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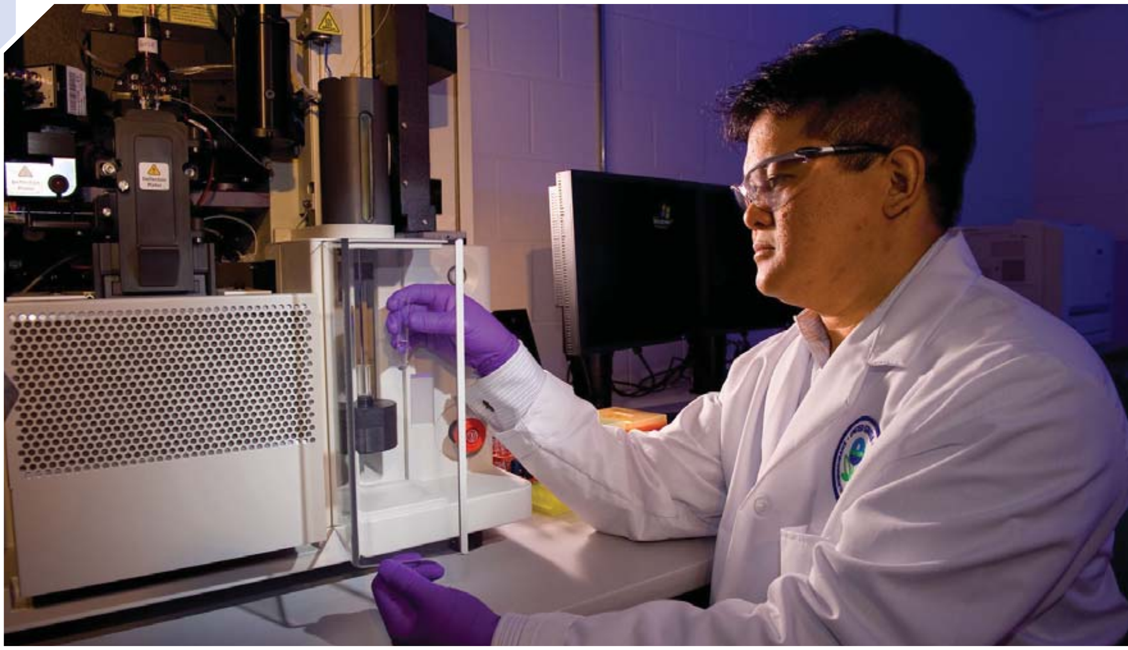
Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods



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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 information related to the 25 presentations given on chemical and analytical methods at the Technical Workshop for the U.S. EPA Hydraulic Fracturing Study held on February 24–25, 2011. This workshop consisted of three sessions or themes: Theme 1–Fracturing Fluid Chemistry; Theme 2–Fingerprinting; and Theme 3–Field and Analytical Challenges. The proceedings include abstracts of the presentations 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 first of four technical workshops on topics relating to the EPA Hydraulic Fracturing Study. The other three workshops are: Well Construction and Operations (Mar. 10–11), Fate and Transport (Mar. 28–29), and Water Resources Management (Mar. 29–30). 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 Chemical & Analytical Methods 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, once again, based on the information submitted to EPA during the attendee nomination process. The workshop lead, Wilma Subra of Subra Company, assisted EPA in finalizing details for the workshop and served as the lead editor of the proceedings document. The theme leads—Cal Cooper of Apache Corporation and Tracy Bank of University at Buffalo for Theme 1, Jennifer McIntosh of University of Arizona for Theme 2, and Kesavalu Bagawandoss of Accutest Labs for Theme 3—served as editors for their respective themes.

Workshop Participants

Name		Affiliation
Michael	Arthur	Pennsylvania State University
Kesavalu	Bagawandoss	Accutest Laboratories
Fred	Baldassare	Echelon Applied Geoscience Consulting
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Susan	Burden	US Environmental Protection Agency
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Cal	Cooper	Apache Corporation
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Robin	Danesi	US Environmental Protection Agency
Jill	Dean	US Environmental Protection Agency
Dennis	Degner	Range Resources
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Mark	Engle	US Geological Survey
Thomas	Fikslin	Delaware River Basin Commission
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Jennifer	McIntosh	University of Arizona
Keith	McLeroy	Texas A&M University

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Harry	Schurr III	CNX Gas/CONSOL Energy
Subodh	Singh	Sinte Gleska University
Mark	Stebbins	CNX Gas Company LLC
Wilma	Subra	Subra Company
Jerry	Swearingen	Baker Hughes
Zoltan	Szabo	US Geological Survey
Kevin	Tanner	Pioneer Natural Resources USA Inc.
David	Thal	Environmental Standards, Inc.
Denise	Tuck, P.E.	Halliburton Energy Services, inc.
Jack	Tuschall	TestAmerica Laboratories Inc
Avner	Vengosh	Duke University
Rock	Vitale	Environmental Standards, Inc.
Frank	Walles	Devon Energy
Rick	Wilkin	US Environmental Protection Agency
Nathan	Wiser	US Environmental Protection Agency

Agenda
Technical Workshops for the Hydraulic Fracturing Study

Chemical & Analytical Methods · February 24-25, 2011

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

February 24, 2011

7:30 am **Registration**

8:00 am **Welcome**

Fred Hauchman, Director, Office of Science Policy, EPA Office of Research & Development
Wilma Subra, Subra Company, Workshop Lead
Pat Field, Facilitator, Consensus Building Institute

Theme 1: Fracture Fluid Chemistry

8:15 am **Technical Presentation Session 1: Fracture Fluid Formulations and Purposes**

HF Fluid Considerations in Marcellus Shale Completions, Dennis Degner, Range Resources

High Rate HF in Non-Marcellus Unconventional Shale, Rick McCurdy, Chesapeake Energy

Cross-link and Linear Gel Composition, Richard Hodge, ConocoPhillips

Old vs. New Trends in HF Chemicals, Denise Tuck, Halliburton

Unconventional Fracturing Fluids: What, Where, Why?, Satya Gupta, BJ Services – Baker Hughes

9:45 am **Break**

9:55 am **Technical Presentation Session 2: Fracture Fluid Interaction with Host Materials**

Inorganic Chemistry of Produced Water in the Appalachian Basin, Elizabeth Rowan, USGS

Produced Formation Water Sample Results from Shale Plays, Nancy Coleman, Chesapeake Energy

Trace Metal Geochemistry and Mobility in the Marcellus Formation, Tracy Bank, University at Buffalo

Fracture Fluid Additives and Formation Degradations, George King, Apache Corporation

11:10 am **Break**

11:20 am **Technical Presentation Session 3: Fracturing Fluid Degradation Products**

What Can You Expect or Not – Chemical Breakdown and Degradation, Denise Tuck, Halliburton

Evaluation of Radionuclides as Degradation Products of Host Materials in Response to Altered Fluid Chemistry Environment, Zoltan Szabo, USGS

12:30 pm **Lunch**

Theme 2: Fingerprinting

1:30 pm **Technical Presentation Session 4: Determining Ambient Groundwater Conditions**

Chemical and Isotopic Tracers of Natural Gas and Formation Waters in Fractured Shales, Jennifer McIntosh, University of Arizona

Distinguishing the Source of Natural Gas Accumulations with a Combined Gas and Co-Produced Formation Water Geochemical Approach: A Case Study from the Appalachian Basin, Stephen Osborn, Duke University

The Origin of Some Natural Gases in Permian through Devonian Age Systems in the Northern Appalachian Basin and the Relationship to Incidents of Stray Gas Migration, Fred Baldassare, Echelon Applied Geoscience Consulting

2:45 pm **Break**

2:55 pm **Technical Presentations 5: Introduced Tracers**

Tracing Fracturing Fluid Movement with Chemical and Gamma-Emitting Tracers with Verification by Microseismic Recording, George King, Apache Corporation

Designing a Water Quality Program for Shale Exploration, Uni Blake, Gastem USA

3:55 pm **Break**

4:05 pm **Technical Presentations 6: Tracing Fracturing Fluids in the Environment**

Elucidating Water Contamination by Fracturing Fluids and Formation Waters from Gas Wells: Integrating Isotopic and Geochemical Fingerprints, Avner Vengosh, Duke University

Isotopic Tracing of Groundwater Contamination: Techniques, Applications, and Practical Considerations, Michael Lawson, ExxonMobil

Inorganic Geochemistry of Pennsylvania Marcellus Flowback Waters, Carl Kirby, Bucknell University

5:20 **Revisit the Major Discussion Points of the Technical Presentation Sessions**
Wilma Subra, Subra Company, Workshop Lead
Cal Cooper, Apache Corporation, and Tracy Bank, University of Buffalo, Theme Leads -- Fracture Fluid Chemistry
Jennifer McIntosh, University of Arizona, Theme Lead -- Fingerprinting

6:00 pm **Adjourn for the Day**

February 25, 2011

Theme 3: Field and Analytical Challenges

8:00 am **Technical Presentation Session 7:**
Sampling Issues – Representativeness, Handling, Preservation
Representativeness of Flowback Fluid Samples: Impacts of Post-Withdrawal Evolution and Temporal Variability of Composition, Mark Engle, USGS

Practical Quantitation and Method Reporting Limits
Quality Assurance, Quality Control and Method Performance Considerations for Chemical Testing: Samples Impacted by Hydraulic Fracturing Fluids, David Thal, Environmental Standards, Inc.

Determination of Total Organic Carbons (TOC) in Difficult Sample Matrices Utilizaing the Supercritical Water-Oxidation TOC Prodedure, Keith McLeroy, Texas A&M University

Practical Quantitation Limits, Method Detection Limits, Interferences and Dilution Challenges in Fracturing Fluid Analyses, Kesavalu M. Bagawandoss, Accutest Labs

9:30 am **Break**

9:40 am **Technical Presentation Session 8: Interference and Dilution Challenges Including Radionuclides**
Radiochemical Analytical Challenges with Hydraulic Fracturing Fluids, Terry Romanko, TestAmerica Labs

Analytical Challenges of Radionuclides in Brines, Zoltan Szabo, USGS

10:55 am **Revisit the Major Discussion Points of the Technical Presentation Session**
Wilma Subra, Subra Company, Workshop Lead
Kesavalu M. Bagawandoss, Accutest Labs, Theme Lead – Field and Analytical Challenges

12:00 pm **Closing Discussions**
Jeanne Briskin, Hydraulic Fracturing Research Task Force Leader, Office of Science Policy, EPA Office of Research & Development
Wilma Subra, Subra Company, Workshop Lead

Summary and Abstracts from Theme 1: Fracture Fluid Chemistry

Summary of Presentations for Theme 1: Fracture Fluid Chemistry

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Technical Presentations

The first set of technical presentations in this theme addressed the formulation and use of fracture fluids.

Dennis Degner, Range Resources, discussed the purposes of and need for the most common chemical additives used in Marcellus Shale fracture treatments. Fracture fluids in the Marcellus, according to Mr. Degner, are typically "slickwater" designed fracture treatments, which are water-based fracture fluids. Mr. Degner identified the most common fracture fluid additives as friction reducers, biocides, and scale inhibitors. These chemicals are added in small concentrations to the fracturing fluid and are monitored throughout the fracturing operations to ensure that the correct concentrations are maintained. Mr. Degner believes monitoring of chemical concentrations is important when produced water is recycled and reused for fracturing.

Rick McCurdy, Chesapeake Energy, discussed the most common chemicals used in fracture fluid in four additional shale plays (Fayetteville, Barnett, Eagle Ford, and Haynesville). Mr. McCurdy discussed the functions of potassium chloride substitute, quaternary amine surfactant, hydrochloric acid (HCl), acid inhibitor, iron control agent, gel, crosslinkers, and breakers in fracturing fluid. Mr. McCurdy described Chesapeake Energy's Green Frac program, which was implemented to evaluate potential environmentally-friendly alternatives to some additives, as well as the potential for eliminating non-critical additives. Specific chemicals added to fracturing fluids were identified, but the range of concentrations of these chemicals was not discussed.

Richard Hodge, Conoco Phillips, discussed the composition of crosslinked and linear gels. Mr. Hodge stated that gelling agents and crosslinkers in fracture fluids increase the molecular weight of polymers in the fluids to increase fluid viscosity for improved transportation and delivery of the proppants into the induced fractures. Breakers are then added into these fracture fluids to "break up" (reduce the viscosity of) the crosslinked polymers at the bottom of the wellbore to promote return of the fracture fluids to the surface.

Denise Tuck, Halliburton, discussed technological advances in HF. Historically, there had been a large number of oil-based operations, but these decreased as the industry focused more on water-based operations, according to Ms. Tuck. The newest technology used by Halliburton is an advanced dry polymer blending. Halliburton uses a scoring index to rank their additives based on health, safety, and environmental impact. Ms. Tuck stated that new fracturing fluid designs used by Halliburton involve chemicals sourced from the food industry.

Satya Gupta, BJ Services–Baker Hughes, discussed the use of unconventional fracture fluids in tight gas formations with adverse capillary effects. In these conditions, water-based fracturing fluids could be replaced by alcohol-based fluids, hydrocarbon-based fluids, or liquid carbon-based fluids, or enhanced by surfactants.

<u>The second set of technical presentations addressed fracture fluid interaction with host materials</u>.

Elizabeth Rowan, United States Geological Survey (USGS), discussed the chemical composition of formation waters in the Marcellus Shale. Her research found that total dissolved solid (TDS) values in produced water from the Marcellus are similar to that of the formation waters in older formations, as well as some Middle-Upper Devonian sandstones; the waters were found to be high in sodium chloride and calcium chloride, and low in sulfate and carbonate. The correlation between radium concentration and TDS suggests that salinity could possibly be used as a predictive tool in the Appalachian Basin. Dr. Rowan observed sodium/bromide and calcium/bromide ratios that suggest evaporated seawater may be the dominant salinity source.

Nancy Coleman, Chesapeake Energy, discussed a review of produced formation water data from four shale formations (Marcellus, Barnett, Fayetteville, and Haynesville) to support Chesapeake Energy's baseline water sampling program. The review found that produced formation waters appear to be variable within and between formations, but that some generalizations can be drawn. The concentrations of TDS and divalent cations, such as barium and strontium, appear to increase with time after fracturing and appear to correlate with each other. Ms. Coleman believes radium-226 and radium-228 are the most useful parameters for gaining information about radionuclides. Ms. Coleman also outlined the most common volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in produced formation water and noted that their concentrations are can vary but are typically low.

Tracy Bank, University at Buffalo, presented a study investigating the trace metal geochemistry of the Marcellus Shale through core samples, well cuttings, and outcrop samples. The study found high concentrations of zinc throughout the Marcellus and no significant differences between the concentrations of most metals in core versus outcrop samples. The study further described the correlation of uranium with total organic compounds throughout the formation (using the new TOF SIMS element mapping technique) and also suggested that there may be some positive correlation between uranium and total organic carbon. Also, extraction studies showed that metals, including uranium, could be mobilized from the shale in fluid-rock interactions.

George King, Apache Corporation, discussed the chemical and physical reactions that can occur in the open wellbore, induced fractures, natural fractures, and the surrounding matrix. These reactions occur as a result of the chemical interactions between fracture fluids and the geologic target formations during the HF process. One of the limiting factors on these reactions is the low permeability of shale, which, according to Mr. King, limits the access of fracture fluids to the formation materials. He also summarized the decomposition reactions of the most common fracture fluid additives, and noted another reaction variable to consider is re-precipitation of compounds over time.

The third set of technical presentations addressed fracture fluid degradation products.

Denise Tuck, Halliburton, discussed broad classes of compounds that can derive from native reservoir fluid, fracture fluid, or raw water. Depending on downhole conditions and water/fluid composition, Ms. Tuck stated that the following classes of chemicals can be found: salts, metals, hydrocarbons, sulfides/sulfates, carbonates/bicarbonates, biocides, pesticides, and naturally occurring radioactive material (NORM).

Zoltan Szabo, USGS, introduced a number of techniques for evaluating the presence of radionuclides in produced waters including: isotope ratios, degradation experiments, microfocused X-ray fluorescence, and fission-track autoradiography. According to Dr. Szabo, further studies should be be based on existing information of NORM distribution in solids to assess what NORM might be expected in produced water. Due to high variability between rock formations, Dr. Sazbo believes there may not be one single technique that will work in every situation for identifying NORM.

Summary of Discussions Following Theme 1: Fracture Fluid Chemistry Presentations

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Crosslinked systems and unconventional fluids. The presenters noted that the purpose of using crosslinked gels is to increase the viscosity of fracturing fluids containing a heavier, coarser proppant while minimizing the amount of gel used. At the end of a fracture job using a crosslinked system, participants discussed the use of breakers to reduce the size of the polymers, thereby reducing the viscosity of the fluids and promoting the return of fracture fluids to the surface. The presenters stated that foams are created immediately prior to injection and continuously from two lines (one containing the foaming agent and one containing the fluid or gas) located at the wellhead. The presenters also stated that diesel has not been widely used as a fracturing fluid in the United States since the 1970s. A participant mentioned that analyses for diesel range hydrocarbons (DRH) may not be an accurate assessment of hydraulic fracturing impacts to groundwater because DRH is often found in flowback water though they are not part of the fracturing fluid.

High pH conditions in the wellbore. Participants discussed the pH conditions in the wellbore and strategies of managing pH. Raising the pH of HF fluids is accomplished in various ways according to participants, such as the addition of sodium hydroxide or potassium hydroxide; potassium hydroxide, in particular, is often used in conjunction with borate fluids. In addition, the presenters stated that when brines of different composition are mixed for injection, reactions occur that can lead to the precipitation of compounds from the fluids.

Viscoelastic surfactant-based (VES) systems. The presenters noted that a majority of VES system use is in Canada. One presenter stated that very few jobs (<5%) in the United States use this type of HF system.

Recycling. A number of workshop participants asked questions and expressed concern about the repeated reuse of produced water. The presenters emphasized that the fracture fluid composition is monitored and fewer chemicals (such as friction reducers and scale inhibitors) might be added based on what monitoring identifies as already present in the (recycled) fluid from the initial injection. One participant noted that much less fluid is recovered than is injected into the well. The fate of the water not recovered depends on the formation. Many companies test produced water from their wells 30, 60, and 90 days after injection and throughout the life of the well, according to one participant. High salinity sample matrix and lack of appropriate methodology were mentioned as analytical limitations to analyzing flowback solutions for metals. In the case of testing for biocides in the flowback water, participants claimed the success of the initial treatment is assessed and follow-up treatment of the well is performed as necessary. The presenters stated that there are limiting factors to the reuse of flowback water, such as the changing downhole conditions that may affect viability of recycled flowback water or the (high) cost of treatment systems to appropriately treat the water for reuse.

Similarity of fluid chemistries. The presenters noted that the typical fracture fluid chemistries used across the industry are very similar with minor differences due to proprietary additives. Presenters noted that when unconventional fracture fluids are employed, the composition of these fluids is usually disclosed. Several participants indicated that the specific fluid composition used in a particular fracture job is highly dependent on the geologic formation and its compositional properties and also on location-specific physical properties such as depth, pressure, temperature and geomechanical properties.

USGS study. Participants asked specific questions about the USGS study described in Dr. Rowan's presentation. In this study, radium concentrations were measured using gamma ray spectrometry. Radium was present in formation waters below its solubility limit and is not affected by changes in temperature and pressure (which can accompany extraction of flowback water). Thorium has been investigated in previous studies but was only found at levels below the detection level and was not included in the study as a possible tracer. From a comparison of calcium bromide versus sodium bromide concentrations, USGS found that a large component of the salt in the Marcellus Shale is likely derived from evaporated ancient seawater rather than from halide dissolution. Only the VOCs and SVOCs mentioned in Dr. Rowan's presentation were targeted for analysis.

Chesapeake Energy's Produced Water Sampling program. A participant asked about glycols with regard to the Chesapeake review. Although glycols were investigated as part of the review, Chesapeake is not satisfied with the analytical methods used and was unable to draw conclusions about the occurrence of glycols in the produced formation waters from the target shale formations studied. Total as well as dissolved arsenic was investigated by Chesapeake and found to be below the detection limits for most samples.

