhibition, San Antonio, TX, USA, 24-27 September.
- DeMong, K., Hands, R., Affleck, B.: "Advances in Efficiency in Horn River Shale Stimulation," SPE 140654, SPE Hydraulic Fracturing Technology Conference, 24-26 Jan 2011, The Woodlands, TX, USA.

- Ferguson, M.L.: Comparing Friction Reducers' Performance in Produced Water From Tight Gas Shales," SPE Technology Update, J.P.T., November 2009, pp 24-27.
- Gaudlip, A.W., Paugh, L.O., Hayes, T.D.: "Marcellus Water Management Challenges in Pennsylvania," Paper SPE 119898, presented at the 2008 SPE Shale Gas Production Conference, Ft. Worth, TX, USA, 16-18 November.
- Grieser, B, Hobbs, J., Hunter, J., Ables, J.: "The Rocket Science Behind Water Frac Design," Paper SPE 80933, presented at 2003 SPE Production Operations Symposium, OK City, OK, USA, 22-25 March.
- King, G. E.: "Thirty Years of Gas Shale Fracturing: What Have We Learned?", SPE 133456, SPE Annual Technical Meeting and Exhibition, Spet 20-22, 2010, Florence, Italy.
- King, G.E., Lee, R.M.: "Adsorption and Chlorination of Mutual Solvents Used in Acidizing," SPE Production Engineering, Cvol.3, No. 2, May 1988, pp 205-209.
- King, G.E., Warden, S.L.: "Introductory Work in Scale Inhibitor Squeeze Performance: Core Tests and Field Results,"Paper SPE 18485, presented at 1989 SPE International Symposium on Oilfield Chemistry, Houston, TX, USA, 8-10 February.
- Palisch, T.T., Vincent, M.C., Handren, P.T.: " Slickwater Fracturing-Food For Thought," Paper SPE115766, presented at 2008 SPE Annual Technical Meeting, Denver, CO, USA, 21-24 September.
- Pond, J., Zerbe, T., Odland, K.: "Horn River Frac: Past, Present, and Future," SPE 138222, 2010 Canadian Unconventional Resources & International Petroleum Conf., 19-21 October, Calgary, Alberta, Canada.
- Schein, G.: "The Application and Technology of Slickwater Fracturing," Distinguished Lecturer Presentation, SPE 108807, presented 2004-2005.
- Steinsberger, N.: "The Barnett Shale and the Evolution of North American Shale Plays," Presentation and Slides, presented at 2009 SPE GCS Westside Study Group.

## **Summary and Abstracts from Theme 3: Disposal Practices**

## ***Summary of Presentations from Theme 3: Disposal Practices***

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### ***Technical Presentations***

The first set of technical presentations in this theme addressed treatment technologies and processes prior to disposal.

**David Alleman**, ALL Consulting, described three potential options for managing produced water: deep injection, treatment and disposal via surface discharge or beneficial use, and reuse in HF activities. He explained that there are a number of treatment challenges including the variation in produced water characteristics, generally high TDS concentrations, makeup of the waste stream after treatment, and differences between treatment in the laboratory and in the field. He explained that the high TDS concentrations effectively limit the technologies that are capable of treating shale gas produced water for discharge to reverse osmosis and thermal distillation. He noted that while there are a number of vendors who offer such treatment technologies, only a few have demonstrated the capability to treat shale gas produced water, and, among those, most do not have facilities and experience in all of the active shale gas plays. Thus, the availability of effective treatment technologies in any given location is limited. ALL Consulting has developed a mixing and scale affinity model with DOE that allows operators to model the chemical reactions taking place downhole and identify potential scaling issues. He stated that this model has helped smaller operators in particular design the appropriate fracture fluid for their water base.

**Pei Xu**, Colorado School of Mines, presented on her research team's recent literature review and technical assessment of a number of different emerging treatment technologies for produced water. She stated that factors such as the particular water chemistry of the produced water and the pressure and thermal resources of the formation should be taken into account when selecting treatment technologies. She suggested that a good treatment technology should fulfill a number of requirements including low chemical and energy demand, flexibility, robustness, low maintenance, high rejection of contaminants, and high recovery.

The final set of technical presentations addressed disposal practices and potential impacts.

**Joseph Lee**, Pennsylvania Department of Environmental Protection, stressed that much more water monitoring is needed in Pennsylvania. He commented that there are a number of causes of water pollution in the state, including large numbers of coal mines and orphaned and abandoned extraction wells, but there has not yet been any evidence of HF directly impacting underground sources of drinking water (USDWs). He noted that it is known that surface and ground waters in the Marcellus Shale area are already stressed by the legacy of past mineral extraction. Mr. Lee concluded that Pennsylvania has recently updated state well construction

regulations and he emphasized that these and other oil and gas regulations are adequate to protect water resources.

**Andrew Havics**, pH2, LLC, presented a risk assessment of the chemicals present in pit fluids on site at drilling operations in Colorado. The selection of chemicals in the assessment was driven by what was present and the risk factors associated with fate and transport for those chemicals. Benzene, toluene, ethylbenzene, and xylene (BTEX) were the most important chemicals investigated. The study found that there was no significant risk to human health from these chemicals based on the potential for exposure. The presenter emphasized that, when conducting a similar assessment elsewhere, the local geologic and hydrogeologic conditions should be thoroughly characterized.

**Rick McCurdy**, Chesapeake Energy Corporation, presented an overview of the Underground Injection Control (UIC) program, outlining the different well classes and discussing the particulars of Class II injection wells. Of approximately 144,000 Class II wells in the United States, 80% are used for enhanced oil recovery and 20% are used for disposal. Brine disposal in Class II wells is safe and environmentally sound, and is the most economic solution in many areas. He stated in some areas, However, these benefits are offset by high transportation costs if a Class II disposal well is not located near drilling operations. In these cases, he commented that other options for disposal such as treatment and reuse may become more viable. He provided an example from Chesapeake, which has developed their reuse program (AquaRenew) in areas such as Pennsylvania where the local geology is not conducive to constructing Class II wells.

**Paul Ziemkiewicz**, West Virginia University, presented a study investigating the sources of TDS loads in the Monongahela River following the high loads measured in 2008. He explained that the major sources of TDS in the Monongahela watershed are coal mines (including acid mine drainage), coalbed methane wells, and wells in the Marcellus Shale. Brine from the Marcellus and mine water have different chemical signatures, with the Marcellus water dominated by sodium chloride and mine water by sodium sulfate. In the Youghiogheny River (a large tributary to the Monongahela), the study found that sodium chloride was much more dominant during the winter wet season and the average TDS increased greatly compared to the summer. The study did not find TDS concentrations over 500 mg/L since 2009. Dr. Ziemkiewicz noted that a mass balance approach can be useful for evaluating the effectiveness of TDS control options.

## ***Summary of Discussions Following Theme 3: Disposal Practices Presentations***

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*Emerging technologies literature review.* Dr. Xu clarified that for well-understood technologies, the research team was able to consider a variety of factors that affect the cost of the technology including chemical and energy demand and depreciation. For an assessment of a new technology, the team was only able to look at the cost of acquiring the technology. When assessing general water quality after treatment, they looked only at whole effluent toxicity. However, the research group did try to cover constituents of concern for beneficial use, and considered indirect potable water use as an option.

*Colorado pit fluids modeling study.* Mr. Havics clarified that his study found no difference in arsenic concentration between soil samples taken at the study sites and background soil concentrations obtained from USGS data. In addition to soil concentrations, he suggested that ground water concentrations of arsenic be measured at increasing pH, simulating the chemistry of the pit fluids. The presenter added that the concentration of arsenic found in the soil at the Colorado study sites was an order of magnitude lower than what would be considered a risk.

*Clarification on items in the other technical presentations.* The mixing model described by Mr. Alleman is based on USGS's PHREEQC model and is available to the public free of charge. Mr. Lee clarified that chloride and bromide ratios in the Monongahela study were also used to fingerprint the different brines in the study, and matched the other results of the study. Mr. Lee also clarified that when he called for additional monitoring in Pennsylvania, he specifically meant ground water monitoring.

*Well construction and casing.* A participant asked why the casing of some wells is not cemented to the surface. The presenters answered that the feasibility of cementing to the top of the well depends on local conditions. In some areas, there is a zone above which the well cannot be cemented. The presenters also noted that mud logging can be used to identify shallow gas zones and cement the problem areas without cementing the entire sequence from top to bottom. Some participants recommended referring to the meeting summary from Workshop 2 for further information.

*Disposal wells in the Marcellus.* Some participants stated that it is currently more economic for many operators to reuse produced water in the Marcellus than to inject it for underground disposal. A participant suggested that the reason underground disposal is not common in the Marcellus is due less to geologic concerns and more to past and present practices in the state which give operators opportunities to dispose of fluid much more easily than through injection. One participant asked if injection wells are even needed in the Marcellus, given the trend toward exploring reuse options and the low water volume output of the play. A participant

recommended that if there is a need for the development of injection capacity in the Marcellus, operators should cooperate to find suitable zones. The presenters emphasized that the decision of how to dispose of produced water is a practical and economic one: they stated that in some cases, underground injection is the safest and most cost-effective and in other cases reuse is safer and more cost-effective.