University at Buffalo study. A participant asked about the HCl extractions described in Dr. Bank's presentation. Dr. Bank explained that the determination of the time periods for HCl extractions of uranium was estimated based on industry practice. The HCl extractions demonstrated different metal extractabilities between core and outcrop samples. Differences among organic carbon compounds in the shale were not investigated in Dr. Bank's study.

Radium in flowback water and as a possible tracer. Participants suggested that treatment of radium-containing flowback water could, due to the half-life of radium, cause a buildup of radium in the treatment sludge and pose a solid waste disposal issue. Some participants suggested that radium could be used as a potential tracer because the isotopic ratio of radium species in the Marcellus is different from the ratio in other aquifers. Other participants noted that there could be problems distinguishing the source of a radium tracer (e.g., from the Marcellus or from other subsurface sources) in the Marcellus Shale (which also has different radium isotopic ratios than those found in the shallower black shale horizons). In addition, radium can be mobile in groundwater. Participants noted that is important to have baseline and background information on formation waters so that the composition of flowback water (a composite of fracture fluids, native formation fluids, and any products of the interaction of the two) can be better understood. Participants indicated that uranium is less useful as a tracer due to its much longer half-life. Analysis of well cuttings can indicate the chemicals, elements, or compounds, in addition to uranium and radium, present in the formation. Participants stated that uranium and radium decay products such as polonium and radon can be distributed in the rock matrix and can be found in solution in formation fluids or flowback water.

Degradation products. Participants noted that some materials (e.g., endocrine disruptors and carcinogens) are not present in flowback water and analytical tests could be conducted to confirm this and reassure the public. Participants indicated that petroleum distillates found in flowback water come from some carrier fluids in the fracturing fluids as well as from some additives. Treatment of petroleum distillates can break down the hydrocarbons (e.g., mineral oil) used as carriers in fracture fluids.

Abstracts for Theme 1: Fracture Fluid Chemistry

Abstracts were submitted to U.S. EPA by the presenters for use in this proceedings document. Not all presenters submitted abstracts of their presentations.

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Hydraulic Fracturing Fluid Considerations in Marcellus Shale Completions

Dennis L. Degner
Range Resources Appalachia, LLC

Hydraulic fracturing (completion) has become a key operation when developing shale gas reservoirs. Like all industries and even families, the natural gas industry uses certain chemicals as a normal part of its daily business. Chemicals used during the fracturing process are a vital component to a successful completion. The chemicals used help reduce surface treating pressures, aid in placement of the propping agent (sand) within the deep, downhole formation, and help maintain fluid properties that meet design specifications. The chemicals most commonly used in Marcellus Shale fracture treatments are friction reducer, biocide, and scale inhibitor. These chemicals are mixed in very low concentrations with water (referred to as a slickwater frac) and make up < 1% of the total job volume.

A friction reducer (FR) is one of the common chemicals used in Marcellus hydraulic fracturing operations. The friction reducer is necessary to reduce the frictional effects (extra pressure) that occur as water is pumped down the long pipe (wellbore) during the hydraulic fracture treatment. In Marcellus completions, there is often 10,000 ft of pipe cemented into the ground. Without using a friction reducer, the surface pressure would be higher than desired to reach the required pump rate during the treatment. Friction reducers are commonly a polyacrylamide polymer that is added at low concentrations (± 0.5 gal/Mgal). Once FR is added to the base fracturing fluid the viscosity remains close to that of water (< 5 cps) while the frictional effects are greatly reduced. FR often comes from the manufacturer in dry powder form, but is most commonly pumped as a liquid by mixing with a mineral oil base fluid to stabilize the material until it's injected into the water stream and pumped downhole. Historically they have worked best with fresh water fluids, but recent advancements in technology have made it possible to pump salt tolerant versions when re-using produced salty water in Marcellus completions. Flow loop testing was conducted in the development of these new chemicals to aid in selection based on fluid salinity. When using produced water in the completion, pre-job water testing is done to verify which FR is required to ensure proper application. A polyacrylamide is commonly used in many industries and can be found in children's toys, and used for soil stabilization in addition to several other uses.

Hydraulic fracture treatments are pumped with various water sources ranging from ground, surface, and produced water environments. Once the source water is identified, samples are captured and tested to determine the amount of bacteria present. The source water and ambient temperature can be strong drivers in the amount of bacteria present, similar to the drivers controlling growth of pond algae. Based on the level of bacteria already present in the water a biocide chemical will be added to the water at a proper loading rate to prevent microbiological influenced corrosion of the downhole pipe, formation souring (H_2S), or other safety/production concerns. Biocide is also added to prevent microbial growth from occurring downhole which could restrict flow from the created hydraulic fracture network. Due to the high biomass content already existing in the water sources used for Marcellus Shale fracturing, an organic biocide is required to achieve the necessary sterilization. A similar chemical approach can be seen in medical equipment sterilization and hand sanitation. Similar to the friction reducer, the biocide is added in a liquid form to the water pumped downhole during the hydraulic fracturing process. Once the well is completed, post-job samples are taken, and testing performed to assess effectiveness of the treatment and for future design optimization. Additional sampling and culture testing occur during the life of a well to ensure bacteria levels remain low.

Based on minerals present in the various fresh and produced frac water sources, there is a potential to create scale during production. Extensive water analysis performed prior to fracturing can detect the tendencies to form scale and identify types most likely to form based on the minerals present in the water and in the Marcellus Shale. Two common scales that can generate in this environment are calcium carbonate ($CaCO_3$) and barium sulfate ($BaSO_4$). Both are expensive to clean within the pipe if they occur, so the purpose of this chemical is to inhibit their formation. $CaCO_3$ can be simple to remove with remedial chemical treatment while $BaSO_4$ requires mechanical removal. To prevent scale from generating, a solvent based scale inhibitor is added into the water pumped downhole. As the volume of produced water used for fracturing increases, the need for adequate scale control will also increase due to minerals dissolving from the shale reservoir into the produced water. Scale inhibitors are added in low concentrations (± 0.1 gal/Mgal) with low level residuals observed after fracturing that help prevent scale from occurring. Similar applications can be seen in municipal water treatments, de-icing agents and household cleaners.

Lastly, a surfactant chemical is pumped on a low percentage of Marcellus Shale completions. The addition of a surfactant reduces surface tension on the fracture face making it easier to recover produced fluids. Testing results have varied resulting in basin specific application. Examples of surfactants can be found in soaps and foaming agents.

Each chemical is electronically monitored and manually strapped for accuracy during the treatment ensuring proper loading. With site specific testing and new chemical development with service companies, industry is able to optimize chemical application while reducing environmental impact in hydraulic fracturing. Best practices with chemical use are shared with industry partners, state agencies and trade groups for transparency and responsible chemical use in Marcellus Shale completions.

High Rate Hydraulic Fracturing Additives in Non-Marcellus Unconventional Shales

Rick McCurdy
Chesapeake Energy Corporation

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Introduction

In a sister publication presented during this workshop, another operator discussed the use of hydraulic fracturing additives in the Marcellus Shale. To avoid unnecessary repetition, this paper will focus on additives used in four other major U.S. unconventional shale plays – the Barnett Shale located in North Texas, the Eagle Ford Shale located in South Texas, the Fayetteville Shale in Arkansas and the Haynesville Shale that lies beneath East Texas and Northwestern Louisiana. The additives used in each play will be discussed, along with comments regarding why they are used, the general chemistries involved with each and the normal usage range in fracturing fluids. Finally, a discussion of the recent trends in the selection of additives will be discussed.

Non-Marcellus Unconventional Shales

Of the four unconventional shales listed above, all are traditional gas plays with the exception of the Eagle Ford. Depending on location, a well in the Eagle Ford can produce gas, gas and condensate or gas and oil. The table below illustrates some comparable physical data for the four shales.

Table 1. Physical data for four shales

Shale Play	Fayetteville	Barnett	Eagle Ford	Haynesville
Average Depth From Surface (ft)	4,500	7,400	9,000	11,500
Bottom Hole Temp (F)	130	190	260	320
Bottom Hole Pressure (psi)	2,000	2,900	6,200	10,000

Of the four, the Fayetteville is the "shallowest" with an average depth of slightly less than one (1) mile beneath the surface of the Earth. On the opposite end is the Haynesville which, on average, can be found more than two (2) miles beneath the surface. As such, these formations are separated from drinking water aquifers by thousands of feet of multiple geologic strata. Often, temperature and pressure increase with depth and that is seen in the data above. The Fayetteville has the lowest bottom hole temperature and pressure and the Haynesville the highest. Temperature has to be taken into account when selecting additives and concentrations for hydraulic fracturing applications.

Typical Additives

In many articles published in various media over the last few years, the number of additives used in hydraulic fracturing is often grotesquely over-stated. In a recent documentary, a statement was made claiming that hydraulic fracturing fluids could contain as many as "596 toxic compounds". Some hydraulic fracturing activities may use as many as 11 additives, but many times the procedures contain far fewer than that. The 11 that may possibly be used are: friction reducer, biocide, scale inhibitor, potassium chloride (KCl) substitute, surfactant, hydrochloric acid, acid inhibitor, iron control agent, gel, cross-linker and breaker (linear and cross-linked gels, along with a few additives that are occasionally required in these fluid systems, will be discussed by another author and will not be discussed in this paper). Following are the purpose, typical chemistry and use concentrations for each additive.

Friction Reducers

This is the product responsible for the term "slick water". Friction reducers are used to reduce interfacial tension between the fluid and the contact surface of the steel pipe the fluid is being pumped through and to maintain laminar flow while pumping. Maintaining laminar, or non-turbulent, flow is critical to achieving the fluid injection rates necessary for hydraulic fracturing of unconventional formations, including shales. The active ingredient in friction reducers is typically a medium to long chain polyacrylamide. When injected into fresh water, the polyacrylamide hydrates and uncoils and prevents turbulent vortices in the moving water. An average usage rate for most friction reducers is 500 to 1,000 parts per million (ppm) and they are injected throughout the entire fluid. On a total fluid basis, they typically account for 0.05% - 0.1% of the total fluid volume pumped.

Biocides

The source water that makes up 99+% of the average hydraulic fracturing stimulation often contains varying concentrations of bacteria that have the potential of causing problems with the additives being used, the overall integrity of the wellbore and surface production equipment and can impart undesirable contaminants to the produced gas stream. Many bacteria can degrade the gels used for building fluid viscosity and have the potential to aggressively attack the metal equipment used both downhole and on the surface for producing natural gas and liquids from the well. Biocides are added to the source water to sanitize the fluid and greatly reduce the concentration of bacteria.

There are several chemistries utilized as biocides in hydraulic fracturing. Historically, glutaraldehyde and blends of glutaraldehyde have been used. Glutaraldehyde has been in use in several industries for many years and has a long history as a disinfectant for medical and dental equipment. Since the late 1990's, a product commonly referred to as THPS (tetrakis hydroxymethyl phosphonium sulfate) has been used in many areas because it degrades in the environment more rapidly that glutaraldehyde. Another product that is highly biodegradable is DBNPA (2,2-dibromo,3-nitriloproprionamide). There are some operators who use sodium hypochlorite (the active ingredient in household bleach) for sanitation of source waters. Regardless of the chemistry being used, it is important to note that all biocide usage is regulated by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and accordingly, each product must be registered for use by the U.S. Environmental Protection Agency (EPA) and by each State in which it will be applied. Biocides are commonly applied throughout the whole hydraulic fracturing fluid at a rate of 75 to 500 ppm and represent 0.075% - 0.05% of the total fluid volume.

Scale Inhibitors

Water used during the hydraulic fracture stimulation often has a potential of producing a mineral scale when coming in contact with naturally occurring water in the producing formation. Additionally, physical changes imparted on produced water (temperature, pressure, etc.) during initial production can cause mineral solids to precipitate from the fluid. To prevent this, Operators use a scale inhibitor injected throughout the hydraulic fracturing fluid. Owing to their compatibility with other fracturing additives, the most commonly used chemistries are carboxylic acid and acrylic acid polymers. Scale inhibitors are usually used at relatively low dosages throughout the frac fluid (75 to 120 ppm) and make up 0.0075% - 0.012% of the total fluid volume.

KCl (Potassium Chloride) Substitute

Most of the unconventional shales contain varying concentrations of water sensitive clays. These clays swell when contacted by fresh water and can potentially shut off flow paths. To prevent this, Operators historically mixed powdered potassium chloride (KCl) in their fresh water at the surface prior to pumping the water downhole. The KCl in the water prevented absorption by the water sensitive clays. With the advent of high volume stimulations of unconventional reservoirs, the process of manually mixing powdered KCl in surface tanks became cumbersome and research was conducted to identify substitutes for powdered KCl. Laboratory testing indicated quaternary amines could prevent adsorption of fresh water by coating the clay particles present in the shale. The most popular chemistry for this application was a product referred to as TMAC (tetramethylammonium chloride).

In 2009, Chesapeake Energy initiated a program focused on looking at the overall environmental footprint of hydraulic fracturing additives to determine if improvements were possible. One of the first targets of this effort was TMAC. Through extensive lab and field testing, a new product, choline chloride, was identified as a very suitable replacement. Choline chloride is commonly used as a nutritional supplement in animal feed, especially as a growth aid for young chickens and it is also used as a nutritional supplement for humans. Chesapeake now uses choline chloride in most areas where KCl substitutes are necessary in hydraulic fracturing activities. Average use concentration for choline chloride is 500 to 2,000 ppm or 0.05% - 0.2% of the total fluid pumped.

Surfactants

Surfactants have been historically used in hydraulic fracturing to reduce interfacial tension between fluid and the shale and between different phases of fluid. In the first instance, the desire is more robust initial water production from the well and in the second, the goal is the elimination of emulsions in shales containing oil and water. The term “surfactant” covers a multitude of products and those used in hydraulic fracturing can be as simple as a laurel sulfate (similar to the ones used in household shampoos) to complex fluoro- and nano-surfactants. Where used, surfactants are typically used at 500 to 1,000 ppm throughout the fluid which would account for 0.05% - 0.1% of the total fluid volume.

Hydrochloric acid

Hydrochloric acid (HCl) is not used throughout the fracturing fluid, but rather usually is used to lead the fluid for each stage. This is done to clear the production casing string of any debris and to dissolve near-wellbore acid soluble minerals present in the shale. Dissolving these minerals promotes additional flow paths for gas and/or oil to make its way to the wellbore and thus improving the production from the well. Calcite ($CaCO_3$), a mineral commonly found in unconventional shales, rapidly reacts with, and is dissolved by, hydrochloric acid. Once this reaction is complete, the only remaining by-products are a soluble calcium salt, water and carbon dioxide.

The hydrochloric acid used in hydraulic fracturing operations is usually 7.5% or 15% active. The amount used is dependent on the number of perforations (openings to the shale reservoir) per well and the mineral composition of the shale. For the major shale plays mentioned earlier, typical usage range is 0.08% - 2.1% of the total fluid pumped (as volume of 15% HCl). However, when looking at the active component, this would actually equal to 0.012% - 0.31% of the total fluid pumped.

Acid Corrosion Inhibitor

While it is desirable for hydrochloric acid remove debris from the production casing, Operators do not want the acid to degrade the integrity of the casing itself. To prevent this, an acid corrosion inhibitor is utilized throughout the entire acid volume. Acid inhibitors tend to be complex products as they are tasked with a protecting the steel casing without reducing the acid’s ability to dissolve iron oxides (mill scale) that is usually present on the surface of the pipe. Acid inhibitors tend to contain amines, amides and/or amido-amines and often contain formic acid as an intensifier for higher temperature applications. Usage rates can vary from 2,000 to 5,000 ppm in the acid only which equates to 0.0004% - 0.0043% of the total fluid volume.

Iron Control

As hydrochloric acid reacts with acid soluble minerals, such as calcite, in the formation and “spends” there is a possibility for any iron oxide mill scale dissolved from the casing to precipitate. This precipitation could potentially block flow channels in the reservoir so iron control agents are used to prevent this from occurring. Iron control products are common organic acids such as citric acid, acetic acid, thioglycolic acid and EDTA (ethylenediaminetetraacetic acid) and incorporate the dissolved iron ion into their structures and prevent it from precipitating. Typical usage in nearly all applications is 5,000 ppm of the acid volume which equals 0.0004% - 0.011% of the total fluid volume.

Recent Trends in Additive Selection

Chesapeake Energy, the American Petroleum Institute and the American Natural Gas Alliance all feel strongly that the risk of contamination to groundwater from hydraulic fracture stimulation of deep shale unconventional gas is extremely miniscule. However, we do realize that there are employees who routinely work around hydraulic fracturing additives and while safety is paramount in our industry, there is always the potential for an accidental surface spill. It was with these two concerns in mind that we forged our Green Frac efforts.

As described above, Chesapeake Energy's Green Frac™ program was initiated in 2009 to determine if it was possible to improve the overall environmental "footprint" of the additives used in our hydraulic fracturing operations. Finding a substitute for the friction reducer, TMAC, was an early, and successful, target of our efforts. Moving forward from that point, Chesapeake has utilized our in-house laboratory, Geophysical, Engineering and Chemical assets to thoroughly evaluate the necessity of every additive in every play. A primary goal was to eliminate any additive that was not absolutely critical to successful completion and operation of our wells. For those we deemed critical, we sought out materials that posed lower risk to personnel and to the environment in the event of an accidental surface discharge. To date, we have either eliminated, have found more desirable substitutes or are in the process of successfully testing substitutes for the majority of additives historically used in hydraulic fracturing of unconventional shales.

Conclusions

- Contrary to what is often published in the media, the typical fluid used to hydraulically fracture an unconventional shale well does not contain "596 toxic compounds". Most frac stimulations contain fewer than eleven additives, including the corrosion inhibitor and iron control agent that is always included in the hydrochloric acid.
- Many of the additives we use are not 100% active. An example is hydrochloric acid which is typically used in a field strength of either 7.5% or 15% active ingredient. If we look at the activity of the various additives, you quickly see that the average hydraulic fracturing fluid contains less that 1% by volume of chemical components. 99% of the liquid volume is water.
- Chesapeake Energy is very proud of our Industry leading program, Green Frac™. Through this program, we have eliminated 20% of the additives used in our fracturing operations. In addition, we have identified and moved to more environmentally friendly substitutes (or have products successfully finishing field tests) for over half of the remaining additives.

Unconventional Fracturing Fluids

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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

Many tight gas formations are water-wet and under-saturated where the initial water saturation in the reservoir is less than the capillary equilibrium irreducible water saturation. The use of water-based conventional fracturing fluids causes water to be trapped in the near-wellbore region, thereby significantly impairing the ability of gas to flow. Formations with sub-irreducible water saturation can be stimulated with fluids that minimize the interfacial tension (such as surfactant gels), minimize the amount of water used in the fluid (such as energized or foamed fluids), dehydrate the formation (such as alcohol-based fluids) or completely eliminate water (such as hydrocarbon-based or liquid carbon dioxide-based fluids). Since the rheology and proppant-carrying properties of these fluids vary, the uses of these fluids are different and will be discussed in detail in the paper. The paper will also present guidelines, based on formation properties, to indicate the need for considering unconventional fluids. Some of the new trends in the development of unconventional fluids are also presented.

Introduction

As the industry moves to extracting gas from tighter and tighter formations, particularly formations such as shales or coalbeds where production is controlled by desorption of the gas rather than matrix flow, fluids that are non-damaging to the proppant pack and formation are becoming increasingly important. Wells with adverse capillary effects due to sub-irreducible water or hydrocarbon saturation also require different fluids to minimize those effects or mitigate effects caused by drilling with the wrong fluid. Several unconventional fluids have been developed and successfully used for these unconventional formations in the last decade.

Adverse saturation in the formation can contribute to productivity impairment. Production has been successfully achieved in formations with matrix permeability as low as 10^{-3} millidarcies (mD). However, adverse capillary forces, which result in high *in situ* saturation of trapped water or liquid hydrocarbons even in very low-permeability formations, make economic production difficult. Low-permeability formations are typically tolerant of only minimal saturation damage due to the sensitivity to capillary retention effects, and rock-to-fluid and fluid-to-fluid compatibility issues. In these wells, the damage from drilling and completion can be overcome by a properly designed frac treatment, which can penetrate beyond the zone of induced invasion and damage.