*Conventional plays.* A participant suggested that, while the technical workshops have focused on tight shales, the participants and presenters keep conventional plays in mind. The participant suggested that the emphasis has been on tight plays because of the volume of water used in slickwater operations. Participants noted that conventional wells are fractured with much less fluid but use higher concentrations of chemicals, so they belong in a different discussion.

### ***Abstracts for Theme 3: Disposal Practices***

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# Novel and Emerging Technologies for Produced Water Treatment

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## Introduction

Development of unconventional gas resources, including coalbed methane (CBM), shale gas, and tight sand is currently one of the most rapidly growing trends in domestic oil and gas exploration and production. The U.S. Energy Information Administration (EIA) projects that shale gas and CBM will make up 34% of total U.S. production in 2035, doubling their 17% share in 2008 [1]. Shale gas is the largest contributor to the growth natural gas production, while production from CBM deposits remains relatively stable from 2008 to 2035.

The rapid rise in production from shale formations is in large part attributed to the advances in horizontal drilling and hydraulic fracturing techniques. Hydraulic fracturing is the most significant technique that has enhanced the commercial shale gas production. Shale formation commonly has low permeability; therefore the wells need to be stimulated by hydraulic fracturing techniques. Hydraulic fracturing involves pumping fluids and proppant (i.e., grains of sand or other material used to hold the cracks open) down the wellbore under high pressure so that the gas can flow to the wellbore. A general estimate of water requirement for multi-stage fracture treatment of a horizontal well varies between 2.3 and 6 million gallons of water [2-4]. Development of shale gas resources also requires significant quantities of water for drilling and plant operations. Additionally, the majority of the frac water, from lower than 15% to as much as nearly 80%, returns to the surface [2, 5]. The flowback water typically contains sand, chemical additives, hydrocarbons, salts, and occasionally low level of naturally occurring radioactive materials (NORM) that are found in many geological formations. In addition to frac flowback water, large volumes of produced water are generated in the early stages of gas production to reduce pressure in the formation before the gas can be produced. Produced water is typically salty and often requires treatment prior to discharge.

Water usage, water quality, and disposal are the pressing issues that may potentially inhibit the projected growth in unconventional gas production, in particular considering new environmental legislation and public perception [6]. Operators must manage flowback and produced waters in a cost-effective manner that complies with regulatory requirements. This requires the treatment processes to be robust, mobile and modular, sustainable, inexpensive, and to have low energy demand. Furthermore, technologies should be versatile and flexible and can be used to treat water with variable quantity and quality containing different contaminants and having different characteristics.

Various treatment technologies have been used or under development to address water supply and disposal issues during oil and gas development. Funded by the DOE/RPSEA program, we conducted a literature review and technical assessment to evaluate existing and emerging technologies that have been used for treatment of produced water and novel technologies that could be tested and considered in the future. The evaluation criteria for technical assessment include commercial status of technology and applications; applicable feed and expected product water quality; removal efficiencies of key constituents; infrastructure considerations (modularity, mobility, etc); energy use and consumption; chemical demand; life cycle and costs; operation and maintenance considerations (ease of operation, reliability, etc); pre- and post-treatment; and waste disposal. Laboratory and field testing were conducted to explore the most appropriate and cost-efficient technologies for treatment of CBM produced waters that will allow beneficial use of the treated water. A modeling framework was developed to evaluate the technical aspects, institutional complexity, and economic viability of multiple beneficial use and discharge options. The decision making framework is comprised of four modules: 1) Water Quality Module (WQM); 2) Treatment Selection Module (TSM); 3) Beneficial Use Screening Module (BSM); and 4) Beneficial Use Economic Module (BEM). The detailed description of this RPSEA project and the downloadable tools and technology factsheets can be found at the website “Produced Water Treatment and Beneficial Use Information Center” ([http://aqwatec.mines.edu/produced\\_water/index.htm](http://aqwatec.mines.edu/produced_water/index.htm)).

This paper will summarize briefly the technical assessment and testing results of novel and emerging technologies for produced water treatment.

### **Electrochemical Charge Driven Separation Processes**

Electrochemical charge driven separation processes separate dissolved ions from water through ion permeable membranes or conductive adsorbers under the influence of an electrical potential gradient. These processes include electrodialysis (ED), electrodialysis reversal (EDR), electrodeionization (EDI), and capacitive deionization (CDI). An ED stack consists of a series of anion exchange membranes (AEM) and cation exchange membranes (CEM) arranged in an alternating mode between anode and cathode. The positively charged cations migrate toward the cathode, pass the cation exchange membrane, and rejected by the anion-exchange membrane. The opposite occurs when the negatively charged anions migrate to the anode. This results in an alternating increasing ion concentration in one compartment (concentrate) and decreasing concentration in the other (diluate). The EDR process is similar to the ED process, except that it also uses periodic reversal of polarity to effectively reduce and minimize membrane scaling and fouling, thus allowing the system to operate at relatively higher water recoveries.

Electrodeionization (EDI) is a commercial desalination technology that combines ED and conventional ion exchange (IX) technologies. A mixed-bed ion exchange resin or fiber is placed into the dilute cell of a conventional electrodialysis cell unit to increase the conductivity in the substantially non-conductive water. The IX resins are regenerated via water splitting under current. The process can be performed continuously without chemical regeneration of the IX resin, and reduce the energy consumption when treating low salt solutions.

Capacitive deionization (CDI) is an emerging desalination technology. In CDI, ions are adsorbed onto the surface of porous electrodes (e.g., activated carbon, carbon aerogel, carbon fibers, etc) by applying a low voltage electric field, producing deionized water.

Electrochemical charge driven separation processes are typically used in desalination of brackish water (up to about 8,000 mg/L TDS for EDR) and not highly saline water. This is because the cost of these processes and energy consumption increase substantially with increasing salinity or TDS concentration. ED and EDR have been successfully used at a number of municipal water and wastewater treatment plants to desalinate brackish water and reclaimed water. Laboratory experiments and pilot scale testing have been conducted to investigate the feasibility of these technologies to treat produced water. Although these processes are less prone to fouling as compared to reverse osmosis (RO) and nanofiltration (NF) membranes, the efficiency of ED, EDR and EDI is degraded by fouling/scaling. Sparingly soluble inorganic salts (e.g.,  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ) and multivalent ions (e.g., iron and manganese) can still scale the IX membranes by precipitation and fixation. This can be controlled by pretreatment of the feedwater with processes such as filtration for suspended solids, softening or pH lowering, and addition of antiscalant into the concentrate compartments. A disadvantage of these processes is the limited removal of non-charged constituents, including organics molecules, silica, boron, and microorganisms.

### **Ceramic MF/UF membrane**

Ceramic ultrafiltration and microfiltration membranes are made from oxides, nitrides, or carbides of metals such as aluminum, titanium, or zirconium. Ceramic membranes are much more resilient than polymeric membranes and are mechanically strong, chemically and thermally stable, and can achieve high flux rates. Typically, a tubular configuration is used with an inside-out flow path, where the feed water flows inside the membrane channels and permeates through the support structure to the outside of the module.

Ceramic membranes are capable of removing particulates, organic matter, oil and grease, and metal oxides. Ceramic MF/UF membranes alone cannot remove dissolved ions and dissolved organics. Pre-coagulation, injection of a chemical coagulant upstream from the membrane, improves removal efficiencies of dissolved organic carbon and smaller particulates. As with conventional ultrafiltration and microfiltration, a strainer or cartridge filter is necessary as pretreatment for ceramic membranes. Numerous research studies have been conducted on using ceramic membranes to treat oil-containing wastewater and produced water [7-8]. These research studies have shown that ceramic membranes perform better than polymeric membranes on oil-containing waters. Ceramic membranes have also been employed commercially as part of a large treatment train consisting of multiple unit process at the Wellington Water Works to treat oilfield produced water [9].

Energy requirements for ceramic membranes are lower than those required for polymeric membranes. Ceramic membranes have a higher capital cost than polymeric membranes. The

application of ceramic membranes for produced water treatment may increase as more research and pilot studies are conducted.

## **Membrane Distillation**

Membrane distillation (MD) is a novel thermally driven membrane separation process that utilizes a low-grade heat source to facilitate mass transport through a hydrophobic, microporous membrane [10-11]. The driving force for mass transfer is a vapor pressure gradient between a feed solution and the distillate, and is the only membrane process that can maintain process performance (i.e., water flux and solute rejection) almost independently of feed solution TDS concentration. MD is most likely capable of producing ultra-pure water at a lower cost compared to conventionally distillation processes; however, compounds with higher volatility than water, such as BTEX and other organic compounds, will diffuse preferentially faster through the membrane. Membrane materials commonly employed for MD include polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidenefluoride (PVDF). MD membranes may be packaged in either flat-sheet or hollow-fiber configurations. For pretreatment, MD processes require a pre-filter to screen out large particles and the complete removal of any surfactants present in the feed stream. If surfactants are present in the MD feed stream they will wet the hydrophobic pores of the MD membrane and cause pore flooding, which results in a substantial reduction in membrane solute rejection.

MD is flexible for most variations in feed water quality and quantity. It may become a potential technology for produced water treatment with the improvement in MD membranes and system design.

## **Osmotically Driven Membrane Processes**

Forward osmosis (FO) is an osmotically driven membrane process. During FO, water diffuses spontaneously from a stream of low osmotic pressure (the feed solution) to a hypertonic (draw) solution having a very high osmotic pressure. Unlike RO and NF, FO systems operate without the need for applying hydraulic pressure. The membranes used for this process are dense, non-porous barriers similar to RO and NF membranes, but are composed of a hydrophilic, *cellulose acetate* active layer cast onto either a woven polyester mesh or a micro-porous support structure.