Fluid Retention

The major cause of productivity impairment in gas wells during drilling, completion and fracturing or workover operations is fluid retention effects. These can include the permanent retention of water or hydrocarbon based fluids or the trapping of hydrocarbon condensate fluids retrograded in the formation during gas production. Bennion and his collaborators have labeled these phenomena aqueous and hydrocarbon phase trapping (Bennion *et al*., 1994, 1996). Capillary forces in the formation are the reason for fluid retention. Capillary pressure forces are the difference in pressure between the wetting (typically water in gas reservoirs) and non-wetting (gas) phases in the matrix. The imbibition effect has been observed as a particularly severe problem in reservoirs where sub-irreducible water saturation exists. Sub-irreducible water saturation may have been created by a combination of factors, including dehydration, desiccation, compaction, mixed wettability, significant height above the free water level in oil reservoirs due to drainage, and diagenetic effects occurring during geologic time. Laboratory capillary pressure measurements supply good approximations of the irreducible water saturation that would normally be expected, but actual reservoir water saturation can be substantially lower, i.e., a sub-irreducible level. The high capillary pressure associated with low-permeability microporous reservoirs is illustrated in Figure 1. Measured capillary pressure values for four rocks with permeability from 0.001 to 1.0 mD are presented to illustrate the greater imbibition effects of water in lower-permeability formations. The capillary pressure of the 0.001-mD core at 40% water saturation is 325 psi greater than that of the 0.01-mD core at initial saturation. This illustrates the higher capillary pressure available in tighter reservoirs to imbibe and trap aqueous liquids due to capillary imbibition. Injecting water-based fracturing fluids into a high-capillarity reservoir results in the creation of a zone of high water saturation in the near-wellbore or near-fracture face area. The relative permeability curves in Figure 2 show how increasing water saturation above the irreducible water saturation results in a dramatic decrease in gas relative permeability.

Gas production results in the affected zone reverting to the irreducible water saturation dictated by the capillary effects of the system and not the sub-irreducible saturation that existed before. The net effect is that the critical producing area of the well retains the increased water saturation, a lowered relative permeability to gas and therefore lower productivity. Several diagnostic techniques are available to estimate these effects (Gupta, 2009). These correlations can be used to estimate compatibility of the formation to water-based fracturing fluids. These are just guidelines, and exceptions abound, particularly for over-pressured reservoirs where the capillary imbibition effects can be overcome in a relatively short time frame (Bennion *et al*., 1996).

Fracturing Fluids

Conventional fracturing fluids include water-based and polymer-containing fluids, hydrocarbon-based fluids, energized fluids and foams. These are not covered in this paper. Unconventional fracturing fluids include non-polymer-containing fluids such as viscoelastic surfactant fluids, methanol-containing fluids, liquid CO_2-based fluids and liquefied petroleum gas-based fluids. The most cost-effective solution is to fracture the formation with the simplest of fluids. Low-viscosity water or hydrocarbon with the fewest additives would be the simplest fluids. However, these have very low proppant transport properties, very little leak-off control and, if pumped at high rates, will result in unacceptable friction. Various additives can control friction, but if the formation has adverse saturation effects, even in tight gas formations with very little leak-off, desired stimulation may not be achieved. Using salts in the fluids can control compatibility with clay containing formations. Depending on pumping conditions, i.e., the shear regime the fluid would experience, there may be need for shear-tolerant or shear-recoverable fluids. For higher-temperature applications, these can be achieved by the use of organometallic or borate crosslinked water-based fluids and crosslinked oil-based fluids. If the gas formations are under-pressured, the fluids can be energized with N_2 or CO_2 or foamed with N_2 or CO_2 or a combination of the two. The foam fluids also provide good leak-off control. If compatibility with water may be an issue due to wetting issues, the use of viscoelastic surfactant fluids can be considered. They also do not damage the proppant pack and can also be energized or foamed. If incompatibility is due to capillary and unloading issues, methanol-containing fluid can be considered. If the incompatibility is severe, then crosslinked methanol-based fluid, liquid CO_2-based fluid or LPG may be the answer.

Viscoelastic Surfactant Fluids

Viscoelastic surfactant (VES) gel systems have been described in the patent literature for friction reduction and as well treatment fluids (Teot, 1981). Its use in everyday life has been around for some time. Its use in fracturing fluids is relatively a new phenomenon, but the patent literature has exploded in this area in the last few years.

Principally, these fluids use surfactants in combination with inorganic salts or other surfactants to create ordered structures, which result in increased viscosity and elasticity. These fluids have very high zero-shear viscosity without undue increase in high-shear viscosity. Thus, they tend to be shear-degradable fluids. As explained by Asadi *et al.* (2002), zero-shear viscosity has been found to be an essential parameter in evaluating proppant transport. Therefore, these fluids can transport proppant with lower loading and without the comparable viscosity requirements of conventional fluids.

The technology of VES systems can be broken down into several categories based on the structure the system creates: worm-like micelles, lamellar structures or vesicles.

As the concentration of surfactant increases in water, micelles start to form. Further increasing the concentration exceeds the critical micelle concentration (CMC) for the surfactant in water; these molecules start interacting with each other. These interactions are based on ionic forces and can be amplified by adding electrolytes (salts) or other ionic surfactants. Depending on the ionic charges and the size and shapes of the surfactants and these counter ions, ordered structures start to form, which increases viscosity and elasticity. The reverse mechanism is true for breaking these systems. The structures can be disrupted by adding other surfactants, ionic additives and hydrocarbons (from the formation or mutual solvents or other solvents) or can be diluted by additional formation water. The most common commercial systems use cationic surfactants with inorganic salts (Teot *et al.*, 1988) or with anionic surfactants (Zhang, 2002).

Anionic surfactants with inorganic salts are also common (di Lullo *et al.*, 2002). Zwitterionic and amphoteric surfactants in combination with inorganic salts have been used (Dahanayake *et al.*, 2004).

The common VES fluids have a temperature limit in the range of 160 to 200 °F without foaming. High-temperature stabilizers have been known to increase the temperature limit to 250 °F. Not all of these fluids are compatible with CO_2. They have been shown to be economical replacements for conventional borate fluids for tight gas applications (Rieb, 2007). At least with one of these fluids, the flowback water from these treatments can be recycled (Gupta and Tudor, 2005, Gupta and Hlidek, 2009). This particular fluid uses a cationic surfactant neutralized with an anionic surfactant. The flowback water, in gas wells, tends to return some of the cationic surfactant and most of the anionic surfactant. The flowback water is typically collected for 24 hours into a tank. Initially, the fluid was filtered to remove any formation fines. Based on experience, it was found that allowing the fines to settle was sufficient to remove the fines. After settling, the middle 75% of the flowback water was transferred to a frac tank and the rest of the required water for the fracturing treatment was made up with fresh water. Using analytical or viscoelastic measurements, additional surfactants were used to reconstitute the fluid. Russell (2001) reported the procedure and well production results from using the recycled fluid in field study in Canada showing no effect of recycling on well production.

These VES fluids are operationally very simple as only one or two additives are added on the fly without any need to hydrate polymers. They do not require any biocides because they do not contain any biopolymers. They do not require additional flowback surfactants because they have inherently low surface and interfacial tension. No additional clay control additives are needed: They contain either salts or cationic surfactants, which have properties similar to KCl substitutes. The surfactants have molecular weights of hundreds, as opposed to the guar polymer with millions.

Viscosity is broken by altering the surfactant properties, by adding other hydrocarbons or by altering the salinity or pH. The regain permeability with these types of systems approaches 100%. Because of the wetting tendencies of the surfactants in some of the VES systems, they are useful even in formations with sub-irreducible water saturation and liquid-trapping issues, despite being aqueous-based.

Viscoelastic Surfactant Foams

A natural extension of VES fluid technology is the VES foams (Zhang, *et al.*, 2002). These foams can be formed with N_2 or CO_2. As mentioned before, not all VES systems are compatible with CO_2. No additional foamers are needed with these systems. The foam viscosity can be adjusted by adjusting foam quality and the viscosity of the base VES system. They have been successfully used in gas formations to 250 °F (Gupta and Leshchyshyn, 2005a). In formations with potential to form water blocks, these fluids are particularly suited because the leak-off fluid still contains the surfactants, which reduce surface tension in the matrix, overcoming capillary forces and helping in recovery of the fluid. These fluids have been shown to be suited for fracturing coalbed methane wells that contain water because the foams control leak-off into the cleats without damage from polymer residue.

With the advent of ultra-lightweight proppants (ULWP), an extension of this technology has been very successful in under-pressured tight gas fields. A liquid suspension of the ULWP in a viscoelastic gel can be added to a stream of nitrogen or CO_2 in the field to form a very high quality (> 85 quality or volume percent) mist as a fracturing fluid, resulting in a partial monolayer frac treatment. This technology has been utilized very successfully in dry, low-pressure, tight formations in shales and coalbed methane wells in the US and Canada.

Emulsion of Carbon Dioxide with Aqueous Methanol Base Fluid

Certain formations have potential to retain even limited water used in foams and VES foams of over 70 quality. These fluids may damage these sensitive formations because of sub-irreducible water saturation and liquid trapping. In these formations, replacing 40% of the water phase used in conventional CO_2 foams (emulsions) with methanol can minimize the amount of water. Gupta *et al.* (2007) showed that a 40% methanol aqueous system yielded the highest viscosity of aqueous methanol mixtures, has a freeze point close to –40 °C (the lowest operating limit for fracturing equipment in the field) and surface tension around 30 dynes/cm. These emulsions use surfactants, which are methanol-compatible foamers, in the place of conventional foamers. Typical CO_2 quality approaches 85, which has resulted in high regained permeability and rapid clean up and production results in several Canadian gas formations (Gupta *et al.*, 2007).

Non-Aqueous Methanol Fluids

In formations with severe liquid (aqueous and hydrocarbon) trapping problems, non-aqueous methanol fluid may be a solution. Over the years, several authors have identified the advantages of alcohol-based fluids (McLeod and Coulter, 1966; Smith, 1973; Tiner *et al*., 1974; Thompson *et al*., 1992; Hossaini *et al*., 1989; and Hernandez, *et al*., 1994). These advantages include, but are not limited to, low freezing point, low surface tension, high water solubility, high vapor pressure and formation compatibility. Methanol is also the fluid of choice for formations with irreducible water and/or hydrocarbon saturation (Bennion *et al*., 1994, 1996b). Three concerns with methanol all relate to safety: low flash point, high vapor density and flame invisibility. With special precautions, as previous authors have identified (Thompson *et al*., 1992; and Hernandez *et al*., 1994), methanol can be safely used in the field.

Several approaches to increasing the viscosity of methanol have been described in the literature (Thompson *et al*., 1992; Hossiani *et al*., 1989; Boothe and Martin, 1977; Crema and Alm, 1985; and Gupta *et al*., 1997). These range from foaming methanol to gelling with synthetic polymers (e.g., polyacrylamide and polyethylene oxide) and modified guar. Attempts were also made to crosslink gelled methanol with metal crosslinkers. However, Ely (1994) described limitations that restrict the use of gelled non-aqueous methanol: solubility of these polymers in both aqueous and non-aqueous methanol, ability to crosslink, ability to break the polymer, and temperature limit.

The most recent development (Gupta, *et al*., 1997; and Mzik, 1993 and 1994) describes a modified guar dissolved in anhydrous methanol crosslinked with a borate complexer and broken by an oxidizing breaker. This system has been successfully used in the field. In under-pressured wells, it has been energized with N_2. There has been an interest in a CO_2-energized methanol fluid for similar formations with severely under-pressured wells. Hence a new polymer that is soluble in non-aqueous methanol and compatible with carbon dioxide was identified. These non-aqueous base gels can be crosslinked with borate at pseudo-high pH (non-aqueous fluids do not have pH) or with zirconium crosslinker at pseudo-low pH for CO_2 compatibility. The special version of this HPG can hydrate in 100% methanol to give viscosity to the base gel and is also compatible with CO_2 without precipitation (Gupta *et al*., 2003).

These fluids can be completely broken with special breakers, resulting in very high regained permeability in the proppant pack and in very sensitive formations. These fluids should be selectively used in gas formations with special safety considerations due to flammability of methanol. These new-generation fluids also do not require any water for hydration or for breaking.

Liquid CO_2-Based Fluids

Fluids based on liquid CO_2 are the real unconventional fluids. The concept and applications of these fluids require outside-the-box thinking. These fluids have been very successfully used in tight gas applications in Canada and several US formations. Their chemistry and physics have been extensively published, as summarized in a paper by Gupta and Bobier (1998) and described in brief here. The family of these fluids consists of pure liquid CO_2 and a binary fluid consisting of a mixture of liquid CO_2 and N_2 to reduce costs.

Conventional fracturing fluids rely on viscoelastic properties to inhibit leak-off from the fracture into the reservoir. Filter cake deposition from long-chain polymers or high filtrate viscosity in oil gel systems provides fluid loss control to establish adequate fracture width. Sufficient fracture width is required to allow proppant placement in the fracture. Liquid CO_2 has very low viscosity (Gupta and Bobier, 1998) and thus does not have the viscosity or filter cake properties to establish fracture widths when pumped at typical rates (i.e., 20 BPM).

Low-viscosity, low-temperature fluids have higher leak-off rates than conventional fluids, but this characteristic has an upper limit that is dependent on reservoir parameters. The use of a gas or liquefied gas makes the fluid compressible. Pumped at high pressure and low temperature, the fluid volumetrically expands when exposed to lower pressure and higher temperature in the formation. The fluid is not in steady state, and thus positive transient effects occur. This thermal expansion effect inhibits leak-off near the fracture face and promotes the development of fracture width. A combination of thermal expansion, relative permeability effects and possible turbulence through small reservoir pore throats curtails leak-off of liquid CO_2 from the fracture into the reservoir.

Several papers have described the unique nature of liquid CO_2 and liquid CO_2/N_2 mixtures as fracturing fluids (Lillies, 1982; Tudor *et al*., 1994; Mazza, 1997; and Gupta and Bobier, 1998). In these systems, the proppant is placed in the formation without causing damage of any kind, and without adding any other carrier fluid, viscosifier or other chemicals. As was described previously, “the use of a reservoir friendly substance like liquid CO_2” (and inert N_2) “offers unique advantages through the elimination of capillary fluid retention and clay swelling” (Mazza, 1997).

These low-viscosity fluids are not an obvious choice of fracturing fluid. However, a large number of jobs have been successfully performed with them (Gupta and Bobier, 1998). One of the major limitations of this technology has been their high treatment cost. Although stimulation treatments using the low-viscosity liquid CO_2 system have been successful, the high rates required to place these jobs and the associated frictional losses raised horsepower requirements.

Liquid CO_2-Based Foam Fluid

Several attempts have been made to increase the viscosity of CO_2-based fluids while trying to maintain the conductivity and formation compatibility of these fluids — with very little operational success (Bullen *et al*., 1987). The liquid CO_2-based foam fluid consists of a foam of N_2 gas in liquid CO_2 as the external phase stabilized by a special foamer soluble in liquid or supercritical CO_2 (Gupta, 2003). The main advantage of this fluid is the additional viscosity gained by the foam over liquid CO_2. The use of 75 volume percent of N_2 also makes the fluid very cost-effective and applicable to project frac applications where multiple jobs can be performed in a single day. The fluid has also found niche application in coalbed fracturing in Canada on dry coalbeds where any water introduced into the formation damages the cleats.

Gelled Liquefied Petroleum Gas

Recently, Liquefied Petroleum Gas (LPG) has been discussed in a patent application as a hydraulic fracturing fluid (Loree and Mesher, 2007). The application proposes that LPG can be viscosified and proppant added to the fluid much like conventional fracturing fluid. The application further describes a unique and novel process that safely handles LPG and meters proppant into the gelled LPG stream for fracturing treatments. LPG gases are a mixture of petroleum and natural gases existing in a liquid state at ambient temperatures and moderate pressure (less than 200 psi). Unlike conventional hydrocarbon-based fracturing fluids, the common LPG gases, propane and butane, are tightly fractionated products with over 90% purity. There are many advantages in using liquefied petroleum gases for hydraulic fracturing if it can be done safely. The properties of density, viscosity and surface tension with complete solubility in formation hydrocarbons are very beneficial. Recovery of the LPG very nearly approaches 100%, clean up is very rapid (often within 24 hours), phase trapping is virtually eliminated, and LPG properties allow for extended shut-in times without detriment. Additionally, direct flowback to an available pipeline can be readily achieved. The result is a potential cost-effective stimulation with effective fracture lengths, excellent post-treatment production and the potential for zero flare clean-up.

New Developments

New developments in the area of unconventional fluids have been in increasing the temperature of use of viscoelastic fluids, the use of associative polymers that associate with surfactants that can be used as straight fluid or foams (Gupta and Carman, 2011) and fluids based on produced water that are also based on associative polymers.

Conclusions

Several unconventional fracturing fluids are described in this paper to minimize or eliminate phase trapping issues associated with stimulation of tight gas wells. Proper selection of the fluid depends on the severity of the issues and economics.

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Figure 1. Effect of capillarity on water saturation (after Holditch, 1979)

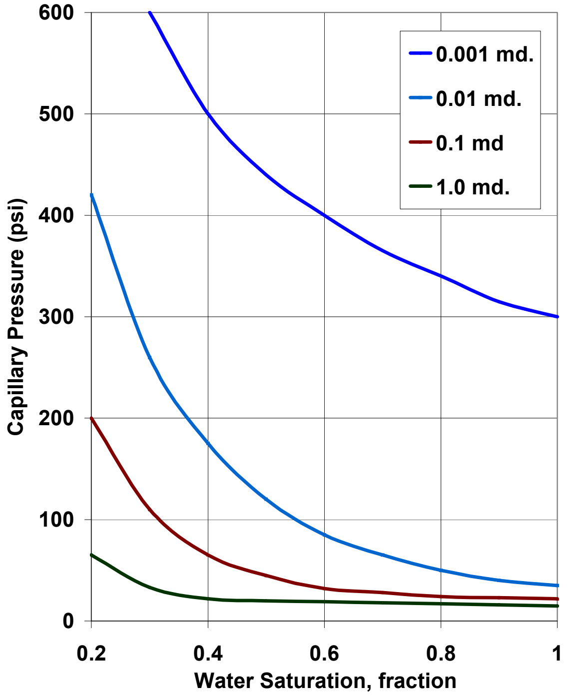
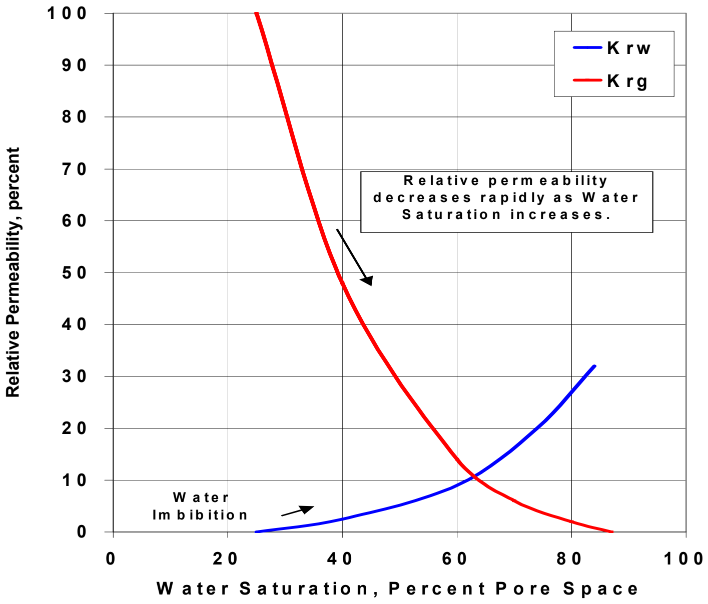


Figure 2. Effect of water imbibtion on relative permeability changes (after Keelan, 1975)



Produced Formation Water Sample Results from Shale Plays

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Chesapeake Energy Corporation (Chesapeake) and Environmental Consultants reviewed non-potable produced formation water sample results available from the literature and other sources. The data review was specifically directed at the chemical characteristics of source water used for hydraulic fracturing fluids, hydraulic fracturing fluids, produced formation water from natural gas wells following hydraulic fracturing activities (i.e., less than 30 or 90 days following hydraulic fracturing), and produced formation water from operating natural gas wells.. The largest amount of data represents sampling conducted of produced formation water from the Marcellus Shale, including the GTI study (Hayes, 2009) and the USGS Produced Water database (USGS, 2010). Additional data was available from private sources. This data set included limited data for three other shale formations, the Barnett, Fayetteville and Haynesville. Some of the data evaluated is subject to attorney-client privilege (herein after “privileged data”).