Typically, the FO draw solution is composed of NaCl, but other draw solutions composed of NH<sub>4</sub>HCO<sub>3</sub>, sucrose, and MgCl<sub>2</sub> have been proposed. During FO the feed solution is concentrated while the draw solution becomes more dilute. FO requires the continuous reconcentration of the draw solution for sustainable system operation. One option is the use of RO for reconcentrating the draw solution and producing fresh product water for beneficial use or discharge.

FO membranes are capable of operating with feed TDS ranging from 500 mg/L to more than 35,000 mg/L, and rejecting all particulate matter and almost all dissolved constituents (greater than 95% rejection of TDS). These attributes also allow FO to achieve very high theoretical

recoveries while minimizing energy and chemical demands. An additional benefit of FO is that the process occurs spontaneously, without the need of applied hydraulic pressure. Therefore fouling layers that accumulate on FO membranes may be readily removed with cleaning (e.g., increasing cross-flow velocity, osmotic backwashing) or with chemicals, and irreversible flux decline is minimized [12]. FO membranes may be packaged in flat sheet or spiral-wound configurations. These packages allow for relatively small process footprints, but are still not optimized to the extent of pressure driven processes.

The testing results of FO process for produced water treatment at laboratory and field are promising. With the development of more suitable draw solution and appropriate semi-permeable membrane, FO process can become a potentially industrial technology to address the challenges of shale gas flowback and produced water treatment.

## References

- [1] U.S. Energy Information Administration, Annual Energy Outlook 2010 with Projections to 2035. Report #: DOE/EIA-0383(2010). Release Date: May 11, 2010. Available at: <<http://www.eia.doe.gov/oiaf/aeo/gas.html>>. [cited October 16, 2010].
- [2] GWPC and ALL, Modern Shale Gas Development in the United States: A Primer. Prepared for the U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory (NETL). Prepared by the Ground Water Protection Council and ALL Consulting. April 2009. Available at: <<http://www.oilandgasinvestor.com/Files/DOEShaleGasPrimer.4.14.09.pdf>>.
- [3] Railroad Commission of Texas web site: June 4, 2007. "Water Use in the Barnett Shale." Available at: <[http://www.rrc.state.tx.us/divisions/og/wateruse\\_barnettshale.html](http://www.rrc.state.tx.us/divisions/og/wateruse_barnettshale.html)>. [Cited October 16, 2010],
- [4] D.B. Burnett and C.J. Vavra, Desalination of Oil Field Brine - Texas A&M Produced Water Treatment. Available at: <<http://www.pe.tamu.edu/gpri-new/home/BrineDesal/MembraneWkshpAug06/Burnett8-06.pdf>>. [Cited October 16, 2010].
- [5] J. Veil, Water Management Technologies Used by Marcellus Shale Gas Producers. Prepared for: United States Department of Energy National Energy Technology Laboratory. Final Report July 2010.
- [6] PADEP, Notice of Final Rulemaking Department of Environmental Protection Environmental Quality Board [25 PA. CODE CH. 95]. Wastewater Treatment Requirements. Available at: <<http://files.dep.state.pa.us/PublicParticipation/Advisory%20Committees/AdvCommPortalFiles/WRAC/Preamble%20TDS%20Final%20Rulemaking%20to%20WRAC.pdf>>. [cited October 16, 2010].
- [7] R.S. Faibisoff, and Y. Cohen, Fouling and rejection behavior of ceramic and polymer-modified ceramic membranes for ultrafiltration of oil-in-water emulsions and microemulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 191 (2001) 27-40.
- [8] G. Gutierrez, A. Lobo, D. Allende, A. Cambiella, C. Pazos, J. Coca, and J.M. Benito, Influence of Coagulant Salt Addition on the Treatment of Oil-in-Water Emulsions by Centrifugation, Ultrafiltration, and Vacuum Evaporation, *Separation Science and Technology* 43 (2008) 1884 - 1895.
- [9] D.R. Stewart, Developing a new water resource from production water. Available at: [http://www.crwcd.org/media/uploads/Dave\\_Steward.pdf](http://www.crwcd.org/media/uploads/Dave_Steward.pdf). [cited October 1, 2010]

- [10] T.Y. Cath, V.D. Adams, and A.E. Childress, Experimental study of desalination using direct contact membrane distillation: A new approach to flux enhancement, *Journal of Membrane Science* 228 (2004) 5-16.
- [11] K.K. Sirkar, and B. Li, Novel membrane and device for direct contact membrane distillation-based desalination process: phase II, 2003, Bureau of Reclamation, Denver, Colorado.
- [12] T.Y. Cath, A.E. Childress, and M. Elimelech, Forward osmosis: principles, applications, and recent developments, *Journal of Membrane Science* 281 (2006) 70-87.

# Simple Modeling of the Disposition of Fluids On-Site in a Pit

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The fracing process begins with wellpad siting, proceeds through completion and ends with production (and the eventually decommissioning or abandonment). The steps in the process include: site selection, well pad development, drilling, fracing, and production. Using the term *waste* to mean any disposal, whether in use or afterwards, one realizes that there are a number of *waste* materials produced during these steps including: drilling fluids, pit solids, pit liquids, frac fluids, flowback fluids, and produced water. An investigation involving sampling and analysis of these materials was conducted along with a followup risk assessment (RA) to assess the impact of fracing in four energy basins in Colorado which was completed in the spring of 2008 [URS, 2008; QEPA, 2008]. The focus of this presentation will be on three media: flowback fluids, frac fluids, and produced waters, although other media (e.g., pit solids as waste) and subsequent pathways were considered and were evaluated in both the sampling and analysis [URS, 2008] and in the RA [QEPA, 2008].

## Chemical Analysis

In 2008, in a project funded by the Colorado Oil and Gas Association (COGA), QEPA, pH2 through QEPA, and URS were contracted to devise a sampling and analytical plan as part of a risk assessment for proposed changes in the Oil & Gas (O&G) regulations in Colorado [COGCC, 2008]. This first necessitated the identification of chemicals for analytical evaluation (CAE) and eventual selection of the chemicals [URS, 2008]. A list of chemicals was prepared that included data suggested by a review of Material Safety Data Sheets (MSDS) from COGA member companies. It also included standard chemicals of interest in the O&G industry such as Benzene, Toluene, Ethyl Benzene, Xylenes (BTEX), Polynuclear Aromatic Hydrocarbons (PAHs), Boron, Chloride, Total Extractable Petroleum Hydrocarbons (TEPH), etc. [CDPHE, 2007; COGCC, 2008]. Primary metals (and metalloid) included were the 8 Resource Conservation and Recovery Act (RCRA) metals consisting of arsenic, barium, cadmium, chromium, lead, mercury, silver, and selenium; and an additional 15 target analyte list (TAL) metals were added from EPA Method 6020A which included Aluminum, Antimony, Beryllium, Calcium, Cobalt, Copper, Iron, Magnesium, Manganese, Nickel, Potassium, Sodium, Thallium, Vanadium & Zinc. Based on a review of potential agents associated with raw material derived from subsurface deposits, gross alpha and gross beta were selected for analysis. A small subset of samples from pit wastes was analyzed by EPA's Toxic Characteristic Leaching Procedure (TCLP) for 8 RCRA metals in addition to pH, reactive sulfides, and reactive cyanides to evaluate waste disposal considerations. However, this presentation will only cover flowback fluids, frac fluids, and produced waters, of which there are 32, 3, and 16 sample data points, respectively, including duplicates.

## **Chemical Selection for Disposition Modeling**

Based on the analytical results, measurable values of the 173 analytes were narrowed. Although a number of PAHs were present, their fate-transport and subsequent risk were not shown to be significant human health risks; however, some were modeled. A few chemicals were removed from the modeling of liquid waste disposition based on previous modeling of solid wastes (our scenarios 1 to 8) indicating minimal opportunity for significant risk given basic maximum concentration as well as subsequent fate and transport. Chloride and boron were not selected for modeling as these had Colorado regulatory limits not tied to human health and these limits were not expected to be exceeded in these materials once accounting for dilution, fate, and transport. For instance, the boron maximum was 7.6 mg/L versus a limit of 2 mg/L limit, not including any dilution from transport.

The glycols were initially considered but dismissed based on the risk assessor's qualitative order-of-magnitude assessment with regard to having a *defacto* dilution attenuation factor (DAF) under the modeled circumstances of an initial 4-100 dilution before significant transport. This *diluted* value when compared to drinking water standards and in consideration of fate and transport resulted in their de-selection from the liquid disposition modeling. For instance, only 5 of 33 data points in the flowback fluids and none of the produced water samples detected glycols. The maximum in any medium was 120,000 ug/L, and with a 100 fold dilution (DAF) the result would be 1,200 ug/L. Using a 300-fold safety factor to calculate an acceptable limit based on the more toxic of the glycols (ethylene) [Blood, 1965] would result in 0.14 mg/kg/day acceptable exposure rate. For a 70 kg man consuming 2 L/day, that would be a drinking water limit of 4,900 u/L, higher than any suspect concentration at the point of exposure (POE). Similarly, data for 2-butoxyethanol (2-BE) revealed several detects in pit solids (as solids), pit fluids, flowback fluids, and drilling fluids. The highest of these was 7.1 mg/L in flowback flow fluids. A total of 5 additional hits were noted as tentatively identified compounds (TICs) with suspect validity, the highest estimated concentration from these was 20 mg/L. The ATSDR MRLS for 2-BE are 0.4 mg/kg/day and 0.07 mg/kg/day for intermediate and chronic exposure [ATSDR, 1998]. These were converted to surrogate drinking water limits assuming 55-70 kg female or male humans and using a reasonable maximum likelihood estimate of water intake of 2 liters per day [EPA, 1989]. This results in intermediate surrogate drinking water limits of 11-14 mg/L, and chronic limits of 1.925-2.45 mg/L. One also notes that these limits have uncertainty/safety factors of 90 and 1000, respectively. Using the 20 mg/L and presuming typical DAFs of 100+, 2-BE would not present a significant risk.