The zones in the four shale plays from which natural gas is being produced vary in average depth below the surface from 4,500 feet in the Fayetteville to 11,500 feet in the Haynesville. The average depth from the surface to the natural gas producing zones in each of the four shale plays are thousands of feet below the geologic zones which produce potable groundwater. Furthermore, temperatures and pressures found at these depths vary from 130°F and 3,000 pounds per square inch (psi), respectively, in the Fayetteville to 320°F and 10,000 psi, respectively, in the Haynesville. These temperatures and pressures have marked effects on the sampling and field analysis of produced formation waters and create potential safety issues for sampling personnel.

The primary purpose of the produced formation water data review was to support Chesapeake’s baseline water sampling program for potable water. Of major interest was the identification of potential sentinel chemicals and/or radiochemicals that could be included in the baseline potable water sampling program. Further, the review was intended to assist in decision making regarding disposal or treatment for reuse or recycling of produced formation waters.

Data available from the GTI study included general chemistry parameters and metals as well as volatile organic compounds and semi-volatile organic compounds from 70 wells in the Marcellus. The data evaluation included a review of chemicals currently being used in Chesapeake wells during hydraulic fracturing. Initially, Chesapeake had chosen the parameters for analyses based on their potential mobility in groundwater water systems, toxicity, and the availability of analytical methods. Eventually, the complete list found at 40 CFR Part 264, Appendix IX, and commonly associated with groundwater monitoring, was selected. The complete list was specified because many of the chemicals in the treatment fluids are proprietary or not disclosed in information available to Chesapeake. All of the analyses were conducted using EPA analytical methods and analyses were performed by certified laboratories. The majority of analyses were conducted by one laboratory.

Some additional data was available in the privileged data for special volatile organic compounds, primarily glycols, and radiochemistry data. The glycols had been included because of the frequency of use in hydraulic fracturing fluids and in order to evaluate their usefulness as sentinel species.

Both the authors of the GTI study and the sources for the privileged data indicated that there are significant issues regarding sampling of produced formation water. Natural gas is contained under high pressure in specialized equipment that is not designed for producing high quality environmental samples. The sample matrix itself presents challenges such as foaming and changes in surface tension.

Analytical techniques are also impacted by the presence of elevated concentrations of total dissolved solids and chloride. The inorganic and wet chemistry methods were most affected by the presence of high total dissolved solids. Radiochemistry methods are particularly affected by the elevated concentrations of barium and total dissolved solids.

As anticipated total dissolved solids and the divalent cations, including barium and strontium, are elevated in produced formation water samples. The concentrations noted in the data evaluated are consistent with that gleaned from the literature (USGS, 2010). Concentrations of these parameters appear to increase with time following hydraulic fracture activities and remain at high concentrations in the produced formation water from operating wells in each shale formation. The concentrations of barium and strontium appear to correlate to the concentrations of total dissolved solids. Chloride represented the most abundant anion. These data are consistent with the generalized data available in the USGS database.

The literature supports the interaction and release of arsenic from host rock in the presence of refined hydrocarbons products, therefore, a specific review of the arsenic data was conducted. In general, arsenic concentrations were not found in many of the samples above method detection limits. The GTI study found some detectable concentrations of arsenic with produced formation water sampled on day five following hydraulic fracturing having the highest concentration, 124 µg/L. Data available from analysis of produced formation water from the Marcellus prior to disposal confirmed the general absence of arsenic. There were four detected concentrations from 87 fluids samples. The highest detected concentration was 4.2 µg/L. Arsenic was not detectable in the limited data available for the Barnett, Fayetteville and Haynesville formations; detection limits ranged from 1 to 10 µg/L.

In consultation with health physicists from SAIC and IEM, Chesapeake has determined that radium 226 and 228 represent the most useful parameters to provide meaningful information regarding radionuclides. This decision is based on the fact that radium 226 and 228 are more soluble in water, are more potentially mobile, and represent 80 percent of the potential ingested dose of radiation in drinking water. Based on experience with radionuclide analyses in produced formation water, it appears that gamma spectroscopy (EPA Method 901.1) and isotopic analyses of the select decay series provide the most accurate and usable information. It is important for the activity results to be presented accompanied by the standard deviation and minimum detected concentrations in order to put the data in context, particularly for non-detected activity levels.

Certain volatile organic compounds, namely glycols, were also evaluated. Glycols were selected because of their frequency of use in treatment fluids used in natural gas production. EPA Method 8015 has been found to be insufficiently robust to overcome the matrix issues which are attendant to the analysis of produced formation water. The range of detection limits seen in the available data sets ranged from 10,000 to 50,000 µg/L, which does not provide meaningful results. EPA Method 8270 has some utility for larger glycols, such as glycol ethers; however for the smaller, more soluble, ethylene and diethylene glycols, the extraction methods are not useful. Sample results for produced formation water prior to disposal had similar issues with elevated detection limits even when total dissolved solids levels were lower. In these samples, ethylene glycol was found in 14 of 87 samples. Glycols may prove to be problematic for use as sentinel compounds because of their other uses in natural gas production, such as winterization of equipment similar to their use in automobiles, recreational vehicles, etc.

Measured concentrations of volatile organic compounds were available for the Marcellus from the GTI study and more limited data had been provided for the Barnett, Fayetteville and Haynesville formations. The most consistently detected volatile organic compounds were benzene, toluene, ethyl benzene and xylenes (BTEX). This finding is consistent with data available in the literature and would be anticipated as these compounds are closely associated with hydrocarbon producing geologies from which the produced formation water comes. There were no trends evident for the BTEX data. The appearance of BTEX was somewhat inconsistent and when present was internally inconsistent. That is, the highest concentrations of benzene were not in the same samples as the highest concentrations of the other three. In the iterative sampling, there was no consistent timing for occurrence of the highest concentration. This may well be due to the differences in water solubility in the presence of elevated total dissolved solids for the individual BTEX components. The data is suggestive that there are differences in BTEX levels between and within shale formations. There were few other volatile organic compounds found in produced formation water; however, they were found on an inconsistent basis.

The semi-volatile organic compounds (SVOCs) were generally not present in detectable concentrations. The most frequently detected SVOC was pyridine in both the GTI Study and in the other data available. In the GTI study data set, six of 70 samples had detectable levels of pyridine in the hydraulic fracture fluids. The author speculated that presence of pyridine was due to its use as a precursor in the manufacture of one of the hydraulic fracturing additives. Certain service companies have alkyl pyridines available as corrosion inhibitors (Weatherford, 2011). In the additional data evaluated, only two of eleven sampled hydraulic fracturing fluids had detectable concentrations of pyridine. In one of these samples, the concentration was related to the reuse of produced formation water as makeup water for the hydraulic fracturing fluid. Pyridine has been reported as naturally occurring in oil shales (ATSDR, 1992). The additional data sets may indicate support mobilization of the naturally-occurring pyridine since it is soluble in water or may represent a degradation product. There appear to be differences between the shale plays; however, the data set is small and therefore, does not support the development of generalizations.

The iterative (time series) sample results presented by GTI and in other available data does not reveal a consistent trend of increasing or decreasing concentration of volatile organic compounds or SVOCs with increasing times after hydraulic fracturing.
The major conclusions from the review of produced formation water data are:

- Produced formation water appears to be highly variable within and between shale plays.
- Analytical techniques used for chemical and radiochemical characterization of the produced formation water must be robust to the matrix interferences presented by total dissolved solids.
- Few volatile organic compounds and SVOCs are consistently found in produced formation waters. Benzene, ethyl benzene, toluene and xylenes are expected to be present in varying concentrations in natural gas. The concentrations of volatile organic compounds and SVOCs are generally low and tend to preclude their use as sentinel chemicals.
- The most reliable sentinel compounds appear to be total dissolved solids, chloride and divalent cations.

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Trace Metal Chemistry and Mobility in the Marcellus Shale

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Drilling and “fracing” of the Marcellus shale causes fluid-rock interactions that have the potential to mobilize metals that are naturally enriched in the shale. While the concentrations of these metals are low, their mobilization from the solid, through redox reactions and leaching, is cause for further study.

In a series of studies, the trace metal geochemistry of the Marcellus Shale and the extractability of select metals through fluid-rock interactions have been determined. The studies were completed on 16 shale samples including outcrop, well core, and well cuttings from western New York and Pennsylvania. Instrumental neutron activation analysis (INAA) was used to determine the concentrations of metals in the shale samples prior to any chemical treatment. The analysis indicates that the Marcellus Shale is enriched in barium, uranium, chromium, and zinc, among other metals (Table 2). For comparison, the maximum contaminant level (MCL) in the United States for barium, uranium, chromium, and zinc are 2 ppm, 30 ppb, 50 ppb, and 5 ppm, respectively. It is likely that the barium concentrations reported here are elevated due to contamination from drilling mud which commonly contains barium. This would explain the very high concentration of barium in cuttings and the increased concentration in core compared to outcrop samples (which would not be contaminated).

Table 2. Selected Metal Concentrations in Marcellus Shale

Metal	Outcrop Average (range) n = 3	Core Average (range) n= 9	Cutting Average (range) n=4	Sample Average (range) n=16
Barium	670 ppm (500-900 ppm)	1000 ppm (*BDL–2000 ppm)	1925 ppm (900-3600 ppm)	1314 ppm (BDL–3600 ppm)
Uranium	30 ppm (11-53 ppm)	28 ppm (10-50 ppm)	17 ppm (9-34 ppm)	26 ppm (9-53 ppm)
Chromium	70 ppm (53 – 100 ppm)	86 ppm (70-100 ppm)	98 ppm (70-120 ppm)	86 ppm (53-120 ppm)
Zinc	515 ppm (*BDL – 660)	526.3 ppm (BDL-2290 ppm)	403 ppm (BDL-530 ppm)	496 ppm (BDL-2290)

*BDL = Below Detection Limit (Ba = 100 ppm, U = 0.5 ppm, Cr = 10 ppm, Zn = 50 ppm)

The concentration of metals in the shale generally increases as the concentration of total organic carbon increases. This is likely because conditions that favor the preservation of organic matter during shale formation also favor the deposition of metals in a reduced state. This is of interest because natural gas developers naturally target regions with the higher concentration of organic matter which are also the most metal-rich.

To determine the extent that these metals could be mobilized during reactions that occur between drilling and/or fracing fluids and the shale, several chemical extractions have been performed. Batch extraction studies were completed using a measured mass of ground and sieved shale and a known volume of chemical extractant. The batch systems were either shaken or stirred for the duration of the extraction (which varied from just a few minutes to 24 hours). Metal concentrations in the shale were measured prior to the extraction test and following the extraction. Also, in some cases metal concentrations in the batch fluid were measured at the end of the extraction study. The extraction studies included: 1) a dilute sodium bicarbonate solution which could remove easily exchangeable ions from the rock, 2) a hydrochloric acid extraction to dissolve carbonate minerals and strongly sorbed metals, 3) a hydrogen peroxide treatment to oxidize organic matter and associated metal, and 4) a sodium dithionite solution which would remove oxide and hydroxide minerals and their associated metals. The results of the sodium bicarbonate study indicated that little to no metal could be solubilized from the shale during a 24 hour reaction. The results of the sodium dithionite study were also negligible because there are so few oxide minerals in the shale. The hydrogen peroxide treatment indicated that some metals were associated with the organic matter in the shale. An average of 20% of the zinc in the samples was solubilized with an extractable range from 3-80%. Additionally, up to 35% of the uranium was solubilized, but a greater amount of uranium could be removed from the outcrop samples compared to the core. Up to 30% of the chromium was removed, but an average of only 8.5% was removed from the shale.

The results of the hydrochloric acid extraction provided the largest amount of data and indicated potential for metals to be solubilized and mobilized from the shale. HCl is used prior to fracing a well to dissolve carbonate cement and increase flow pathways for the natural gas. In this study, finely ground shale was reacted with 3 M and then 1.5 M HCl for a total of two hours. The amount of metal solubilized in the batch solution was measured using inductively coupled plasma mass spectrometry (ICPMS). Additionally, the solid sample was re-analyzed following the extraction test. Interestingly, the results of this study varied depending on whether the sample was outcrop or core; outcrop samples contain up to 70% HCl extractable uranium while core samples contain only about 25% HCl extractable uranium. Zinc and chromium were both moderately extractable in both sample types, up to 60% and 20% respectively. Up to 40% of the barium was removed during the extraction but results vary from sample to sample and are probably affected by contamination from drilling muds.

This study shows that metals may be mobilized from the shale into wastewater produced during natural gas development. Additionally, the results of this study indicate that many of the heavy metals in the shale are potentially leachable and may present a disposal issue. Drill cuttings that are removed during drilling of thousands of feet of well hole need to be properly disposed. These cuttings contain reduced metals that will oxidize over time if exposed to air and water. Proper disposal of these cuttings needs to be considered.

Fracture Fluid Additive and Formation Degradations

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The focus of this presentation is on reactions that describe the degradation of fracturing fluids and formations during the hydraulic fracturing process and the clean-up period of 2 to 6 weeks following the fracturing application. A description of the primary chemical reaction controls, namely permeability and area-to-volume ratio, precedes a discussion of the better known and more common degradation reactions. Although shale formations will be highlighted because of media attention, other formations will be covered as well.

Reactions in wells are subject to most normal catalytic and restriction influences, but also have a set of specific limiters that are found in few other places in chemical industry. Reaction influences of temperature and pressure are reasonably predictable, but other reaction controls such as reaction rate are strongly influenced by the area and mixing constraints described by location of the reaction, the area-to-volume ratio and the behavior and stability of the by-products. The reaction zones include:

- Open wellbore - a zone of high energy but small area in which reactions are possible but segregation of sequenced reactants can be enforced by turbulence during their one-time passage through the wellbore where area-to-volume ratio is sub 1:1.
- Hydraulic fracture – mostly singular in a vertical well and usually narrow (~3mm to 25mm) slit where chemical reactions that depend on diffusion are limited by the pump rate and reactants may be quickly lost to the natural fractures or matrix through leak-off generated by pressure differential and controlled by the permeability to those side connections. Area-to-volume ratio is 8 to 50 for normal fracture widths.
- Natural fractures – very narrow (~0.01mm to 1mm) but numerous slits that may or may not be continuous in even a small area. Area-to-Volume ratios range from 100:1 to over 1000:1.
- Matrix or interstitial porosity – a potentially highly reactive zone because of the ratio of the very large surface area-to-volume of fluid ratio (order of 20,000:1 to 30,000:1).

Reactive target potential in the previously described zones include rock and minerals, metal, cement and a typically short-list of chemical additives used in the wells to facilitate control of natural mineral reactions, transport of solids (e.g., cuttings and proppant), and permit physical reactions (i.e., fracturing) that can create, widen and/or stabilize a flow path of improved permeability to allow the formation fluids to flow to the wellbore.

The primary down-hole limit to any chemical or physical reaction is access. Permeability (a measure of ability to flow a fluid through a rock) is the fundamental restriction to fluid flow.

Once the potential reactant has reached the zone of reaction, the area-to-volume ratio is a primary influence on most reactions. Diffusion, the ability to get reactants to the site and move products away, is controlled by area-to-volume ratio, the permeability of routes to and from the reaction and the type and behavior of by-products themselves.

Degradation reactions involving well construction and operation issues include pipe stability and cement stability, which are mostly chemical concerns. Although physical reactions such as pipe collapse, burst, tension failures and erosion are known to occur, their behavior has been well described and adequate controls appear to be in place based on the population of 50+ year old wells still producing and passing mechanical integrity tests.

Cementing stability and degradation have been addressed in the petroleum engineering literature by more than eleven thousand general papers and over six hundred that comment directly on cement degradation reactions and blocking mechanisms. This discussion has covered mineral and organic acids, CO_2, H_2S, thermal, low pH waters, sulfate effects, cyclic pressure behavior, long term performance and other issues. Reactions that deteriorate cement are easily demonstrated in the laboratory in beakers but are reduced exponentially when issues of access are considered. All reactions depend on access and the low permeability of the formations surrounding the numerous formation barrier seal areas, coupled with the extremely low permeability of the cement itself make significant deterioration reactions unlikely if not practically impossible. Added to this are instability and quick precipitation of common reaction by-products that form an impenetrable barrier on most reaction surfaces. Additives that reduce cement degradation include those for sulfate resistant cement, special thermal compositions for very high temperature wells, a variety of additives that reduce cement permeability, improve strength and chemical and physical treatment to improve bonding. Problems with cement almost universally are traced to poor application during well construction.

Pipe reactions are mostly corrosion and erosion-corrosion. These reactions are also well known with over two thousand papers in petroleum engineering literature of direct application of wells and pipelines. These reactions are most common in long term production with acid gases (CO_2 and H_2S) and the short term contact of mineral and organic acids during acid stimulation. Because of the short duration of the frac and the very small amount of weak mineral acid used as a breakdown stage, the effect of corrosion or erosion-corrosion during a fracturing job is negligible.

Formation degradation during fracturing is possible, but sharply limited by access. Higher permeability conventional formations, sandstones and carbonates with permeability over about 1 mD, are largely inert to reactions with waters used in fracturing except for the limited swelling reactions of smectite and a few mixed layer clays. Reactions in shale are still being researched, but access is still the dominant control. Examples of reactions in the accessible zone of fracture between proppant, shale formation and waters are being researched and results of two recent papers are presented.

Chemical additive reactions resulting in degradation or disappearance of the chemicals are presented. These reactions include gel breaking, adsorption, absorption, capillary trapping and precipitation. Examples of each of these mechanisms will be discussed. Nearly fourteen thousand papers in the petroleum engineering literature deal with subjects of sorption, gel breaking and capillary effects.

Evaluating Interactions of Fracturing Fluids and Degradation Products with Radionuclides Contained in Organic-rich Solid-Phase Host Materials

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In situ contaminants (arsenic, radionuclides, or others) can be released from organic-rich gas-bearing shale host rock when fracturing fluids are injected. This potential release raises questions regarding the nature of wastes created and pumped to surface, and those remaining in the formation. The rate of entry of various radionuclides into return flow liquid matrixes can be studied in the laboratory and matched with corresponding observations in the field to estimate the reactions and their rates, and provide understanding of the solid material degradation processes.

Radionuclides can serve as tracers for rock-matrix degradation processes in both field- and laboratory-based experiments. Uranium (U) and thorium (Th) have multiple isotopes and multiple direct and indirect progeny that also have many isotopes. Concentrations of many of these isotopes, their ratios, or ratios of progeny can be determined and monitored in water or brine to estimate changes in U and Th concentrations in rock. Laboratory characterizations can be utilized to determine sources of U in the solids matrix and to show changes in the distribution of U or progeny radionuclides before and after manipulation (for example, simulated fracking of core materials tested by a variety of laboratory approaches). The combination of simultaneous or near simultaneous solid phase and liquid phase observation of the fate of these materials in the presence of laboratory manipulations with the capacity to make similar observations in the field make for a powerful tool for the study of the rock-matrix degradation processes. The characterization of U occurrence in black shales and its fate has already received attention and will provide useful analogues for design of such experiments.