Although gross alpha and gross beta were present, a set of appropriate phys-chem properties is not available for modeling their fate and transport within the model chosen for the other components. Furthermore, the effect of the anticipated DAF (100+) of disposing of a liquid in a waste pit on-site [where reserve pits at closure tend to be about 75x20 ft to 100x50 ft at depths of 8-10 ft], suggests that in these geologic settings, gross alpha and beta (maximums 274 and 4,030 pCi/L, respectively) would not result in exceedances of 15 and 30 pCi/L EPA suggested levels in absence of isotope data at the anticipated conservatively estimated POE of 72 meters.

The flowback fluids in general produced the highest levels of constituents of concern. The

produced water at the highest levels, for conservatism, were used in the modeling. Maximum values for each constituent were used as opposed to means or upper confidence limits (UCLs). Soil leaching was run simultaneously with the liquid and thus results include both, but are driven by the liquids in the off-site scenarios.

## Fate & Transport

In the study in Colorado, the hypothetical practice of releasing flowback or produced water back into waste pits was modeled using a standard fate & transport model used in the ASTM RBCA standard [ASTM, 2002]. The modeling performed assumed a standard pit had an infinite source of flowback fluid and assumed no liner was present. We chose characteristics of the chemicals based on data from the two basins qualitatively considered more risky in setting, and the hydrogeologic characteristics for these basins as well. The model for transport is a standard Domenico model [Domenico, 1985, 1987] for solute transport with a modification for decay-based attenuation. For no decay, the decay constant in the equation,  $\lambda$ , was set to zero. Other parameters were set to limit errors, and apply a certain level of conservancy while still using more regional/local maximum likelihood estimators (MLEs) for hydrogeologic parameters. The hydraulic conductivity ( $K_{ha}$ ) was selected as 3.63E-3 cm/sec, driven by regulatory concerns [CDPHE, 2007], although the range tends to be lower. The depth to groundwater was varied from 1-3 meters (3.3-9.8 feet) in the 4 scenarios modeled, two with 1 meter and two with 3 meters. The lower range of constituent retardation values from ASTM [ASTM, 2002] was used in the model. The POE for ground water was set at 10-72 meters (33-236 feet), where 72 meters was the nearest well in a survey of 28 sites from the two basins (out the 55 sites from which the full study was conducted). The POE for surface water was also set at 10-72 meters, recognizing that the minimum and 5% quantile values for surface water distance to drilling well at the 28 sites investigated were 15 and 59 meters (49 & 194 feet), respectively. Of the 4 scenarios modeled, two used 10 meters and two used 72 meters; and two assumed decay and two did not. Decay rates were set by chemical by selecting on the lower end of published data.

## Exposure

Several assumptions go into the exposure assessment process and a number of limitations also arise from this. In the study in Colorado the fluids released back into waste pits was modeled using a standard fate & transport model used in the ASTM RBCA standard [ASTM, 2002]. As part of this ASTM process, pathways from soils, groundwater and vaporization were considered. Scenarios that were accounted for included fishing, swimming, well water consumption, inhalation of air and dust downwind, etc. Exposures for commercial building occupancy and a construction worker scenario were modeled and are in the RA (QEPA, 2008), but are not presented here. Because multiple pathways, and thus exposures and doses, were modeled on the same population (e.g., person), an overestimate of real exposure is likely to arise. The RA was completed using a variety of assumptions, details of which are provided in the RA [QEPA, 2008].

The results indicate that benzene is driving the carcinogenic risk with all other agents (e.g., PAHs, phthalates, etc.) having little influence. There was an effect from arsenic, but this would already be seen from background levels present in soils already. The results also indicate that

the non-cancer risk is driven by toluene, followed by xylenes and then ethylbenzene, with all other agents having little influence. The groundwater pathway is clearly more important. Based on the 4 scenarios, with scenarios 10 & 11 the most likely, it does not appear that the fluids present the significant risk that might have been anticipated had the fate, transport, and RA not been performed.

### Acknowledgments

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### References

- ASTM: E1739-95(2002), Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites. ASTM, Conshohocken, PA. 2002.
- ATSDR: Toxicological Profile for 2-Butoxyethanol and 2-Butoxyethanol Acetate. August 1998.
- ATSDR: Toxicological Profile for Ethylene Glycol. 2010.
- ATSDR: Toxicological Profile for Propylene Glycol. 1997.
- Blood, FR: Chronic toxicity of ethylene glycol in the rat. Food Cosmet Toxicol 3:229-234. 1965.
- Colorado Department of Public Health and Environment (CDPHE), Hazardous Materials and Waste Management Division, Table 1 Colorado Soil Evaluation Values (CSEV) – December 2007
- Colorado Oil and Gas Conservation Commission (COGCC), Draft Rules for Oil and Gas Development in Colorado, (HB 1298 & HB 1341), March 31, 200.
- Domenico, P.A.: An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species. J Hydrology 91: 49–58, 1987.
- Domenico, P.A. and G.A. Robbins: A New Method of Contaminant Plume Analysis. Ground Water 23(4): 476–485. 1985.
- QEPA: Pathway Analysis and Risk assessment (PARA) For Solids and Fluids Used In Oil and Gas Exploration and Production in Colorado, pp. 1-930, June 2008.
- URS: Field Activities Report for Characterization of Exploration and Production Pit Solids and Fluids in Colorado Energy Basins, June 4, 2008.
- US EPA: Exposure Factors Handbook, Volume I - General Factors. EPA 600/8-89/043. USEPA: Washington, DC. May, 1989.

# Underground Injection Wells for Produced Water Disposal

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## Introduction

The Oil and Gas Industry first utilized underground injection as a means of disposing of the naturally occurring brine that was often produced along with crude oil and / or natural gas in the 1930's. In 1974, the Safe Drinking Water Act required the U.S. Environmental Protection Agency (EPA) to set minimum requirements for the brine injection wells utilized by the Oil and Gas Industry along with numerous other wells used for disposal of various hazardous and nonhazardous wastes. These requirements are generally referred to as the Underground Injection Control (UIC) program. Since inception of the UIC program, Class II wells (those wells classified for injection of oil and gas liquids including oilfield brine disposal wells) have safely injected over 33 trillion gallons of oilfield brine without endangering underground sources of drinking water (USDW).

## History of Underground Injection

During the 1930's, oil producers first began disposing of the brine produced in conjunction with crude oil back into the same formation from which it had been extracted. In this same decade, the practice of injecting produced brine into a formation in order to push crude oil to an adjacent producing well was initiated, thus starting the practice of enhanced oil recovery (EOR). In the 1940's, oil refineries began using deep well injection for disposal of refinery waste and several chemical plants followed this trend a decade later. As the practice of brine disposal using deep well injection continued to grow, many states began implementing regulations for disposal of oilfield brine in the 1950's. In the 1960's, documented cases of groundwater contamination associated with the underground injection of waste began to surface. Most notably, a waste injection well at the Hammermill Paper Company in Erie, Pennsylvania suffered a casing failure and pulping liquor escaped into the surrounding ground and into Lake Erie. Though never conclusively determined, a black liquid found to be flowing from an abandoned oil well approximately five miles from the Hammermill well was believed to be pulping liquor from the Hammermill well.

In response to this and other cases, the U.S. Congress passed the Safe Drinking Water Act in 1974 and gave the EPA the authority to regulate the underground injection of all wastes in order to protect USDW's. In the following decade, Federal UIC regulations were passed establishing five classes of wells that fall under the UIC program and requirements for States or tribes to have primary enforcement, or primacy, on their lands. Since its creation, the UIC program has been amended to allow for stricter regulations for deep well injection of

hazardous waste and to create a sixth well classification for wells that will be used for geologic sequestration of carbon dioxide (CO<sub>2</sub>).

### **Primary Enforcement (Primacy)**

As mentioned above, the Federal UIC regulations established the requirements necessary for a State or tribe to enforce the program on their lands. In order to assume primacy, the States or tribes had to demonstrate their program for UIC enforcement met the minimum requirements established by the EPA's UIC program. Currently, 33 States and three U.S. Territories have primacy for all of the UIC wells in their jurisdiction. Seven States, but none of the U.S. Territories, share primacy with the EPA, often with a State handling one or more classifications of wells and the EPA overseeing the remaining classifications. The EPA maintains primary enforcement of the UIC programs in the remaining ten States and three US Territories.

### **Well Classification**

Under the Federal UIC regulations, there are currently six different well classifications.