A variety of tools are available for determination of radionuclide occurrences in samples of host rock. Solid phase analysis of the relative abundance of a suite of radionuclides (^{238}U, ^{226}Ra, ^{228}Ra and ^{210}Pb) may include low energy gamma-ray spectrometry that can provide simultaneous, non-destructive determinations in representative samples and important baseline concentration information. The drawbacks to using low energy gamma-ray spectrometry are a large sample size is required (150-250 g) and the actual distribution within the sample cannot be determined. Developed fission-track radiographs or alpha-autoradiographs can be observed under a microscope to reveal the sources of U or other alpha-emitting radionuclides in rock samples. Fission-track radiographs are generated by irradiation of a polished thin section with a thermalized neutron flux that causes fission of ^{235}U in the sample. Fission fragments recoiling from the sample surface are detected by covering the sample with a detector material (low U muscovite). Fission-fragments paths are farther developed by etching the dector material with hydrofluoric acid. The developed fission tracks are observed under a microscope. Although Th is a possible source of fission fragments, the sensitivity of Th to thermal neutron fission is much less than that for an equal amount of U. Autoradiographs are images of the sources of emitted alpha particles, but do not have as high sensitivity and resolution as fission track images. An alpha-sensitive photographic emulsion is spread directly over the thin section and the image of the alpha tracks is observed directly under the petrographic microscope. The alpha autoradiograph captures images of radionuclides undergoing active alpha decay as opposed to images induced by the ^{235}U fission noted in fission tracks.

The use of element mapping utilizing a variety of X-ray analysis techniques can be employed for determination of radionuclide (and other trace element) occurrences in small-scale detail in samples of host rock. Scanning electron microscopy energy dispersive x-ray (SEM/EDX) allows for the capture of high resolution high magnification images as well as dispersive X-ray mapping of the occurrence of the element at points within the image where the X-ray beam is focused. Synchrotron-based spatially resolved micro-X-ray fluorescence (μ-SXRF) allows for small-scale element concentration mapping on individual core samples, whereas synchrotron-based X-ray absorption near edge spectroscopy (XANES or μXANES) can be used to deduce elemental valence state and Extended X-ray Absorption Fine Structure (EXAFS or μEXAFS) can allow for analysis of atom coordination (speciation). The most recent efforts have been to obtain images with μ-SXRF mapping on the same spatial point on the rock sample with the X-ray beam while the leaching experiment is in progress, with chemical effluents collected and analyzed from a split sample undergoing the same procedure. These techniques can be done over small areas within a highly polished sample (approximately 0.3 mm^2 area with a step size of 10 μm and a dwell time of 2s per pixel). The dispersed nature of the U in organic-rich fine-grained rocks may pose difficulty for signal resolution. The intense fluorescence peak of iron in samples can cause interferences. Beamline time would need to be obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory or the Stanford Synchrotron Radiation Lightsource at Stanford University. Images of changes in radionuclide distribution and speciation in the core during such experiments could be captured and compared to changes in radionuclide concentrations in leachate from laboratory-based experiments. Radionuclide concentrations in samples collected at varying stages of fracture fluid flowback in the field could be compared to the results of radionuclide distribution determined in the laboratory for leachate and rock. This series of experiments and field-based observations promises to shed light on the mechanisms responsible for the liberation of radionuclides from gas-bearing shale formations by the fluid fracturing process and could guide the understanding the process of rock matrix degradation.

Summary and Abstracts from Theme 2: Chemical Fingerprinting

Summary of Presentations for Theme 2: Chemical Fingerprinting

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Technical Presentations

This first set of presentations in Theme 2 related to the determination of background ground water and natural gas conditions.

Michael Lawson, ExxonMobil, discussed the use of isotopic tracers and other biogeochemical techniques to understand the sources of contamination that can affect ground water. Major ion chemistry, according to Mr. Lawson, can be used to identify contamination of ground water but may not be able to determine the source of the contamination. Mr. Lawson stated that isotopic tracers can be used along with major ion chemistry to identify the source of contamination and also quantify the contributions of different sources.

Jennifer McIntosh, University of Arizona, presented a comparison of the isotopic and chemical composition of the Devonian New Albany Shale, Pennsylvanian coal beds, and shallow glacial drift aquifers in the Illinois Basin. Dr. McIntosh stated that microbial and thermogenic natural gas from the deeper formations (shale and coal beds) can be distinguished from microbial methane from the glacial aquifers by gas composition and carbon isotopes of methane and carbon dioxide. Associated formation waters in shale and coal beds may be distinguished from ground water in glacial drift aquifers by elemental and isotope chemistry, according to Dr. McIntosh.

Stephen Osborn, Duke University, discussed fingerprinting of formation water and gas in the northern Appalachian Basin using carbon isotopes. According to Dr. Osborn, the gas in the Appalachian Basin is primarily thermogenic, although there is some indication of mixing between a larger thermogenic reservoir and a smaller biogenic reservoir shown by deviations of linearity in the carbon isotope plots. Dr. Osborn emphasized the need for a multiple analysis approach to understanding the origin of natural gas and formation water.

Fred Baldassare, Echelon Applied Geoscience Consulting, presented a discussion on a number of different sources of stray gas migration in the Appalachian Basin. Sources of stray gas include abandoned and operating coal mines, naturally occurring gas seeps, natural gas pipelines, landfills, and buried organic matter. He emphasized that it is difficult to pinpoint the source of natural gas migrations and that identifying the source requires the synthesis of several different data types. Mr. Baldassare said he has investigated hundreds of stray gas cases in Pennsylvania and found no incidents of gas migration related to HF operations.

The second set of technical presentations addressed introduced tracers.

George King, Apache Corporation, discussed the use of chemical and gamma-emitting tracers in conjunction with microseismic monitoring to optimize fracture operations. Gamma-emitting tracers coat the proppant in a zero-wash coating (non-removable) and can be used to identify where the proppant left the wellbore out to a distance of about 12 inches. The half-life of the gamma-emitting tracers ranges between 64 and 84 days depending on the tracer type. Microseismic data allow estimation of the shape of the fractures (as plotted by acoustic monitoring of the shear fracturing events), and the stimulated rock volume (SRV) is roughly outlined by the densest volume of these events. These techniques provide information for the accurate spacing and separation of wells as well as the development of fractures along the wellbore. Microseismic techniques can also assist in targeting the placement of fracs and, when combined with production logging techniques, can identify the major sources of gas for better fracture placement.

Uni Blake, Majitox for Gastem USA, presented a study design of a water quality monitoring program at the Ross Well site in New York that consisted of baseline water testing, fracture fluid testing, and water quality monitoring. A number of challenges were encountered by the scientists including variability in baseline water quality between residential wells, the variability of different additives used in different fracture jobs, and the subsurface fate and transport of chemicals and compounds. Water samples were collected for 12 months after fracturing in a two-mile radius around the Ross Well site. More study is needed; a next step is determining a potential organic confirmation tracer.

The third set of technical presentations addressed tracing fracturing fluids in the environment.

Avner Vengosh, Duke University, discussed the use of several isotope-fingerprinting methods coupled with a geochemical evaluation of the possible impacts of fracturing fluids and formation waters on the quality of water resources in affected areas. Dr. Vengosh suggested that strontium concentrations and isotopes may be used to identify contributions of formation water in ground water samples. He emphasized the importance of establishing a baseline and using a combination of tracers.

Carl Kirby, Bucknell University, provided a survey of the inorganic geochemistry of Pennsylvania Marcellus Shale flowback waters. Flowback water chemistry (salinity in particular) was shown to change significantly as a function of time. Dr. Kirby suggested that the strontium signature of the Marcellus Shale flowback could serve as a tracer, and he warned against relying on stream conductivity as evidence of formation water or flowback water discharge to a stream. Dr. Kirby noted difficulty in acquiring samples for his study. He also introduced the Bucknell Marcellus Shale Initiative (MSI) database.

Summary of Discussions Following Theme 2: Chemical Fingerprinting Presentations

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The importance of baseline/background data and multiple tracers. A participant noted that many sites do not have baseline water quality data, and local geologic variations complicate the collection of representative background data. One participant suggested that gas companies should take the responsibility to collect and provide baseline/background information. Other participants emphasized the need for multiple tracers. One participant noted that any assessment of potential contamination requires multiple tracers and detailed analytical work, and HF-related testing is no exception. Other participants noted that a multiple tracer approach will be invaluable in situations where stray or migrated gas might have originated from multiple sources. The use of strontium isotopes as tracers has been investigated and participants claimed that the appropriateness of their use, as with all tracers, depends on whether different formations have different and distinct isotopic ratios. Participants indicated that phenols have been used in the petroleum sector but there is no indication in the literature that they might be appropriate tracers in a HF context.

Analyzing tracers. In the studies discussed in the presentations, samples were collected at the wellhead where water and gas are already separated. A presenter stated that samples from shallow aquifers consisted of methane dissolved in water. Generally, in the experience of the participants, the amount of the tracer recovered is proportional to the amount of fracture fluid recovered. Participants claimed that chemical tracers cannot provide information on the location of fractures through which water has moved (though microseismic survey data can help provide this information). Participants also mentioned that chemical variability within formations needs to be taken into account when trying to determine contamination pathways. Participants noted that concentrations of volatiles or total organic solids can be high in samples collected from trucks or tanks in which the water has been sitting for some time.

Gamma-emitting tracers and microseismic recording. Participants noted that iridium, selenium, and antimony are the most commonly used gamma-emitting tracers due to their reasonably short half-lives and rarity in shales and other formations.

The New York water quality study. Ms. Blake clarified that most sampling was done within three months of fracturing, with very few samples taken on the same day as a fracture job. Participants noted that high methane content is possible in drinking water wells due to naturally occurring methane seeps, and their belief that high methane levels in drinking water are not necessarily an indication of fracturing activities.

Well drilling and operations. Participants explained that well construction and operation are in part characterized and optimized through the use of tracers and microseismic data before and during drilling. In shales with extensive natural fracture systems, participants noted that less energy and pressure is required to hydraulically fracture the formation than is required for formations that do not have significant natural fracture systems. The success rate of re-fracturing a shale play is 85% compared to 30% in non-shale rock, according to one participant. Some participants emphasized that with good fracture treatment design, fractures do not propagate upward for a significant distance (toward sources of drinking water). Some participants stated that problems related to well-construction and the possible surface spillage of fluids are the two main issues regarding the potential for pollution from HF. Participants also discussed mechanical integrity tests (MITs), which are periodic tests of well operations prescribed by state regulators. Participants indicated that, historically, western states have had more comprehensive state regulations than Pennsylvania and New York, though Pennsylvania recently implemented some new aspects of HF regulations.

Water fate and flowback. Participants stated that, in areas with low permeability where leakoff is observed, injected water is most likely exploiting natural fractures and fissures that are common in shale formations. In this situation, participants explained that the capillary blocking pressure can increase and potentially result in damage to the formation.

Recycling. A participant asked about the effects of recycling water on tracers and fingerprinting. Participants mentioned that recycling and mixing could pose challenges by altering water composition. However, several participants noted that regardless of the source of the recycled water, its chemical signature is likely to be distinct from fresh water, which should enable it to be traced.

Migration and contamination scenarios. A participant noted that the mobility of gas is greater than that of water and asked if the presence of a water-based tracer could ever be detected without gas intrusion into the ground water. Other participants described a spill or other surface accident that could cause ground water impacts. However, participants indicated that, for most subsurface migration scenarios, the arrival of the gas at a particular monitoring point would precede the arrival of the water. A participant noted that a leak related to a compromised well might also be anticipated by observed pressure changes in the well.

Injection pressure in the Marcellus Shale. A participant asked about the typical injection pressure in the Marcellus Shale and how the pressure dissipates after HF is completed. A participant stated that the average injection pressure (measured at the surface) is in the range of 8,000 psi and does not exceed 9,000–10,000 psi. The participant continued to explain that instantaneous shut-in pressure is 3,000–3,500 psi, which dissipates slowly over time; in addition, the participants noted that pressure will not dissipate completely, but rather stabilize at a level higher than the natural level.

Abandoned wells. A participant asked about abandoned wells and the possibility of fracture communication with these wells. Participants noted that this is always a concern, especially if there is any kind of wellbore within a few hundred feet of the injection well. Pressure effects can be communicated between wells across as much as 250–300 meters, according to one participant. This participant stated that the potential for well communication is one reason why well operational records are so important. The participant went on to explain that in Texas and Oklahoma, the records are fairly good regarding a list of abandoned wells, and an industry tax contributes to the plugging of abandoned wells. In addition, the participant noted that permits in Texas are often denied if there are any wells too close to the proposed injection/HF well. On the other hand, a participant stated there may be 100,000 abandoned wells unaccounted for in northwestern Pennsylvania. However, participants noted that it is important to distinguish between shallow and deep abandoned wells. Marcellus Shale HF wells should not be affected by properly abandoned shallow wells according to participants.

Cooperation among industry, academia, and regulatory agencies. Participants expressed appreciation that representatives from industry, academia, commercial labs, and the government all attended the workshop. Participants called for more cooperation among the stakeholders and suggested that industry give universities more access for sample collection and analysis. One participant noted that, outside the industry, people do not know many details about the long-term effects of HF.

Analytical techniques. A participant noted that conductivity pens are very inexpensive compared to chemical analysis. Other participants pointed out that conductivity may not be a good indication of the source of contamination since there can be multiple sources of salinity (e.g., road salt in surface water) other than subsurface brines, and that chemical analysis is not that expensive compared to how critical it is. A participant noted that chemical analysis may cost $1,000, which is worth the investment over the life of operations, research or investigations. Participants argued that chemical analysis should not be complicated or overwhelming; collectively, the various analyses provide critical information for managing operations.

Drilling muds. A participant asked about the composition and use of drilling muds. Other participants explained that mud basics are fairly simple, but that details and specifics can get complex. Basic mud is a mix of fresh water with some added minerals and chemicals. One participant explained that mud composition depends on the downhole temperature and pressure, the type of formation, the need to lift cuttings, the drill bit, the size of the hole, and other factors. The participant continued to explain that the characteristics of drilling muds can change over time as drilling progresses and more information is collected. Participants noted that the use of oil-based muds is limited due to concerns about environmental consequences if they are spilled at the surface. Participants stated that there are also very expensive specialized muds, but, for most shale HF drilling purposes, simple mud systems are sufficient. According to participants, functions of mud are to keep the well under control, allow pressure to be read, and circulate fluids through the well bore. When a vertical well turns horizontal, participants explained that mud and fluids can become more complicated and more expensive. Managing mud composition and characteristics, claimed participants, is a day-by-day or hour-by-hour job.

Compressed air can also be used instead of mud, even when drilling to depths of 5,000–6,000 ft, as noted by participants.

HF fluids. A participant explained that there are essentially 12 different types of fracture fluids currently in use; the fluids used in the Eagle Ford Shale are typically hybrid jobs: slickwater or base gels, followed by crosslinked borate gels. The Eagle Ford formation is deeper and hotter than the Marcellus according to participants.

"Bad" wells and methane hazards. One participant asked about the causes of wells going bad. Other participants noted that saying the well is "bad" could mean several things. One participant explained that if the well does not flow in commercial quantities, then the company did not correctly select the location or the stimulation—that is "going bad" in the economic sense. However, well blowouts are almost universally due to human error, according to participants. Participants stated their belief that there are very few areas where drilling cannot occur and drilling has occurred in some very difficult areas; however, any large industry will have accidents. One participant emphasized the importance of identifying potential methane hazards when drilling.

The role of the caprock. A participant asked about the mechanisms that would stop fracture fluid from moving to the surface in different situations. Other participants explained that there will always be a caprock or seal present above gas zones; the seal is necessary to create the gas zone in the first place.

EPA's study. A participant asked how EPA plans to use the results of the technical workshops to revise the draft study plan. The purpose of the workshops is for EPA to collect more information on specific topics and thematic areas. The workshops will provide EPA with more up-to-date information to inform the study as it develops.

Abstracts for Theme 2: Fracture Design and Stimulation

Abstracts were submitted to U.S. EPA by the presenters for use in this proceedings document. Not all presenters submitted abstracts of their presentations.

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Chemical and Isotopic Tracers of Natural Gas and Formation Waters in Fractured Shales

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Introduction

Fingerprinting the chemical and isotopic composition of formation waters and natural gas associated with organic-rich shales is critical for evaluating potential environmental impacts of hydraulic fracturing for gas production. This paper summarizes recent results from Schlegel et al. (in press) comparing the chemical and isotopic composition of formation waters and natural gas in an organic-rich shale (Devonian New Albany Shale) in the Illinois Basin to other gas accumulations in overlying Pennsylvanian coalbeds and shallow glacial drift aquifers (Figure 3) to determine the best analytical tools for distinguishing gas and fluid sources. Previous data are included from Coleman et al. (1988), Strąpoć et al. (2007), and McIntosh et al. (2002).

Geologic Background

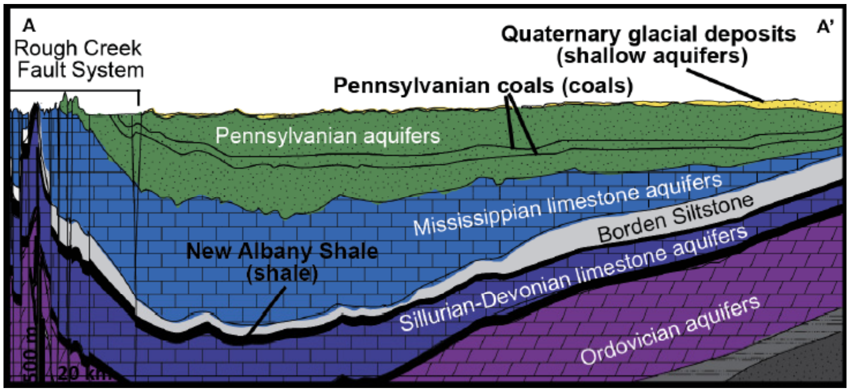

Figure 3. Cross-section of Illinois Basin from Schlegel et al. (in press)

The New Albany Shale is an organic-rich (black) shale along the eastern margin of the Illinois Basin and grades into a grey-green shale along the western margin (Barrows and Cluff, 1984; Hassenmueller, 1993). The shale contains predominantly type-II kerogen (sapropelic-marine), with up to 16 wt% total organic carbon (TOC) and has low thermal maturity (R_o <0.6%; e.g. Barrows and Cluff, 1984) except in the south near the Shawneetown-Rough Creek fault system where the shale reaches R_o values >1% (Fig. 3b; Cluff and Byrnes, 1991). Previous studies have shown that the shale contains both microbial and thermogenic gas. Thermogenic gas is distributed throughout the basin, while microbial gas is predominantly located along the northeastern and eastern margins of the basin where meteoric water infiltration likely stimulated microbial methanogenesis by decreasing formation water salinity and transporting in near-surface microbial communities into paleo-pasteurized sediments (McIntosh et al., 2002; Schlegel et al., in press). New Albany Shale wells in areas of predominantly microbial methane typically contain copious amounts of formation waters, which must be removed for gas production.

Pennsylvanian coalbeds are composed of type-III kerogen (typical of terrestrial organic matter; Hatch et al., 1991), and have low thermal maturity (R_o <0.6%) except in the south where tectonic activity locally increased the geothermal gradient and produced higher coal maturity (R_o ~0.7 to 0.8%; Fig. 3a; Drobniak et al., 2004; Hower et al., 2005). Pennsylvanian coals contain thermogenic gas in the central and southern basin with little to no co-produced formation waters. The coals contain microbial gas, associated with variable salinity formation waters, across the northern and northeastern basin margins (Strąpoć et al., 2007).

Glacial drift sediments containing detrital organic matter overlie much of the northern portion of the Illinois Basin; these sediments are up to 120m thick and constitute an aquifer with high quality drinking water (Swann, 1968). The glacial sediments contain up to 17.2 wt% TOC, which is relatively thermally immature (Glessner and Roy, 2009). Many water supply wells screened in glacial drift aquifers contain dissolved methane that is microbial in origin, and sourced from biodegradation of in-situ organic matter and/or in underlying shallow Paleozoic sediments (Coleman et al., 1988).