*Table 7. UIC well classifications*

Class I	Wells that inject hazardous wastes, non-hazardous industrial wastes and municipal wastewater beneath the lowermost USDW.
Class II	Wells that inject fluids for enhanced oil recovery, dispose of fluids associated with oil and gas production and inject liquid hydrocarbons for storage.
Class III	Inject fluids for the extraction of minerals such as salt, sulfur and uranium.
Class IV	Originally used for wells that injected radioactive or hazardous waste above a USDW, but this process has been banned. This classification is now limited to wells that are being used for an authorized clean-up of a contaminated site or groundwater source.
Class V	Wells that inject non-hazardous waste above a USDW. Basically is composed of all wells that do not fit into any other category.
Class VI	Newest well classification. Intended for wells that will be used for sequestration of carbon dioxide.

### **Class II Wells**

At present, there are approximately 144,000 Class II injection wells in the U.S. Of these, roughly 80% are wells used for enhanced oil recovery (EOR). Most prominent of this group are water injection wells that re-inject brine taken from a producing formation back into that formation in an effort to pressure more crude oil to the producing wells. This subset of Class II wells also includes wells used to inject steam into formations containing viscous crude and wells used to inject various mixtures of gas and / or brine to improve crude production. The smallest subset of Class II wells is the wells that are used to inject liquid hydrocarbons into underground storage caverns. Most recognizable of this set of wells are those utilized for the U.S. Strategic Petroleum Reserve. The remaining Class II wells, approximately 20% of the total, are those wells that are used to dispose of the fluids associated with oil and gas production, more commonly referred to as saltwater disposal wells.

## **Saltwater Disposal Wells (SWD)**

This special subset of the Class II UIC wells has allowed for the safe disposal of fluids associated with oil and gas production since the 1930's and has a long track record of protecting USDW's under the UIC program. Oil and Gas Companies have come to rely on the safe and economic operation of these wells for disposal of the naturally occurring brine that often accompanies the production of oil and / or gas. Whenever an Oil and Gas Company or a commercial SWD Operator decides to establish a SWD in a new area, the first consideration is site selection.

The surface location of an SWD well is important as it needs to be an area where it is easily accessible by Operators who need to dispose of brine from their oil and gas production efforts; however, surface location is not the only consideration when selecting a site for the SWD well. Additionally, the SWD Operator needs to understand the geology beneath the surface location. The first consideration is for a porous and permeable, non-hydrocarbon bearing zone that is not considered an aquifer under the UIC program. A previously productive oil and gas zone that is now depleted and is porous and permeable is also suitable for brine disposal. In either of these options, there must be a clear barrier between the zone of interest and all USDW's and the area to be drilled must be relatively clear of any geologic faults. Once the site selection is complete, the well may be drilled and completed provided certain minimum requirements in the UIC program are adhered to.

Once drilling commences on the well, the first requirement under the UIC program for the area is the depth at which surface casing must be run. Usually, surface casing is run from surface to a depth that is several hundred feet beyond the deepest known aquifer in an area. Once surface casing is set, cement is circulated into the void between the steel casing and the borehole, forming an impermeable seal across any aquifers. The well is then drilled to the desired depth for the zone targeted for disposal. Again, steel casing is run from surface to the total depth of the well and cement is circulated into the annular space between the casing and the borehole from the bottom of the well to surface, forming another dual layer of protection to isolate the injected fluids from any USDW. A cement bond or evaluation log is usually run at this point. The cement evaluation log is a sonic tool that can give a 360° interpretation of the quality of the cement bond to the casing's outside diameter. At this point, a special tool is used to open holes in (or perforate) the casing and cement across the disposal zone.

Injection tubing (usually internally plastic coated to protect the pipe from corrosion) and a packer are run into the well. The packer is a device that seals the annular space between the casing and tubing and prevents the fluid being injected via the tubing from coming back up the annular space. The UIC program often dictates the depth at which the packer must be located, but it is usually somewhere between 50' and 100' above the uppermost perforation. After running the packer and tubing into the well, a packer fluid is circulated through the tubing and back up the annular space to surface before the packer is "set" or activated. Packer fluids serve three primary purposes: 1) protect the casing inside diameter and tubing outside diameter from corrosive agents, 2) provide a hydraulic fluid to allow for instantaneous notification on the surface should the packer leak injection fluid into the annular space and 3) provide hydrostatic

head pressure to help offset the pressure on the bottom of the packer from the injection fluid. After the packer is set, UIC regulations require that the mechanical integrity of the injection casing and packer seal be tested and verified. This is usually done by applying pressure to the annular fluid and using a chart recorder to document that the pressure remains constant in a static condition for a period of time (e.g. 30 minutes). Once a well has been placed in service, the UIC regulations require that, as a minimum, the wellbore integrity be verified via a recorded pressure test once every five years and the normal operating annular pressure be observed and recorded once per month. Many of the oil and gas regulating divisions in States with primacy have more stringent requirements. In Texas, for example, a recorded pressure test for casing integrity (H5 test) must be performed annually on each Class II well.

The next required step in the UIC process is a step rate test to determine maximum surface injection pressure. In a step rate test, a fluid similar to that expected to be injected into the well once it is in service is pumped into the well at gradually increasing rates. Each rate is maintained for a required period of time, usually either 30 or 60 minutes. Bottomhole pressure is recorded during this period. When plotting the dynamic bottomhole pressures for each injection rate, the point at which the fracture gradient for the targeted formation is exceeded will be seen as an inflection in the slope of the line through the pressure points. After noting that the formation has “broken down” or indicated that fracture formation has initiated, pumping may be stopped and the instantaneous shut in pressure (ISIP) recorded. Maximum surface injection pressure is often set at or just below the ISIP, allowing for hydrostatic head of the injected fluid and friction loss in the injection tubing. In the event that formation breakdown is not noted in the test, maximum surface injection pressure is usually set to reflect the highest pressure seen during the step rate test. UIC regulations generally require that all step rate tests be witnessed by a representative for the local UIC administrator.

After a saltwater disposal well has been properly constructed, the economics of operation often complement this time-proven method of brine disposal. For a saltwater disposal well that is operated by an Oil and Gas Company for disposal of the brine produced during normal operations, the average cost of disposal is often less than \$0.25 per barrel of fluid disposed. A commercial SWD well will typically charge between \$0.50 and \$2.50 per barrel of fluid. As with most things in life, this price disparity is usually related to supply and demand. In areas where disposal wells are plentiful and generally operate below capacity, competition drives the price down. In areas where there is a strong demand for brine disposal, but the disposal infrastructure has not been developed or the subsurface geology is not conducive to underground injection of oil and gas fluids, the commercial operators can receive a premium for their services.

A second cost associated with disposal of oilfield brine is transportation of the brine from where it is gathered and stored at the well site to the disposal well. On average, the transportation of brine will cost an Operator \$1.00 per barrel of brine per hour of transportation time. In an area such as the Barnett Shale in North Texas where SWD wells are plentiful, brine transportation may only add \$0.50 per barrel to the cost of brine disposal. Conversely, in northern Pennsylvania, where the nearest commercial disposal well may be in

Ohio or West Virginia, the cost of transportation can easily add \$4.00 to \$6.00 per barrel to the cost of disposal.

Lastly, in addition to the cost of transportation in this area, an Operator needs to consider the wear and tear on local roads from the long distance transportation of the brine along with contribution of carbon dioxide emissions from the trucks required to transport the brine.

Consideration of these three items led Chesapeake Energy to develop our unique Aqua Renew™ program to allow for reuse of produced brine from our Marcellus wells. By filtering and reusing the brine in an upcoming completion, Chesapeake not only reduces the amount of fresh water required for the completion, but we can also eliminate seven hours of truck time that would have been used to transport brine to an out of State disposal well. This reduction in truck transportation of brine will also reduce 52,500 road miles of wear per well and eliminate 88 metric tons of carbon dioxide emissions per well.

The subsurface geology in Pennsylvania has not proven to be conducive to brine disposal. To date, there are only eight permitted Class II wells devoted to saltwater disposal in the entire state. Of these eight, three utilize the Oriskany formation for disposal and two use a combination of the Oriskany and Huntersville formations. One well injects into the Balltown formation and another the Gatesburg zone. Lastly, the highest disposal volume of the set injects into a mine void. As a group, the eight wells account for 8,667 barrels per day of brine disposal capacity. By comparison, the Mann #1 SWD well operated by Chesapeake near Cleburne, Texas (Barnett Shale) averages 26,000 barrels per day of brine disposed. The Mann #1 injects brine into the Ellenburger Formation, a porous strata located 1 ½ miles beneath all known aquifers in the area. Tarrant County, of which Fort Worth, Texas is the county seat, has more saltwater disposal wells (ten) than the entire State of Pennsylvania. Overall, the State of Texas has approximately 12,000 Class II saltwater disposal wells.

While the overall subsurface geology in Pennsylvania may not be ideally suited to subsurface brine injection, Chesapeake did attempt to drill and complete a Class II well in the Trenton / Black River formations. Originally budgeted for three million dollars, ultimate capital spent on this well was just under seven million dollars and numerous tests indicated very limited brine uptake capacity. A permanent bridge plug was set above the targeted formations and the well was temporarily abandoned.

### **Reclamation / Disposal Combinations**

In areas where disposal opportunities are limited or disposal capacity in a given well is less than plentiful, it may be advantageous to utilize some form of water reclamation upstream of the disposal well. Of the reclamation systems available to the industry, all have differing costs and efficiencies associated with brine concentration and some are limited in consideration by organics or the total dissolved solids concentration of the fluid to be treated. To an Operator, another key consideration is whether the unit produces a distilled water or water vapor. If it is distilled water and the unit is east of the 98th Meridian, the distilled water must be trucked back to a completion location to be used in an upcoming stimulation. A provision of the Clean

Water Act allows Operators to request permission from the EPA to surface discharge treated produced fluids for the beneficial use of agriculture or for wildlife propagation – provided the discharge location is west of the 98th Meridian. If discharge of treated water is not allowable and available water resources are abundant, a reclamation system that produces water vapor while concentrating the brine for disposal will save road wear and reduce carbon dioxide emissions from truck traffic.

By concentrating the brine prior to disposal, these units may make economic sense in area where disposal capacity is limited. If the produced brine chemistry allows for recovery of 75% of the treated water volume as vapor, the remaining brine volume will be reduced by a factor of four. Reclaiming this fluid prior to disposal allows for a disposal site that has a maximum daily capacity of 500 barrels of water to process 2,000 barrels of fluid per day. Of the processed 2,000 barrels, 1,500 are returned to the water cycle as vapor and the remaining 500 barrels of concentrated brine are sent down the Class II disposal well.

Chesapeake Energy is trialing such a unit at our Brentwood disposal site just east of downtown Fort Worth. Two EVRAS (evaporative reduction and solidification system) units manufactured by Layne Christensen's Intevras Division utilize waste heat from the Ark Park compressor site to treat 1,200 barrels per day of produced water. Of these 1,200 barrels, roughly 700 are evaporated as water vapor. The result is that the initial 1,200 barrels are concentrated down to 500 barrels before injection into the Brentwood SWD well. Though not economically favorable to the standard Barnett Shale practice of straight disposal of oilfield brine, the Brentwood application allows us to properly test out application of the technology for other areas.

## **Conclusions**

- The Oil and Gas Industry has utilized underground injection of brine since the 1930's and Class II UIC wells currently inject two billion gallons of fluid per day for enhanced oil recovery, disposal and storage.
- Wells used exclusively to dispose of fluids from oil and gas production account for 20% of the 144,000 Class II Wells in the U.S.
- Brine disposal in Class II wells is safe, environmentally sound and is the most economically viable option in most areas.
- In areas of limited disposal capacity or where water resources are stressed, reuse of produced brine is proving to be an effective alternative to underground injection.

# Wastewater from Gas Development: Chemical Signatures in the Monongahela Basin

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The West Virginia Water Research Institute began monitoring the Monongahela River and its major tributaries in July 2009 after reports of increasingly high dissolved solids concentrations in the River near Pittsburgh in the late summer of 2008. A sampling network of sixteen stations was established extending from mile 23 at Elizabeth PA to the Rivers two major sources, the Tygart and West Fork Rivers. Based on earlier surveys by the Pittsburgh District, US Army Corps of Engineers and PaDEP, the chemical constituents of interest were determined to be: sodium, sulfate, chloride, calcium, magnesium and alkalinity. Total dissolved solids (TDS), iron, aluminum and manganese were also determined in the laboratory. Field parameters including pH and electrical conductivity were also measured. It was decided that loadings were needed in order to identify significance of the various ion sources so sampling stations were located near gauges where possible and flows were estimated in non-gauged streams. Sampling took place every two weeks, data were compiled and results placed on a publicly available website: monWQ.net.

While sampling made no assumptions as to the sources of the high TDS readings we suspected that two sources would predominate: treated coal mine discharges and brines from the gas industry. The former were easy to characterize as the coal mine discharges are regulated under the NPDES program of the Clean Water Act. Brines are not. Streams dominated by coal mine discharge were characterized by sodium sulfate as the dominant ions. Brines are characterized by sodium chloride and three streams in Pennsylvania: the Youghiogheny, Ten Mile Creek and Whiteley Creek show a distinct sodium chloride signature suggesting heavy brine loadings. So, after 20 months it is possible to identify the major sources of TDS and their chemical signatures. The results also indicate seasonality with respect to higher TDS concentrations during low flow periods. This has led to a successful program with the coal industry whereby pumping rates are restricted during sensitive, low flow periods in late summer and fall with corresponding, higher discharges during high flow periods. As a result, the data show substantially reduced TDS concentrations on the Monongahela River since adoption of the managed discharge program in December 2009 and our data show no instances of TDS concentrations exceeding 500 mg/L on the Monongahela since December 2009.

The presentation focuses on major ion loadings and concentrations in the Monongahela River and its tributaries, the relative contributions of the major ions to TDS and their proportional contribution per tributary.

## **Revisiting the Major Discussion Points of the Technical Presentation Sessions**

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**John Veil** of Veil Environmental, the workshop lead noted that local issues may be more important than overall water availability in most shale plays. He suggested that with appropriate planning, the available water can accommodate most needs. In addition, he suggested saline ground water, surface water, and reused water are often viable alternative options to fresh ground water, and as technologies advance, some of these options will become more widely adopted. He emphasized that technology is also allowing HF to become more water efficient; operators are using larger well pads with more wells and more stages, resulting in less required water per unit of gas produced. Mr. Veil noted that it is important for all parties to be aware of the actual costs and prices of procuring, treating, recycling and disposing of water. Mr. Veil mentioned the success story of operators switching to surface water in Louisiana, as well as the challenges posed by landowner relations in the Eagle Ford. He encouraged all of the participants to continue to participate in the discussion and noted that regulatory and policy issues will continue to affect energy production and water use.

**Gary Hanson** of Louisiana State University – Shreveport, the Water Use and Sustainability theme lead, described his experience working in multiple sectors and noted that even agreeing upon common units for water use (e.g., acre feet, gallons) can be a challenge. He also noted that while the oil and gas industry is a business with financial incentives, the last two years have seen significant improvements in the way the industry addresses water use issues on a state-by-state basis. In addition, he noted that the industry has been rapidly adapting and improving their technologies, recognizing the potential benefits of using high-saline water in fracturing fluids. Mr. Hanson concluded that water will be a very important issue in the future and there will continue to be advances in technologies using reclaimed or recycled water.

**Tom Hayes** of the Gas Technology Institute, the Flowback Recovery and Water Reuse theme lead, reiterated the definitions of flowback and produced water, and he summarized the main points of the presentations and discussions. The presenters emphasized the variability of different plays and the necessity of tailoring water management to the specific characteristics and challenges of each unique play. He stated that many operators are currently streamlining and simplifying approaches to water management as new industry standards are developed. He concluded by noting that a number of innovations are facilitating the development of new concepts in water management, including continuing adaptation of water treatment technologies, new well pad design options, pipeline conveyance, and a variety of water storage options.

**Matthew Mantell** of Chesapeake Energy Corporation, the Disposal Practices theme lead, summarized the main discussion points from the Theme 3 technical presentations. He noted that treatment involves moving contaminants from one phase to another and introducing different disposal issues. He stated that a number of innovative technologies have been developed, but availability is still a limiting factor. He suggested that Underground injection wells are currently the most popular disposal method due to economic and practical considerations. Mr. Mantell also noted that in areas such as Pennsylvania, where there are large numbers of abandoned wells and mines, ground water monitoring is essential. He stated that the example of high TDS levels in the Monongahela River in 2008 and the subsequent study tracing the source of salinity underscores the need for monitoring. He remarked that the study's perspective on Dunkard Creek and other tributaries to the Monongahela illustrates that what may become the focus of the news media is not always the real issue.

**Bob Puls** of U.S. EPA, the Hydraulic Fracturing Study Technical Lead, thanked the participants in the workshop for their contributions. The presentations and discussion were very useful to EPA and will inform the way that the study is developed. Dr. Puls summarized key points made by the presenters. First, he noted that it is important to understand how water availability in different regions may affect the potential impacts of water withdrawal. Second, he noticed that there were many presentations on reuse of produced water. He noted that the field has changed in this area in just one year and that more meetings on this issue could be a good idea due to the quick changes in industry and concern for environmental protection. Dr. Puls noted that some presentations suggested that the salts in produced water might be beneficial for injection, and using recycled water for injection could reduce costs with little to no impact on production efficiency. He also noted that some presentations advised that there are significant differences between regions in that some formations are more consistent regarding volume and quality of produced water, and other formations are more variable. It was also noticed in the presentations that there are differences in formation chemistry, in treatment and disposal options, and in the regulations in different states. Dr. Puls observed that some of the presenters expressed concern that reusing produced water is potentially not only an issue of water availability and cost considerations, but also of community and public concerns. Dr. Puls concluded by thanking the leaders and organizers of the workshops.

## **Poster Abstracts**

Posters were submitted to US EPA for display during the technical workshops. Authors also submitted poster abstracts for use in this proceedings document.

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# Chemical Transformations of 2, 2-Dibromo-3-nitrilopropiamide

Uni Blake

MajiTox for Gastem USA

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## Introduction

As a part of determining the potential extent of the impact of a chemical on a target receptor, exposure pathways and the environmental fate of the contaminant of concern (COC) need to be addressed. Predictive modeling of the exposure pathways can be used to determine how the anthropogenic chemical moves through the environment and how the chemical would effectively avail itself to receptor response. Potential COC that result from chemical transformations are also used in the modeling process.