Chemical and Isotopic Fingerprint of Natural Gas

In general, gas accumulations in the Devonian New Albany Shale, Pennsylvanian coalbeds, and shallow glacial drift aquifers have different hydrocarbon compositions (methane (C_1) to ethane (C_2) and propane (C_3) ratios; Figure 4). Dissolved gas in the shallow aquifers is predominantly comprised of CH_4 with some C_2 (in addition to atmospheric-derived gases, such as N_2 and Ar), and no detectable C_{3+}. Natural gas in the shale has much lower C_1/C_2+C_3 ratios (12-5931), compared to the shallow aquifers ($>10^6$), due to the presence of thermogenic gas in addition to microbial methane. Coals have C_1/C_2+C_3 ratios (188-163,361) that plot roughly between the shallow aquifers and shale.

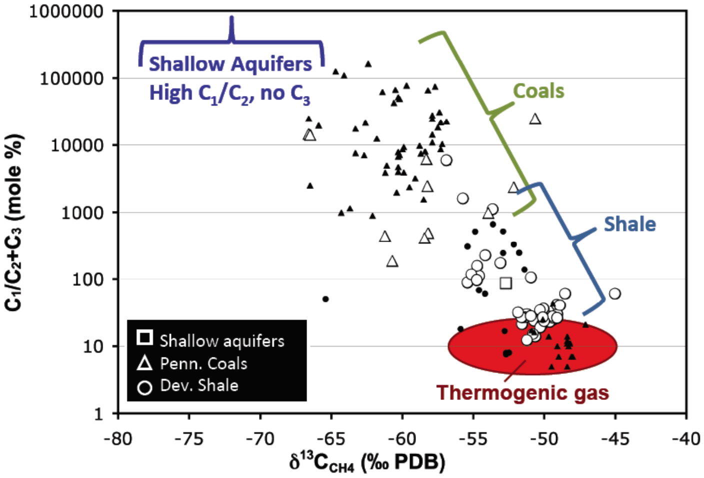

Figure 4. Methane to ethane + propane ratios versus carbon isotopes of methane for various gas

The carbon isotope values of methane accumulations are also distinct between the three organic-rich formations. Shallow aquifers have very low δ^{13}C-CH_4 values (-90 to -68‰), consistent with early stage methanogenesis where the CO_2 reservoir has not been significantly depleted. In contrast, δ^{13}C values of CH_4 from the Devonian shale are much higher (-57 to –45‰) likely due to mixing with isotopically-enriched thermogenic gas, and significant depletion of the CO_2 reservoir during microbial methanogenesis via CO_2 reduction (Schlegel et al., in press). Importantly, microbial CH_4 from the Devonian shales has similar δ^{13}C values to thermogenic CH_4 (-55.9 to –52.7‰), suggesting that carbon isotope of CH_4 alone cannot distinguish mechanisms of shale gas generation. In contrast, $\delta^{13}C$ values of thermogenic and microbial CH_4 in the Pennsylvanian coals are distinct (Strąpoć et al., 2007). In addition, $\delta^{13}C$ values of microbial CH_4 (-67 to –51‰) in the coals plot between the shallow aquifers and Devonian shale with little overlap (Figure 4).

Microbial methanogenesis produces (and consumes) CO_2 in addition to CH_4, with high $\delta^{13}C$-CO_2 values. Carbon isotope fractionation factors ($\alpha_{CO2\text{-}CH4}$) for methanogenesis via CO_2 reduction typically range from 1.05 to 1.09 (Figure 5), while $\alpha_{CO2\text{-}CH4}$ values for acetate fermentation typically range from 1.03 to 1.05 (Whiticar et al., 1986). The majority of CO_2 and CH_4 from the Devonian shale, Pennsylvanian coals, and shallow aquifers plot along a carbon isotope fractionation line of ~1.05 to 1.09, except for a few coal samples influenced by methane oxidation and sulfate reduction (Strapoc et al., 2007), and one outlier glacial drift sample. Thermogenic gas in the Devonian shale was not analyzed for $\delta^{13}C$-CO_2 as it contains very little CO_2 (<0.1 mole %). Thermogenic gas in the Pennsylvanian coals has much lower $\delta^{13}C$-CO_2 values than microbial gas, within the range of C_3-type organic matter.

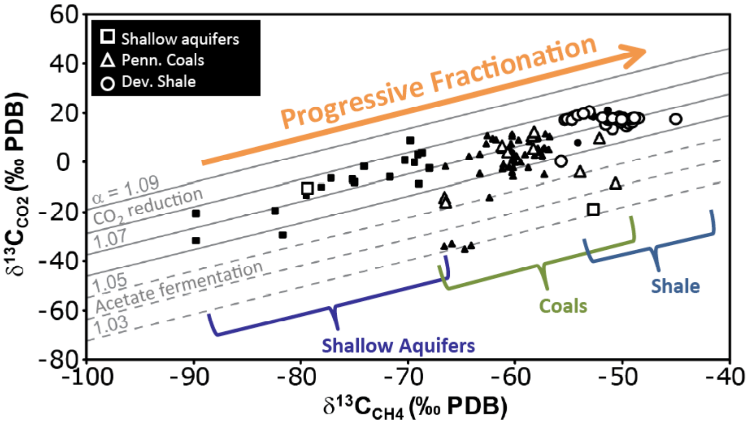

Figure 5. Carbon isotopes of carbon dioxide versus methane for various gas sources

Gas samples show a progression along the carbon isotope fractionation line (Figure 5) from more negative $\delta^{13}C$ values of CO_2 and CH_4 in the shallow aquifers to more positive values in the shale, with coal samples plotting in between. This may be due to mixing between a thermogenic and microbial methane source, or the progressive depletion of the carbon (CO_2) reservoir, causing increased $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$. Mixing between microbial and thermogenic methane would be seen in an increasing trend of $\delta^{13}C_{CH4}$ versus C_{2+}%. Though the $\delta^{13}C_{CH4}$ of microbial and thermogenic methane for the shale have similar ranges (up to -47.1‰) (McIntosh and Martini, 2008), a slight increasing trend is observed in the shale from -53‰ to -47‰ for samples with <2% C_{2+}, however no such correlation is observed for the shallow aquifers or the coals. These trends suggest that though some thermogenic methane is mixing with microbial methane, the overall progression of carbon isotopes along the fractionation line may be due to the progressive depletion of the carbon (CO_2) reservoir under closed system conditions (Jones et al., 2008).

Together, the $\delta^{13}C$ values of CO_2 and CH_4, in combination with gas composition (including mole % CO_2, CH_4, C_2, C_{3+}), clearly distinguish microbial and thermogenic gas from the Devonian shale, Pennsylvanian coals, and shallow aquifers.

Chemical and Isotopic Fingerprint of Formation Waters

Formation waters associated with natural gas in coalbeds and fractured shales in the Illinois Basin are enriched in Cl and Br (>1.8 mM and >8.7 µM, respectively), as well as other solutes, relative to shallow aquifers (Figure 6). These saline fluids are likely remnant Paleozoic brines sourced from evaporation of seawater, which have been subsequently diluted by meteoric recharge and modified by water-rock-microbial reactions (McIntosh et al., 2002). In contrast, shallow aquifers contain dilute (Cl <0.8 mM), recently recharged meteoric waters (McIntosh and Walter, 2006).

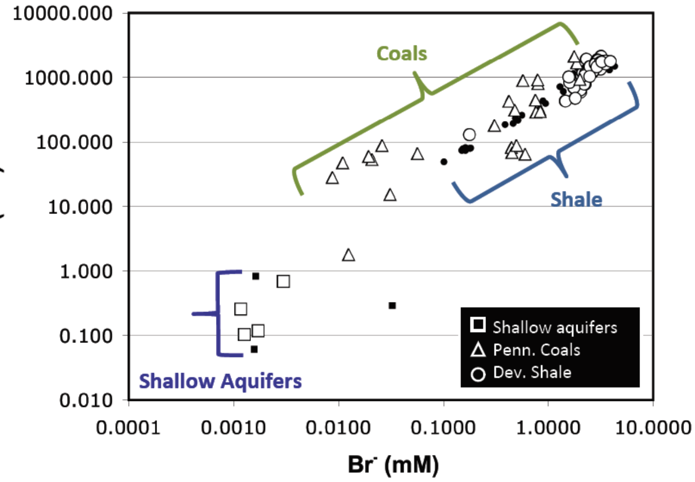

Figure 6. Chloride vs. bromide concentrations (log-scale) of formation waters associated with various gas sources

Groundwaters from shallow aquifers have δ^{18}O and δD values, which plot along the global meteoric water line (GMWL) (-8.6 to –6.6‰, and –57 to –40‰, respectively; Figure 7). Saline fluids in the Devonian shale are more enriched in ^{18}O and ^{2}H (-7.5 to –0.14‰, and –46 to –8‰, respectively) than shallow aquifers, and plot to the right of the GMWL, along a mixing line between Illinois Basin brines and meteoric water. Stable isotopes of water may be useful for distinguishing between fluids sourced from the Devonian shale versus shallow aquifers. Formation waters in Pennsylvanian coals have δ^{18}O and δD values (-7.0 to –1.9‰, and –48 to –13‰, respectively) that overlap the shallow aquifers and Devonian shale, making it difficult to distinguish between water sourced from the coal versus water from the shale or shallow aquifers.

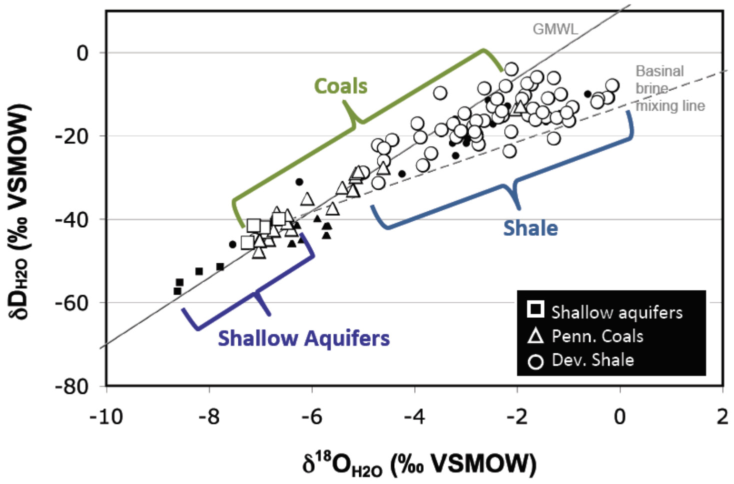

Figure 7. Stable isotopes of formation waters associated with natural gas accumulations

Alkalinity concentrations and carbon stable isotopes provide an additional tracer of fluid sources. Formation waters associated with microbial methanogenesis in the Devonian shale and Pennsylvanian coals typically have high δ^{13}C values of dissolved inorganic carbon (DIC; >10‰), and variable alkalinities (<5 to 37 meq/kg). Shallow aquifers have lower alkalinities (<10 meq/kg), and low δ^{13}C-DIC values (<0‰). Formation waters associated with thermogenic gas in the Devonian shale have low alkalinities (up to 2.4 meq/kg), and low δ^{13}C-DIC values (most near 0‰) (McIntosh et al, 2002).

In short, formation waters sourced from the Devonian shale are saline (with high Cl, Br, and other solute concentrations), enriched in ^{18}O and ^{2}H, and have high δ^{13}C-DIC and alkalinity values, compared to dilute meteoric waters in shallow aquifers. Formation waters from Pennsylvanian coals have similar solute concentrations (Cl, Br, alkalinity) and δ^{13}C-DIC values as Devonian shale fluids. In addition, their δ^{18}O and δD values overlap the Devonian shale and shallow aquifer samples, suggesting that it may be difficult to distinguish fluids sourced from Pennsylvanian coals versus fluids sourced from the Devonian shale.

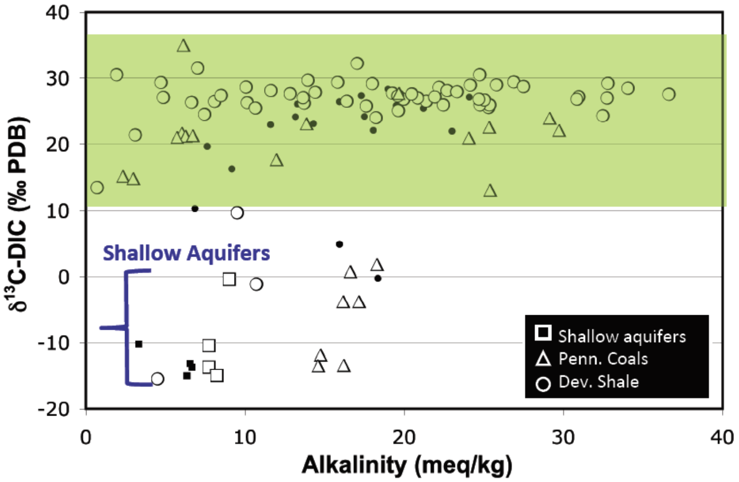

Figure 8. Carbon isotopes of dissolved inorganic carbon (DIC) versus alkalinity concentrations of formation waters associated with natural gas accumulations

Summary

Natural gas (microbial and thermogenic) from the Devonian shale and Pennsylvanian coals can be distinguished from microbial methane sourced from shallow glacial drift aquifers based on gas composition and δ^{13}C values of CH_4 and CO_2. Formation waters from the Devonian shale can be distinguished from dilute groundwater in shallow aquifers using major ion chemistry (Cl, Br, other solutes) and stable isotopes (^{18}O, ^{2}H, ^{13}C). It may not be possible to distinguish between formation waters sourced from Pennsylvanian coals versus the Devonian shale based on major ion chemistry and stable isotope compositions alone. These results are important for evaluation of potential environmental impacts of hydraulic fracturing of shales, such as the migration of brines and natural gas into shallow drinking water resources.

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Distinguishing the Source of Natural Gas Accumulations with a Combined Gas and Co-produced Formation Water Geochemical Approach

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

Introduction

Identifying the source of dissolved gas accumulations in shallow groundwater systems may provide some insight into potential impacts from underlying geologic formations targeted for natural gas production and associated with drilling and hydro-fracturing operations. This presentation describes a combined gas and formation water geochemical approach for distinguishing relatively shallow microbial methane and gas sourced from depth by the thermal-catalytic breakdown of organic matter (thermogenic gas). Recent results from the northern Appalachian Basin, detailed in Osborn and McIntosh (2010), will be presented and highlight this approach using gas composition and carbon isotope ($\delta^{13}C$) values of methane and higher chain hydrocarbons (ethane, propane, and butane) combined with elemental (major) and isotopic analyses ($\delta^{13}C$-DIC) of formation waters.

Distinguishing the Source of Natural Gas

Thermogenic gas has a greater proportion of higher chain hydrocarbons (ethane, propane, butane, and pentane) relative to methane than microbial gas, which dominantly contains CH_4 and CO_2 (Schoell, 1980). Thus, gas composition may be used as a first order approximation distinguishing between microbial and thermogenic gas. Carbon isotope values of methane ($\delta^{13}C$-CH_4) are widely used to further constrain the origin of natural gas. Schoell (1980) suggested that $\delta^{13}C$-CH_4 values less than -64‰ and ethane concentration less than 0.5 mole% (methane to higher chain hydrocarbon ratio greater than 1000) may represent a purely microbial gas end-member, where as more positive $\delta^{13}C$-CH_4 values (up to approximately -50‰) may represent an admixture of thermogenic and microbial gas (Bernard, 1978; Schoell, 1980; Whiticar et al., 1986). Methane to higher chain hydrocarbon ratios less than approximately 100 and $\delta^{13}C$-CH_4 more positive than -50‰ have been interpreted as indicative of thermogenic gas (Bernard, 1978; Schoell, 1980; Whiticar et al., 1986). Studies on thermogenic gas have focused on higher chain hydrocarbons to understand mixing relationships among different sources of gas.

Chung et al. (1988) proposed a kinetic fractionation model (natural gas plot) that assumed a linear correlation between carbon isotope values of methane, ethane, propane, butane, and pentane (C_1-C_5); and the reciprocal carbon number as a qualitative indicator of purely thermogenic gas. Deviations from linearity in the heavier hydrocarbons (C_2-C_5) may be interpreted as a mixture of different thermogenic gas end-members and/or reflecting the heterogeneity within a single organic matter source. Depleted carbon isotope values of methane relative to a linear thermogenic end-member may result from mixed thermogenic and microbial gas. The sole use of gas composition and $\delta^{13}C$ values to determine the origin of natural gas is complicated by microbial production of higher chain hydrocarbons (i.e., ethane and propane) and secondary modifications during microbial oxidation and diffusive fractionation and mixing between multiple gas sources (Barker and Fritz, 1981; Prinzhofer and Pernaton, 1997; Boetius et al., 2000; Taylor et al., 2000; Martini et al., 2003; Hinrichs et al., 2006). Thus, additional indicators from formation water geochemistry are necessary to further constrain the origin of natural gas.

Methanogens extract hydrogen from shale organic matter and in-situ formation waters to produce methane. The covariance of hydrogen isotope values of water and methane have been used as a strong indicator methanogenesis, as well as identifying the predominant metabolic pathways for methane generation, as CO_2 reducing methanogens impart a different hydrogen isotope fractionation factor ($\alpha_{CH4-H2O}$) than acetate fermenting methanogens (Schoell, 1980; Whiticar et al., 1986; Martini et al., 1996). Production of CO_2 causes formation waters associated with methanogenesis to be enriched in alkalinity (>10 meq/kg), and have very positive $\delta^{13}C$ values of dissolved inorganic carbon (DIC) (>10‰).

The geochemical conditions (salinity and redox) favorable for microbial metabolism are also important for identifying methanogenesis. Microbial methane generation is inhibited at high salinities and sulfate concentrations. A salinity level of approximately 2,000 mmole/L chloride has been proposed as a boundary for the onset of toxicity for methanogens, however, a range of tolerances is observed up to 4,000 mmole/L (Zinder, 1993; Ollivier et al., 1994; Waldron et al., 2007). Sulfate reducing bacteria (SRB) begin to out-compete methanogens in freshwater sediments for hydrogen and acetate at sulfate concentrations greater than 1 mmole/L (Lovley and Klug, 1982).

Results from the Appalachian Basin

Together the formation water and gas results suggest that the vast majority of methane in the Devonian organic-rich shales and sandstones across the northern Appalachian Basin margin is thermogenic in origin. Small accumulations of microbial methane are present at shallow depths along Lake Erie and in western NY. This is based on the observation that the majority of natural gases in Devonian organic-rich shales and sandstones at depth (>168 m) in the northern Appalachian Basin have a low methane to higher chain hydrocarbon ratio (3-35 mole%) with high $\delta^{13}C$ values of CH_4 (-53.35 to –40.24‰).

Dissolved gases in shallow groundwaters in Devonian organic-rich shales along Lake Erie contain detectable methane (0.01 to 50.55 mole%) with low $\delta^{13}C$-CH_4 values (-74.68 to -57.86‰) and no higher chain hydrocarbons, characteristics typical of microbial gas. Nevertheless, these groundwaters have only moderate alkalinity concentrations (1.14 to 8.72 meq/kg) and relatively low δ^{13}C values of dissolved inorganic carbon (DIC) (-24.8 to -0.6‰), suggesting that microbial methanogenesis is limited.

The geochemistry of co-produced brines shows evidence for microbial activity. High δ^{13}C values of DIC (>+10‰), slightly elevated alkalinity concentrations (up to 12.01 meq/kg) and low SO_4 values (<1 mmole/L) in select Devonian organic-rich shale and sandstone formation water samples suggest the presence of methanogenesis, while low δ^{13}C-DIC values (<-22‰) and relatively high sulfate concentrations (up to 12.31 mmole/L) in many brine samples point to sulfate reduction, which likely limits microbial methane generation in the Appalachian Basin.

Conclusions

Results from this case study demonstrate the importance of a combined gas and formation water approach for constraining the origin of natural gas in sedimentary basins. This approach may provide useful in understanding the origin of natural gas accumulations in shallow groundwater systems that may be associated with drilling and hydro-fracturing operations.