This abstract briefly describes the various potential chemical transformations of 2, 2-Dibromo-3-nitrilopropiamide (DBNPA) during the well stimulation process to determine if other COC can result from the chemical transformation of the biocide and also potentially act contiguously with DBNPA.

## Background

2, 2-Dibromo-3-nitrilopropiamide has been used commonly as a non-oxidizing biocide; mostly in cooling water systems. In this known use, it has been regulated safely under the National Pollution Discharge Elimination System. The biocide is used commonly because of its ability to hydrolyze completely into benign components. In modeling systems of 2, 2-Dibromo-3-nitrilopropiamide reactions, the pH and temperature effect, down-hole resident time, bacteria kill rate, exposure to microbial time and the original biocide concentration can all be shown to have an impact on the concentration of biocide at discharge. Therefore, to understand 2, 2-Dibromo-3-nitrilopropiamide reactions during the hydraulic fracturing process, different potential reaction scenarios that can affect discharge concentrations are looked at.

## Down hole

Conditions:

- elevated temperatures of 120-150 °F
- high pressure
- potential of presence of unspent acid

Under the above conditions, DBNPA will be expected to undergo complete hydrolysis.

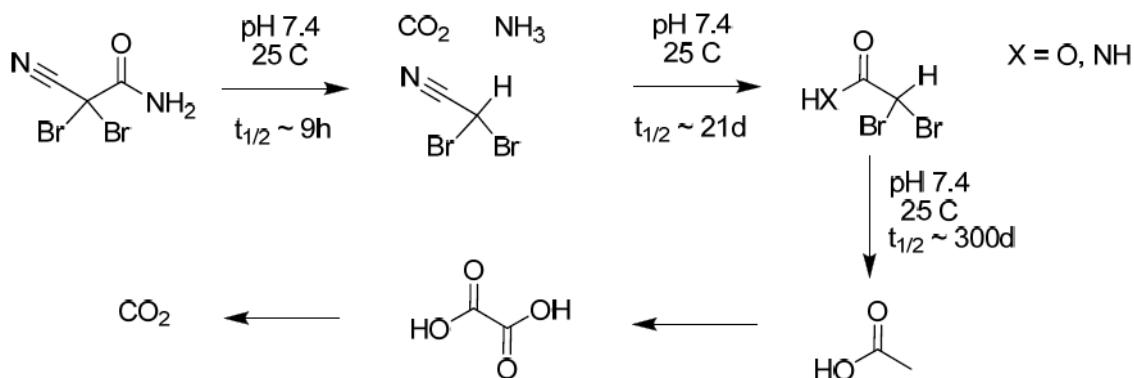


Figure 14. Hydrolytic Degradation Pathway for DBNPA (Williams et al., 2010)

## Transformation in the Environment

### **Reactions in Soil**

These types of reactions would be the result of potential surface spill.

Reactions:

- Biodegradation by microorganisms in the soil
- Adsorption
- Chemical degradation
- Hydrolysis

DBNPA is expected to disappear faster in soil than in surface water mostly due to chemical or microbial degradation (note: if DBNPA is available in concentrations below the inhibitory levels of the microbes). Chemical degradation may also be due to reactions with natural occurring sulfites or bisulfites. Degradates found include dibromoacetic acid and 2-cyanoacetamide which will most likely be biodegraded within 30 days.

### **Reactions in Surface Water**

This scenario would be based on a potential surface water spill.

Reactions:

- Photolysis
- hydrolysis

Potential degradates include cyanoacetic acid, cyanoacetoamide, malonic acid and oxalic acid. Having relatively short half-lives, most of these products will disappear. The most stable is dibromoacetic acid (1/2 life of 300 days at 25°C days). However, DBAA is less toxic on aquatic life than DBNPA. Oxalic acid will decarboxylate to carbon dioxide.

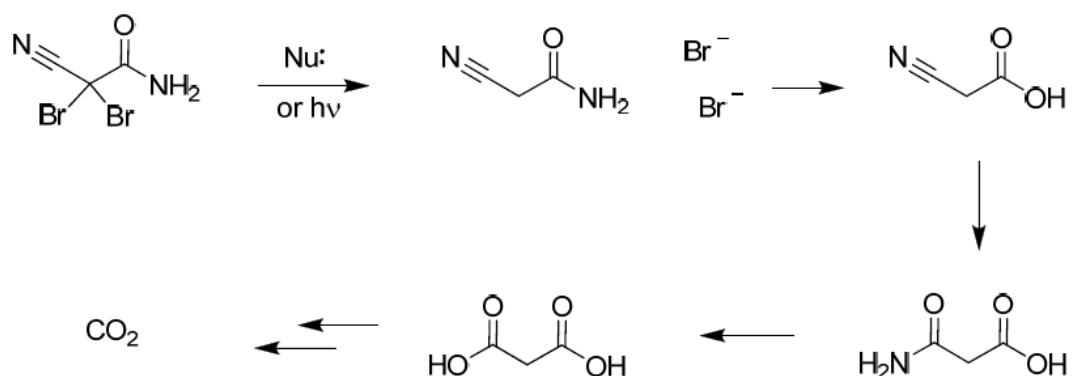


Figure 15. Reaction with DBNPA with nucleophiles and sunlight (Williams et al., 2010)

### Reactions During Flowback Storage

Potential reaction in the storage tank of unspent DBNPA would be pH and resident dependent.

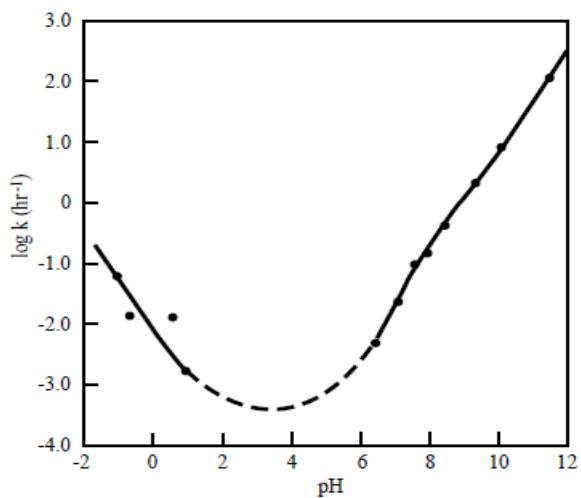


Figure 16. pH profile for the hydrolysis of DBNPA at 25°

pH	$r_{1/2}$	Temp °C
3.9	2,140	23
6	155	25
6.7	37.0	25
7.3	8.8	25
7.7	5.8	25
7.7	145	0
8.0	2.0	25
8.9	0.34	25
9.7	0.11	25
9.7	1.5	0

*Table 8. Rates of Hydrolysis of DBNPA*

Potential products of the incomplete hydrolysis of the biocide in water include dibromoacetonitrile, dibromoacetic acid, tribromoacetonitrile, and tribromoacetoamide.

### **Wastewater Treatment**

Unspent biocide can be deactivated prior to treatment using a reducing agent, however according to literature (Tamblin, 2010), flowback waters from the Marcellus Shale were tested for toxicity prior to the POTWs acceptance of flowback and it was determined that the flowback did not have significant biocide concentrations to impact the function of the wastewater treatment plant.

### **Conclusion**

According to this evaluation of the reactions and the chemical transformations of DBNPA during and after the process of the well stimulation, it does not appear that the biocide will persist in the soil after a potential spill or aquifer communication with flowback fluids. This can be concluded by 2, 2-Dibromo-3-nitrilopropionamide's ability to hydrolyze and biodegrade rapidly in the soil.

In the event of a potential spill on surface water, at the lower concentrations of DBNPA found in flowback, it can be expected that the biocide would degrade rapidly (half-life of less than 5 hours) due to hydrolysis and photolysis.

The next step of the assessment would be to perform a toxicity assessment to determine carcinogenicity on some of the more persistent biocide degradates and then determine their exposure.

### **References**

Exner J. H., Burk G. A. and Kyriacou D. "Rates and products of decomposition of 2,2-dibromo-3-nitrilopropionamide", 1973 *J. agric. Fd Chem.* 21, 838- 842

Terry M. Williams, "Deactivation of Industrial Water Treatment Biocides". The Dow Chemical Company; Heather R. McGinley, The Dow Chemical

Stephen Klaine, George Kobb, Richard Dickerson, Kenneth Dixon, Ronald Kendall, Ernest Smith, Keith Solomon "An ecological risk assessment for the use of the biocide, DBNPA, in industrial cooling towers". 1996. *Environmental Toxicology and Chemistry* 15: 21-30  
Michael E. Tamblin. One POTW's Acceptance of Hydrofractured Water *Clear Water*, Winter 2010, Vol. 40, No. 4 pgs. 40-43  
Kargbo D. M, Wilhelm R. G, Campbell D. J. "Natural gas plays in the Marcellus Shale: challenges and potential opportunities." *Environ Sci Technol.* 2010 Aug 1;44(15):5679-84.

# Shale Gas Development and Related Water-Resource Investigations in New York State –Cooperative Projects to Promote Public Understanding

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The U.S. Geological Survey (USGS), in cooperation with various partners, is performing water resource studies and continue to develop projects to collect, analyze, and provide water-resource information to New York State agencies, the residents of the State, the gas industry, and others to understand, protect, and promote the transparent and sustainable use of the Nation's water resources.

Current projects include valley-fill aquifer mapping and hydrogeologic characterization in the Southern Tier counties of New York and recurring ambient ground-water quality assessments throughout the State as part of the USEPA/New York State Department of Environmental Conservations (NYSDEC) 305-(b) water quality program. USGS has also assisted the Susquehanna River Basin Commission (SRBC) in their implementation of a real-time stream water-quality program in the Upper Susquehanna River Basin in both New York and Pennsylvania. These programs build on over 100 years of unbiased geologic and hydrologic data collection and interpretation by the USGS.

Two USGS reports have recently been released which are quite useful to State regulators, the gas industry, and the general public in understanding surface water characteristics and estimating availability of low-flow in the Susquehanna River Basin in New York - *“Low flow of streams in the Susquehanna River basin of New York”* by A. D. Randall, 2010, U.S. Geological Survey Scientific Investigations Report 2010-5063, 57 p. Relating to groundwater quality and the Marcellus shale, the location of the fresh water/ salt water interface in the Southern Tier of New York was reported in – *“Evaluation of well logs for determining the presence of freshwater, saltwater, and gas above the Marcellus Shale in Chemung, Tioga, and Broome Counties, New York”*, by J.H. Williams, 2010, U.S. Geological Survey Scientific Investigations Report 2010-5224, 27 p.

Pending projects include *“Hydrogeologic Characterization and Water-Quality Assessment in Relation to Marcellus and Utica Shale Gas Development in Otsego County, New York”*. This project will involve the gas industry, Otsego County agencies, one or more local universities, several State agencies, and the USGS to characterize the surface and groundwater resources of Otsego County through the sharing, compilation, and distribution of several sources of information from existing and newly-collected water quality and geologic data. This pilot study

will serve as the basis for an anticipated state-wide, shared database of information available for all to utilize during and following the production of shale gas resources in New York State.

The project would utilize 1.) water well and gas well information collected by the State and the gas industry, 2.) geologic information mapped by the New York State Geological Survey which would be enhanced by the collection of new geologic data during the drilling of gas wells and water wells throughout the County, 3.) the evaluation of surface and ground water-quality data that currently exist and the addition of new water-quality data collected before, during, and following gas well drilling, hydrofracking, and long-term gas production, and 4.) the collection and utilization of natural gas ‘fingerprinting’ (isotopic gas analysis), to identify thermogenic sources of natural gas (old gas) that exist in the bedrock of New York, as well as other (newer) sources of natural gas, such as “swamp gas”, landfill gas, and gas found in unconsolidated glacial deposits “drift gas”.

Another project would document historic water-quality data collected by the USGS to serve as a retrospective assessment of stream water-quality parameters – primarily specific conductance and total dissolved solids and chloride data, where available, from the USGS National Water Information System (NWIS) database. The specific conductance data would serve as a baseline to compare current and future surface-water conditions. This study would be enhanced by targeted programs to collect current specific conductance data in New York streams to confirm and update the previous dataset, as well as studies being carried out by other agencies, for instance, the Susquehanna River Basin Commission. The SRBC currently provides near-real-time water quality data for about 40 selected small and large watersheds throughout the shale-gas region of New York and Pennsylvania within the Susquehanna River watershed.

All of these projects provide various water and geologic resource information which is critical in understanding existing hydrogeologic conditions in New York. These projects would serve numerous water-resource agencies, regulators, the gas industry, and the residents of New York by providing this information to understand and properly protect and manage the use of these resources, as well as increase our ability to evaluate impacts during the long-term development and production of shale gas in New York State. Without these data, stakeholders are missing key information required for the clear understanding and proper management of New York’s surface and groundwater resources, and how shale gas development may or may not impact these resources.

## Glossary of Terms

The sources of the definitions found in this glossary are noted at the end of each definition. Sources include the following:

Abbreviated Source	Full Source Name
SPE	Society of Petroleum Engineers Exploration & Production Glossary ( <a href="http://www.spe.org/glossary/wiki/doku.php/">http://www.spe.org/glossary/wiki/doku.php/</a> )
Schlumberger	Schlumberger Oilfield Glossary ( <a href="http://www.glossary.oilfield.slb.com/default.cfm">http://www.glossary.oilfield.slb.com/default.cfm</a> )

### ABBREVIATIONS

<b>2-BE</b> 2-butoxyethanol
<b>AEM</b> anion exchange membranes
<b>AF</b> acre-feet
<b>ASTM</b> American Society for Testing and Materials
<b>ASWCMC</b> Appalachian Shale Water Conservation and Management Committee
<b>ATSDR</b> Agency for Toxic Substances and Disease Registry
<b>bbls</b> barrels
<b>Bcf</b> billion cubic feet
<b>BCF</b> billion cubic feet
<b>BEM</b> beneficial use economic module
<b>BLM</b> Bureau of Land Management
<b>BOPD</b> barrels of oil per day
<b>BPM</b> barrels per minute
<b>BSM</b> beneficial use screening module
<b>BSWCMC</b> Barnett Shale Water Conservation and Management Committee
<b>BSWMC</b> Barnett Shale Water Conservation and Management Committee
<b>BTEX</b> benzene, toluene, ethylbenzene, and xylene
<b>CAE</b> chemicals for analytical evaluation
<b>CDI</b> capacitive deionization
<b>CEM</b> cation exchange membrane
<b>COC</b> contaminant of concern
<b>COGA</b> Colorado Oil and Gas Association
<b>COGCC</b> Colorado Oil and Gas Conservation Commission
<b>DAF</b> dilution attenuation factor
<b>DBNPA</b> 2, 2-dibromo-3-nitrilopropiamide
<b>DOE</b> US Department of Energy
<b>E&amp;P</b> exploration and production
<b>ED</b> electrodialysis
<b>EDI</b> electrodeionization
<b>EDR</b> electrodialysis reversal
<b>ESP</b> electric submersible pumps
<b>EVRAS</b> evaporation reduction and solidification system
<b>FO</b> forward osmosis
<b>GIS</b> geographic information system
<b>HDPE</b> high density polyethylene

**HF** hydraulic fracturing  
**HRB** Horn River Basin  
**ISIP** instantaneous shut in pressure  
**IX** ion exchange  
**LSU** Louisiana State University  
**MD** membrane distillation  
**MF** microfiltration  
**MGD** million gallons per day  
**MLE** maximum likelihood estimator  
**MMCF** million cubic feet  
**MMCFD** million cubic feet per day  
**MSC** Marcellus Shale Coalition  
**MSDS** Material Safety Data Sheets  
**MVR** mechanical vapor recompression  
**NORM** naturally occurring radioactive material  
**O&G** oil and gas  
**PADEP** Pennsylvania Department of Environmental Protection  
**PAH** polynuclear aromatic hydrocarbons  
**PCB** polychlorinated biphenyls  
**POTW** publicly-owned treatment works  
**PP** polypropylene  
**PTFE** polytetrafluoroethylene  
**PVDF** polyvinylidene fluoride  
**RBCA** risk-based corrective action  
**RCRA** Resource Conservation and Recovery Act  
**RO** reverse osmosis  
**RPSEA** Research Partnership to Secure Energy for America  
**RRAA** Red River Alluvial Aquifer  
**RRC** Texas Railroad Commission  
**RRERP** Red River Education & Research Park  
**SAB** Science Advisory Board  
**scf/d** standard cubic foot per day  
**SRBC** Susquehanna River Basin Commission  
**SWD** saltwater disposal well  
**TAL** target analyte list  
**TCEQ** Texas Commission on Environmental Quality  
**TCLP** toxic characteristic leaching procedure  
**TDS** total dissolved solids  
**TEPH** total extractable petroleum hydrocarbons  
**TIC** tentatively identified compound  
**TOC** total organic carbon  
**TSM** treatment selection module  
**TSS** total suspended solids  
**TWDB** Texas Water Development Board  
**UF** ultrafiltration  
**UIC** Underground Injection Control  
**USACE** United States Army Corps of Engineers  
**USGS** United States Geological Survey  
**WEWG** Water Energy Working Group  
**WQM** water quality module  
**WRCNL** Water Resources Committee of Northwest Louisiana  
**WVDEP** West Virginia Department of Environmental Protection

## **GLOSSARY**

**acre-foot** 1 acre-foot of water = 325,851.4 gallons or 10,344.5 barrels

**connate water** the natural brine occupying the pore spaces. Usually this water is at equilibrium with the minerals in the formation. (SPE)

**evaporite** a formation formed by the evaporation of water from shallow seas. Very low permeability. (SPE)

**flowback** The process of allowing fluids to flow from the well following a treatment, either in preparation for a subsequent phase of treatment or in preparation for cleanup and returning the well to production.  
(Schlumberger)

**kerogen** An initial stage of oil that never developed completely into crude. Typical of oil shales. (SPE)

**pig** a flow line clearing device, pumped through the line with normal flow. (SPE)

**produced water** A term used to describe water produced from a wellbore that is not a treatment fluid. The characteristics of produced water vary and use of the term often implies an inexact or unknown composition. It is generally accepted that water within the pores of shale reservoirs is not produced due to its low relative permeability and its mobility being lower than that of gas. (Schlumberger)

Note: The term produced water is sometimes used synonymously or interchangeably with flowback.

**slick water** a water base fluid with only a very small amount of a polymer added to give friction reduction benefit.  
(SPE)

**sweet** absence of hydrogen sulfide, H<sub>2</sub>S. (SPE)



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