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The Origin of Some Natural Gases in Permian through Devonian Age Systems in the Appalachian Basin & the Relationship to Incidents of Stray Gas Migration

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Introduction

The molecular composition and isotope geochemistry for natural gases of Permian through Devonian age system rocks across the Central & Northern Appalachian Basin reveal gases are microbial, thermogenic, and mixed microbial/thermogenic in shallow systems, and thermogenic gases of different thermal maturities in commercially productive formations.

Since 2008, the pace of gas well drilling to the Marcellus shale has markedly increased in the Central & Northern Appalachian Basin. This pace is expected to continue as demand for natural gas grows. As drilling activity to the Marcellus shale has increased so have the number of reports of stray natural gas migration to shallow aquifer systems.

As allegations of hydraulic fracturing contaminating groundwater supplies received the attention of various media outlets, the link to stray natural gas contamination of aquifer systems created by hydraulic fracturing was simultaneously made, inexplicably. Pennsylvania leads all states in the number of Marcellus shale gas wells drilled and in production. Investigations of stray natural gas migration incidents in Pennsylvania reveal that not one incident of stray natural gas migration to a shallow aquifer system was caused by hydraulic fracturing of the Marcellus shale.

Background

Methane is the principal hydrocarbon detected in all Permian and Devonian age system rocks across the Appalachian Basin and in all stray gas migration incidents. It is the simplest and most abundant gas hydrocarbon, and is generated by microbial and thermogenic processes. Methane has a specific gravity of .555, and a solubility of 28-32 mg/l in water at standard atmospheric pressure (methane solubility increases with increases in hydrostatic pressure).

Though incidents of stray methane gas and stray methane gas migration have received significant attention as gas well drilling to the Marcellus shale has increased, the occurrence of methane gas, and stray gas migration incidents to shallow aquifer systems have occurred long before the start of the Marcellus shale drilling industry. This is particularly evident in Pennsylvania where there are often multiple potential sources of methane and subsurface methane migration. Potential anthropogenic sources of stray methane migration include abandoned and operating coal mines, abandoned and operating gas wells, natural gas storage facilities, coalbed methane wells, buried organic matter, and landfills.

Methane is also naturally occurring in some shallow, near surface environments. Microbial methane is generated by bacterial decomposition of organic matter through CO_2 reduction and acetate fermentation pathways. Thermogenic methane also occurs naturally in some aquifer systems in the Central and Northern Appalachian basin. (Laughrey, Baldassare, 1998; Baldassare, Laughrey unpublished data, 1999-2011; Revesez, and others, 2010)

Genetic Characterization of Natural Gas

Gas-origin/source correlations are determined from geochemical parameters including molecular composition, (relative concentrations of CH_4 to C6 hydrocarbons and non-hydrocarbon gases including He, H, CO_2, and N_2), and stable carbon and hydrogen isotope ratios. Analyses of the molecular composition, stable carbon and hydrogen isotopes of C1 – C5 hydrocarbons, and the radioactive isotope of C1 provide the highest level of geochemical evidence to interpret the origin of methane and other hydrocarbons in the subsurface.

Various researchers have determined by examination of stable carbon and hydrogen isotopes of methane that there are common isotopic compositions for thermogenic gas associated with coal and natural gas, drift gas, and other near-surface microbial gases (Coleman and others, 1977; Schoell, 1980; Whiticar,1986; Baldassare and Laughrey, 1997; Jenden and others, 1993; Kaplan and others, 1997; Rowe and Muehlenbachs, 1999, Revesz, and others, 2010; and Osborn and McIntosh, 2010).

Stable isotope compositions are expressed as

$\delta = (R_{sample} - R_{std})/R_{std}$:

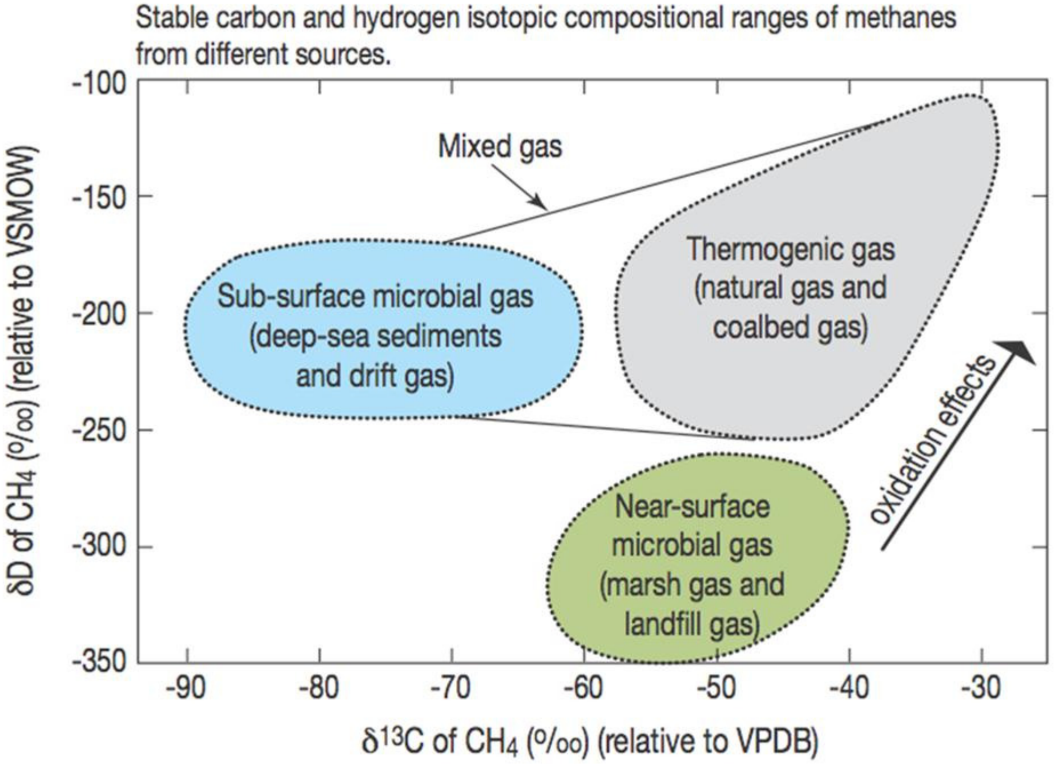
$$\delta^{i}E = \delta(^{i}E) = \delta(^{i}E/^{j}E) = \frac{N(^{i}E)_{B}/N(^{j}E)_{B} - N(^{i}E)_{std}/N(^{j}E)_{std}}{N(^{i}E)_{std}/N(^{j}E)_{std}}$$

where $\delta(^{i}E)$ refers to the delta value of isotope number *i* and *j* (heavy and light isotopes, respectively) of element E of sample B relative to the same element E in an international measurement standard (std); Rsample=$N(^{i}E)B/N(^{j}E)B$ and Rstd=$N(^{i}E)$ std/$N(^{j}E)$std are the ratios of the number of isotopes in unknown sample (B) and the international measurement standard. A positive $\delta(^{i}E)$ value indicates that the sample is more enriched in the heavy isotope than the international measurement standard. A negative $\delta(^{i}E)$ value indicates that the sample is depleted in the heavy isotope relative to the international measurement standard (Revesz, and others, 2010). Stable carbon isotope ratios are relative to Vienna Pee Dee Belemnite (VPDB) standard, and hydrogen isotope ratios are relative to Vienna Standard Mean Ocean Water (VSMOW) standard. (Gat and Gonfiantini, 1981)

In general, microbial methane formed by the acetate fermentation pathway (marsh gas & landfill gas) reveals isotope compositions of δ^{13}C1: -40 to -62 o/oo and δD: -270 to -350 o/oo.

Microbial methane formed via the CO_2 reduction (drift gas) pathway reveal isotope compositions of δ13C1: -62 to -90 o/oo and δD: -180 to -240 o/oo. Thermogenic methane reveal isotope compositions of δ^{13}C1: -26 to -50 o/oo and δD: -110 to -250 o/oo as depicted in Figure 9.

Additionally, δ^{13}C values of dissolved inorganic C (DIC) compared to the DIC in background groundwater can reveal additional evidence of methane origin in groundwater. Microbial processes such as CH_4 production or CH_4 consumption by oxidation can impart unique isotopic signatures to gases and components of the associated waters. Using a combined gas and water approach is significant to constrain the origin of natural gas in water wells. Microbial CH_4 production by acetate fermentation results in C and H stable isotope signatures in associated waters that are different from microbial CH_4 produced by CO_2 reduction (Whiticar and Faber, 1986; Revesz et. al., 2010; Osborn, McIntosh, 2010).



Stable carbon and hydrogen isotopic compositional ranges of methanes from different sources.

After Coleman and others (1993) based on the data set of Schoell (1980)

Figure 9. Isotope geochemistry for Marcellus Shale gas have expanded our view to reveal more thermally mature thermogenic methane than fit within the standard isotope crossplot, and that also reveal isotope reversals (C1, C2) throughout the stratigraphic section. Similarly, stable carbon and hydrogen isotope compositions reveal a broader range for early thermogenic methane.

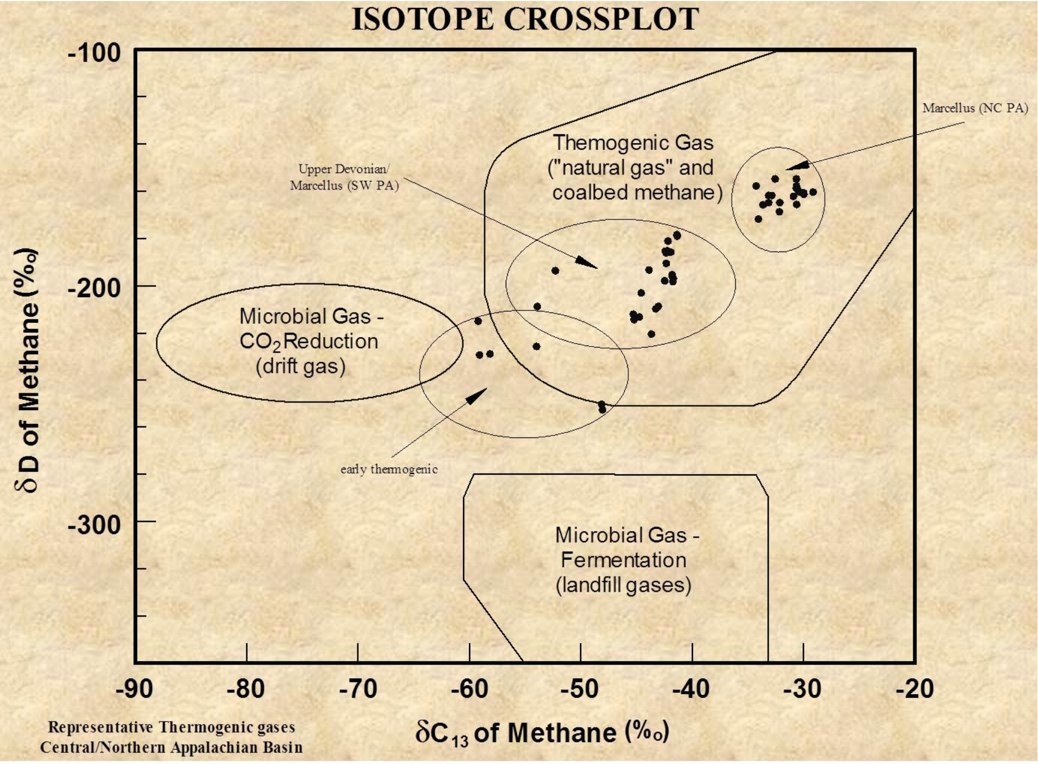


Figure 10 provides a small dataset of a much broader database documenting isotope compositions of thermogenic gases in areas across the Central and Northern Appalachian basin. In addition, recent geochemistry for Marcellus shale gas (unpublished data, Baldassare, 2011) and deeper natural gas resources in areas of the Appalachian basin reveal a complicated thermogenic history that cannot be explained by current hydrocarbon generation models (Burruss, Laughrey, 2010).

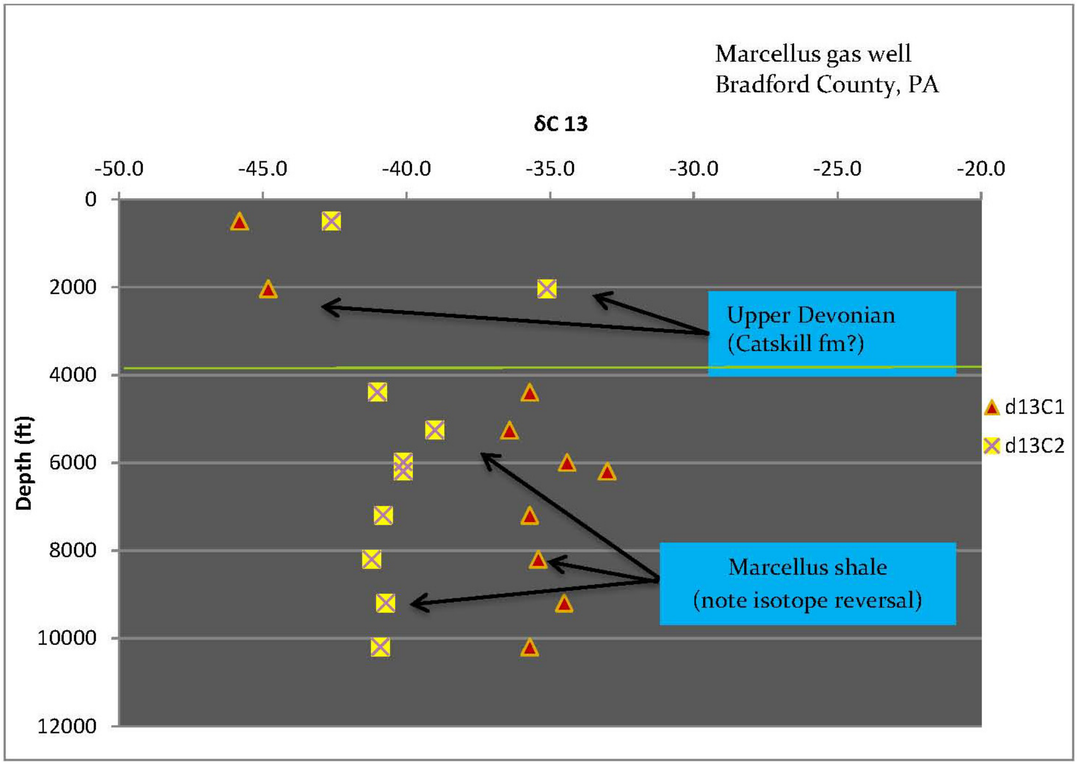


Figure 11 provides a small dataset of a much broader database documenting isotope compositions of thermogenic gases in areas across the Central and Northern Appalachian basin. In addition, recent geochemistry for Marcellus shale gas (unpublished data, Baldassare, 2011) and deeper natural gas resources in areas of the Appalachian basin reveal a complicated thermogenic history that cannot be explained by current hydrocarbon generation models (Burruss, Laughrey, 2010).

Conclusions

Defining the source of natural gas migration requires the investigation and synthesis of different data types, notably gas geochemistry and mechanism of migration. Geochemical evidence reveals that microbial and early thermogenic methane occurs naturally (pre-existing anthropogenic activity) in some shallow aquifer systems in areas of the Appalachian Basin . Water wells drilled to these formations create low pressure zones and potentially a migration point for naturally occurring methane or stray methane from anthropogenic sources. Building structures and other low pressure zones also represent potential migration pathways.

Given the occurrence of multiple potential anthropogenic and naturally occurring stray gas sources, it is essential that a thorough characterization and definition of background groundwater quality is implemented to define pre-existing conditions prior to drilling activity. Stray gas migration incidents should be thoroughly investigated and supported by multiple lines of evidence, principally, geochemistry & analyses documenting a mechanism of migration.

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Tracking Fracture Fluid Movement with Chemical and Gamma-emitting Tracers with Verification by Microseismic Recording

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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.

Chemical tracers, gamma-emitting tracers, microseismic (acoustic monitoring of small breakage sounds made by the rock during fracturing) as well as other simple measurements during and after fracturing can be very useful in describing hydraulic fracture development. The output from such monitoring can supply information on fracture complexity, frac conductivity, height growth, frac barrier effectiveness, well-to-well and frac-to-frac interference, water entry points and general fracturing execution.

This work focuses on both the “certainty” of the data (and sources) and the linkages between measurements with the intent to improve understanding of both the reliability of the data and the unknowns that can be addressed, either in part or in full, by the collected data.

Frac optimization begins with understanding the elements that control the placement and flow behaviors in a well. High permeability, conventional reservoir rocks basically have one-factor-dominated systems of porosity, permeability and fluid saturations. Such formations are relatively easy to describe in numerical units that yield to reservoir models and predictive behavior. As formation grain size, permeability and porosity reach the values in the rocks classified as potential-productive “shales”, the permeability drops into the 100’s of nano-Darcies. Effective, interconnected porosity may exist in fractures, interstitial portions of the fine-grained rock matrix and in openings within the kerogen, created by shrinkage and alternation of the organic content during maturation and subsequent hydrocarbon expulsion. As shale forms gas storage and flow structures, the rock fabric becomes radically different from convention reservoirs with natural fractures and weak zones within the fabric offering potential for complex fracturing and very unusual fluid behavior.

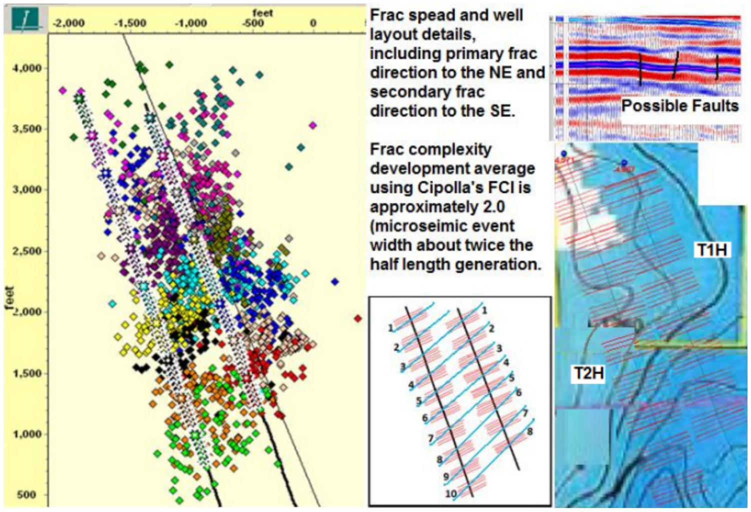
Field data sets are rarely perfect or complete, so having a number of data sources and an understanding of the type of information that can be drawn from often disparate data sources plus the level of accuracy possible from these measurements is very useful. The sources of information in well work may include:

- 3-D Seismic is well known for identification of geologic hazards, but is also important in combination with overlays of microseismic, micro-losses of mud and frac breakdown pressures to identify natural fracture locations.
- Geological structure mapping is valid for locating structures, reefs and areas of uplift that may be associated with increased incidence of natural fractures.

- Shale fabric considerations are part of the wider reaching candidate and sweet-spot identification as well as evaluation of interconnection of shale variables such as mineralogy, multiple porosity types and natural fracture occurrences.
- Frac Design and Pumping Records – pumping behavior (pressure, rate, loading) frequently raise questions about what is happening in frac initiation, frac extension and overall frac growth. Some frac analysis, either during or post frac, have been accepted in shale fracturing while others are of questionable use in the ultra-low permeability shales where most fluid loss is through the fractures in pressure dependent leakoff.
- Microseismic with pressure, rate and prop loading matched to the event time is a useful tool for tracking shear fracturing events that are common in many shale fracs where natural fractures open and form the flow paths and the extensive fracture-to-formation contact areas necessary for shale development. Microseismic is commonly used to describe the stimulated reservoir volume (SRV) in shales. Low-level gamma energy tracer-marking of proppant has developed many uses and supplies conformation of frac initiation points, near wellbore isolation between fracs in multi-frac wells, verifies frac diversion, proppant interference from frac-to-frac and even well-to-well on moderately closely spaced wells.
- Chemical tracers in the backflow from both stimulated wells and offset wells have been utilized for tracking water return from individual stages, polymer clean-up, well-to-well frac interference and possibly helping confirm complex fracture development.
- Recovered brine salinity, volume and ion analysis describe the return of frac fluid, the amount of mixing between frac water and shale connate fluids at time of sampling. Care must be exercised with this technology since single data points are often skewed by irregular flow patterns of the well (e.g., slugging). Using the data as a trend over time is the only accurate use.
- Production logging can be the final word on production from each frac stage; however, flow in horizontal wells is complex and examples of active production and simultaneous counter-current flow (into the well) are well described in both physical simulators and actual wells. Correct application of this technology is very valuable to identification and quantification of fluid entry and exit points.
- Production plots contribute significantly to evaluation of overall frac performance in a well-known area and as a piece of data in evaluating new areas.

Tracing Examples

One of the first necessities is to lay out the wall path with as much support information as possible. Figure 12 illustrates such a layout with well path, structural impacts, faults below and possibly through the play, the potential well-to-well linkage from expected frac direction, and comparison of frac behavior of offset wells.



Frac spead and well layout details, including primary frac direction to the NE and secondary frac direction to the SE.

Frac complexity development average using Cipolla's FCI is approximately 2.0 (microseimic event width about twice the half length generation.

Figure 12. A sequential or zipper fraced well pair in Tier 2 of the Barnett was drilled in a NNW direction in an area with possible faulting in the Ellenberger (immediately below the Barnett) with general primary frac direction of NE/SW. Well T1H has 8 stages; well T2h has 10 stages. Each stage was approximately 200,000 lb 100 mesh sand (1000 lb/ft); 7400 bbls water (40 bbls/ft of lateral); 6 perf clusters per frac stage; 1 bpm/perf; design frac rate was 50 bpm.

In this first example case, the available assessment information includes chemical fluid tracer (CFTs), proppant tracers ("100" mesh sand), microseismic monitoring and frac pump charts. The initial production or IP (24 hr) was 2.3 mmscf/d in the T2H and 1.0 mmscf/d in the T1H.

The first post-drilling information is usually the frac treatment pressure response, Figure 13. The break in pressure in stage 1 after about an hour on the T2H well was unusual, but the microseismic showed that the events were still solidly in the target zone, although frac direction had changed.

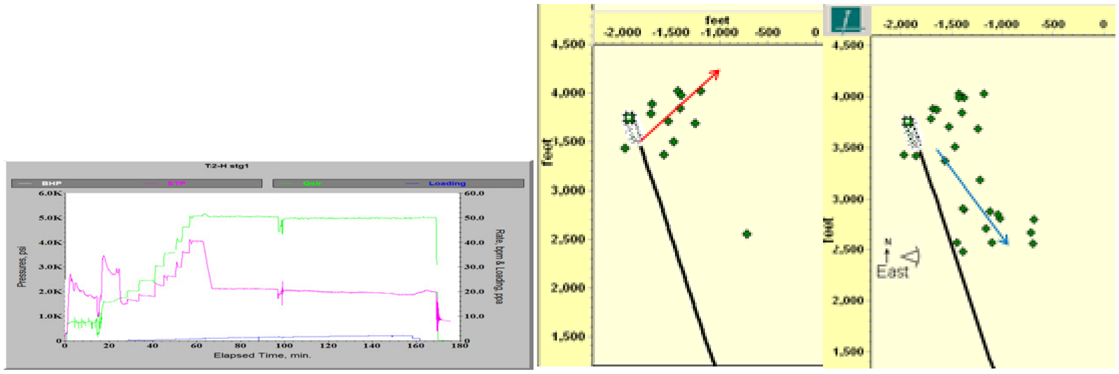


Figure 13 shows an unexplained pumping pressure break at about 60 minutes.

Fracture initiation pressure (breakdown) is low in this area and is marked by frequent frac direction switching along the natural fractures as often captured by the microseismic. The technique of ramping up slowly was common to allow the frac to open natural fractures and initiate active complex fracturing. This avoided both planar fracturing and breaking out of zone (important to avoid the salt water containing Ellenberger formation below the Barnett). Stage 1 (the toe stage) on the T1H well exhibited nearly the same behavior, Figure 14.

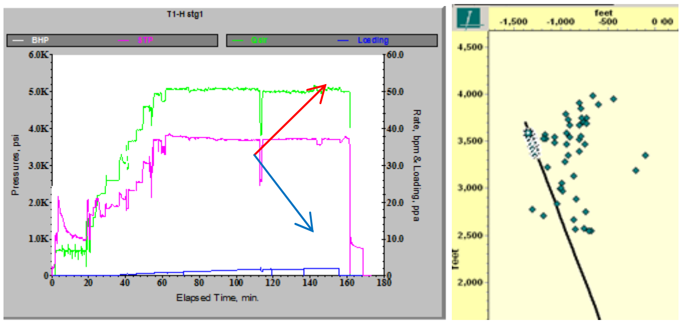


Figure 14. Near identical primary and secondary frac behavior on the T1H stage 1. The breakout pressure shift was hidden in the ramp up but occurs at about 45 minutes.

Flow back monitoring of returning frac and formation fluids was accomplished with chemical tracer monitoring and a logging run to measure the gamma levels along the wellbore. Results are in Figure 15.

Other Information Sources

Surface Treating Pressure (STP) is one source of information that is always available. Understanding the pressure relationship to down-hole events is never an exact method, but there are many cases where this surface information does have a strong linkage to demonstrated events. The closest agreement is often generated in a field-specific study and demonstrated knowledge of the geologic area. One example is the behavior of the net pressure development (rate of increase or decrease) during the fracs. This data has been more useful in specific shales such as the Barnett than any other conventional or unconventional formation (King, 2008; King, 2011).

The earliest data from the frac is the breakdown and the well's reaction to the increases in rate and proppant. Increasing the rate after the initial breakdown in increments of 5 to 10 bpm was recognized as a way to keep the frac in zone, first in the Devonian shale and later in the Barnett Shale (Yost, 1988; King, 2008; King, 2010). The explanation then and now is that the incremental increase gives the natural fractures time to break down and start the initial complexity development. After breakdown, every incremental increase in rate brings a sharp rise in pressure followed by a sharp drop grading into an attenuated decline as the fracture opens and reaches a steady leakoff rate. Notice that the declines in pressure become shallower and less in total in the later stages of rate increase. This is the effect of hydraulic diversion as friction through the perforations begins to control the flow rate into the subject perforations.

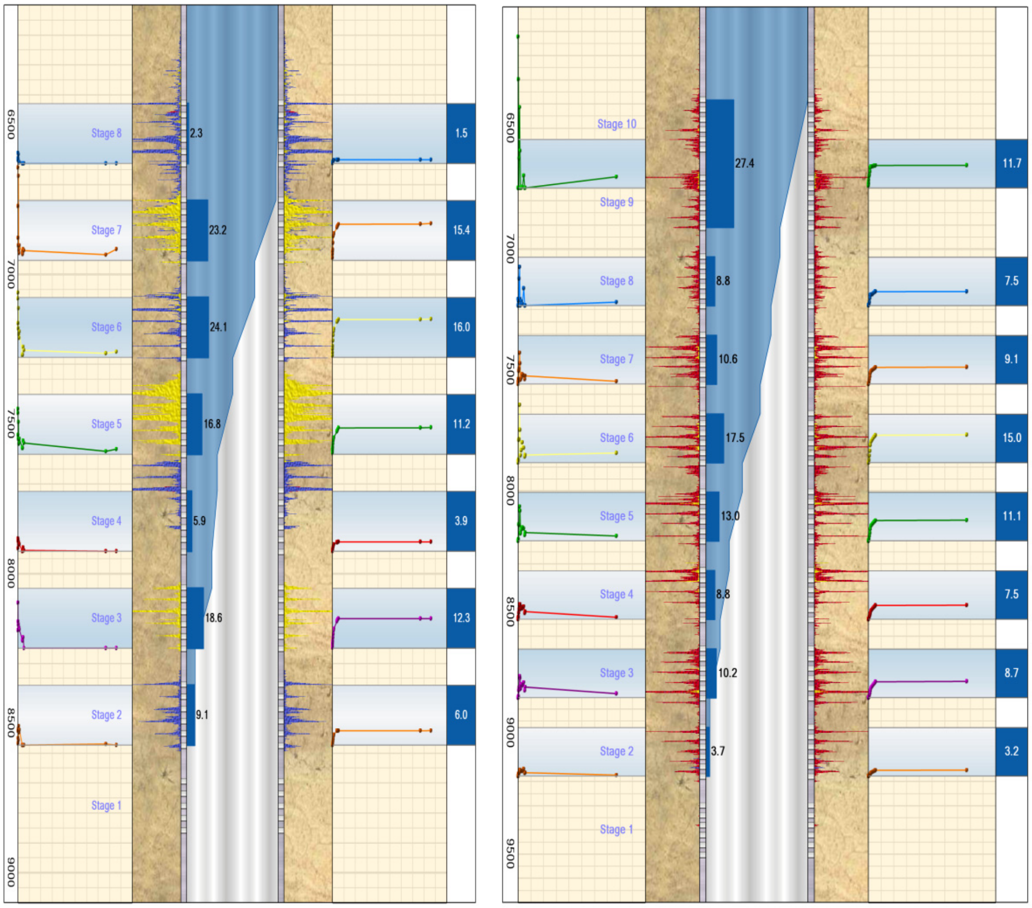


Figure 15 for T1H (left) and T2H (right) are the mass balances of fluid tracer flow coupled with information on frac breakdown from proppant tracer. The information from fluid tracing shows CFT concentration measurements in the backflow against volume produced (left side of each figure) are useful for estimating communication of the frac stage with the wellbore and how that communication changes over time or volume produced. The left side of each figure is the amount of initial fluid tracer recovered from each traced stage and is a reflection of the amount of traced load fluid actually recovered. The shaded area in the center is the contribution of each stage to the flow as calculated from the mass balance.

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Designing a Water Quality Program for Shale Exploration

Uni Blake
Majitox for Gastem USA

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Introduction

Protecting water quality is the key objective of developing a comprehensive water quality monitoring program. The design of an effective program requires characterizing and understanding all the chemical variables associated with the ambient water resources and the natural gas well site. This includes characterizing the: (1) quality of the surrounding water resources before any natural gas exploration activity starts (establishing a baseline), (2) additives used in hydraulic fracturing, (3) flowback fluids, and (4) ambient water after hydraulic fracturing activities. The combination of the above information is crucial when it comes to delineating and differentiating potential contaminations that may occur as a result of hydraulic fracturing.

Project Goals

There is concern about the potential contamination of surface and ground water primarily by the additives used in the hydraulic fracturing process and secondarily by the flowback from the well after the frac job is completed. The flowback contains some additives, salts, metals and organic compounds. Understanding the exact nature of these chemical streams is important especially when it comes to selecting indicator parameters that can be used to trace sources or track a contamination plume.

Project Design

Gastem USA designed a water quality monitoring program for use at the Ross Well site in Maryland, NY.

1. A sampling and analysis plan which incorporated quality assurance and quality control protocols was written to ensure that the data collected was accurate, precise, representative and complete.
2. A two mile radius centered at the Ross Well site was established as the area of interest. This region was determined to have the greatest potential of being impacted by activities at the well site because of proximity.
3. Analytical data from flowback fluid studies was gathered to aid in the development of the monitoring program (Hayes, 2009, Clark, 2009). This data was instrumental in selecting potential sentinel indicators and chemical tracers for potential contamination caused by hydraulic fracturing.

4. Water samples were collected at the surface and ground water (private wells) locations and tested for general water quality indicators and for other parameters that are associated with natural gas exploration and development activities. See Table 3.
5. The Well underwent hydraulic fracturing in the fall of 2008. Day one flowback water was sampled and analyzed. This water contained mostly additives and their chemically transformed constituents.
6. Water samples from the area of concern were collected for a twelve months following the hydraulic fracturing of the Shale.

Table 3. Parameters Tested in Surface Water and Residential Wells

• Dissolved methane, propane and ethane	• Volatile Organic Compounds
• Glycols	• pH
• Conductivity	• Chloride
• Alkalinity	• Sulfate
• Total Dissolved Solids	• Total Suspended Solids
• Calcium	• Magnesium
• Sodium	• Potassium
• Iron	• Manganese
• Arsenic	• Barium
• Chromium	• Lead
• Lithium	• Strontium

Challenges

There were challenges faced when developing the Shale water monitoring.

- Variability in baseline water quality: Residential water wells vary in depth and aquifer location. This variability has an impact on the concentrations of natural constituents found in the groundwater. It is known that drinking water wells located close to natural gas deposits may contain elevated levels of BTEX, methane, and strontium (Lesage et al., 1997). Gastem found that some wells had detectable levels of methane, and some had constituents that exceeded local water quality standards. This variability has an impact on creating a representative baseline water quality database. *Solution: A team of stakeholders in Otsego County are working on developing a program that will characterize groundwater quality.*
- Additives. Additive selection depends on the nature of each frac job, type of well, depth of the well, and the company performing the hydraulic fracturing. *Solution: Comparing fracturing fluids collected during the stimulation of various target formations to determine if the variability has an appreciable impact.*
- Chemical fate and transport. Fate and transport mechanisms of the potential contaminants have the ability to change the distribution and concentrations of the contaminants in the soil and groundwater. *Solution: Literature search on reported fate*

and transport models of the potential indicator parameters to determine their suitability as indicators.

Selecting Chemical Tracers

Specific indicator parameters can help overcome some of the challenges faced when developing a monitoring program. There are different types of chemical tracers and fingerprints that have been recommended to monitor potential chemical migration in hydraulic fracturing.

- Isotopes
- Frac Fluid Constituents
- Added Chemical Tracers

Frac Fluid Constituents as Unique Tracers

In Gastem's water quality monitoring program, frac fluid constituents were used as indicators of potential migration. The process of identifying indicator parameters in potential groundwater contamination is a complex problem because there are both natural and anthropogenic sources of chemically similar contaminants. However, because of flowback aging studies, it is possible to determine which constituents are anthropogenic and which are natural. Table 4, summarizes the constituents that were selected based in their available concentrations in the flowback fluids.

Table 4. Selected Flowback Constituents

Detected Constituents (Highest concentration to Lowest)	Indicator Potential	Source	Notes
Inorganic anions			
Strontium	N	Natural	
Lithium	N	Natural	
Sodium	N	Natural	
Calcium	N	Natural	
Potassium	Y	Natural/Added	
Organics			
Toluene	N	Natural	
Ethylene Glycol	N	Added	Biodegrades rapidly
Inorganic cations			
Chlorides	Y	Natural/Added	

Results

Table 5. Comparison of Select Parameters from Utica Shale Stimulation Results

ANALYTES	RESIDENTIAL WATER WELLS (before)	RESIDENTIAL WATER WELLS (after)	ADDITIVES IN FLUID
Non X-VOC	Non detect	Non detect	Ethylene glycol* 35 mg/L
SVOC	Non detect	Non detect	Acetone* 13 mg/L
X-VOCs	Non detect	Non detect	Chloromethane* 8.0 mg/L
Potassium	0.27-0.97mg/L	0.23-0.98mg/L	61.6 mg/L
Chlorides	0-69 mg/l	1.1-84 mg/l	5070 mg/l

*highest concentration parameter in the chemical group

Indicator parameters selected

Chlorides: Chloride's fate and transport has been extensively studied; as a conservative solute, chloride is commonly used in groundwater transport and plume monitoring studies (barber, 1992). It is modeled using advection and dispersion. However, chlorides are not necessarily unique to hydraulic fracturing. Chlorides are found in the formation brine solutions, and are also used in the region for de-icing road surfaces in concentrations high enough to impact groundwater (Godwin, 2003).

Potassium: Potassium has also served as an indicator in groundwater studies. It is highly soluble and not likely to precipitate. It is found in appreciable concentrations. It is used in well drilling activities as a clay stabilizer. If high levels of chloride are detected in the field in a water resource, and if elevated potassium can be confirmed, then the probability increases that there has been migration of frac fluid.

Table 6. Selected Indicator Parameters

	K^+	Cl^-
Ease of detection in field		X
Ease of detection in laboratory	X	X
Non-reactive with water	X	X
Low Sorption	X	X
Availability in Frac Fluid	X	X
Background interference	K-bentonite from the Utica Shale	Road salt

Conclusion

The possibility exists for potential migration indicators to be drawn from the field of additives used in hydraulic fracturing. The right choices can be a demonstrative and powerful tool. However, deciphering which constituent(s) can serve as a sentinel tracers and which other constituents can serve as confirmation tracers requires meticulous data review. The process includes understanding the chemical additives used, and the chemical processes that occur as a result of mixing at the surface and downhole.

Study Limitations: (1) Impact of produced water is not included within the scope of the study, since is generally understood that produced water does not contain significant concentrations additives (Hayes, 2009), (2) water quality contribution of the introduced supply water, and (3) site specific fate and transport information of organic constituents were not reviewed intensively.

Future: A comprehensive study to determine a potential organic confirmation tracer.

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Elucidating Water Contamination by Fracturing Fluids and Formation Waters from Gas Wells: Integrating Isotopic and Geochemical Tracers

Avner Vengosh, Nathaniel Warner, Stephen Osborn, Rob Jackson
Nicholas School of the Environment, Duke University

This presentation highlights the use of several isotope-fingerprinting methods coupled with a geochemical evaluation of the possible impacts of fracturing fluids and formation waters on the quality of water resources in gas-drilled affected areas. The presentation is based on preliminary data generated as part of Duke University research on the impact of gas drilling and fracturing fluids on shallow groundwater resources in Pennsylvania and New York. The study presented here is based on (1) systematic sampling of shallow groundwater from private wells from the Catskill aquifer in northeastern Pennsylvania in an attempt to establish baseline water quality data in areas that are expected to be affected by gas drilling and hydro- fracturing; (2) systematic analysis of the chemical and isotopic compositions of brines from the Marcellus Shale, one of the major target formations for unconventional gas exploration in the Appalachian basin; and (3) integration of geochemical (major and trace elements), water isotopes ($\delta^{18}O$, $\delta^{2}H$), and dissolved salt isotopes ($^{11}B/^{10}B$, $^{87}Sr/^{86}Sr$, $^{228}Ra/^{226}Ra$) of co-produced waters from a gas well in Pennsylvania. Boron and strontium isotopes were measured by thermal ionization mass spectrometry (Triton mass spectrometer) at Duke University using advanced methods with analytical reproducibility of 0.6‰ and 0.01‰, respectively (http://www.nicholas.duke.edu/tims/). Radium isotopes were measured at the Laboratory for Environmental Analysis of RadioNuclides at Duke University (http://www.nicholas.duke.edu/learn/). Trace metals were measured by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometer (ICP-MS) at Duke University.

The Upper Devonian Catskill aquifer in northeastern Pennsylvania is the focus of the baseline survey and is composed of various amounts of gray to red shale, siltstone, sandstone, and conglomerate (Low and Galeone, 2007). The bedrock aquifer is underlying glacial deposits, particularly in valleys, and overlying the Lock Haven Formation. Groundwater flow in the Catskill aquifer is mainly through fractures. The investigated private wells had a reported depth range 110 to 430 (median=270) feet.

The chemical data of the Catskill groundwater was evaluated based on preliminary sampling of the Duke team combined with archive water-quality database from Pennsylvania Department of Conservation and Environmental Resources (Taylor, 1984). The data show that the Catskill groundwater has low salinity (TDS<400 mg/L) with a typical Ca-HCO_3 composition. All levels of trace inorganic contaminants were below the EPA Maximum Contaminant level (MCL) drinking water guidelines (e.g, arsenic < 1.4 μg/L, barium< 230 μg/L). Preliminary ^{226}Ra data also show activities of 0.1 to 0.5 pCi/L, significantly lower than the MCL guideline of 5 pCi/L for combined ^{226}Ra and ^{228}Ra activities. The stable oxygen and hydrogen isotope ratios of the Catskill groundwater were found to overlap the local meteoric isotopic composition, with δ^2H - δ^{18}O relationships identical to the Local Meteoric Water Line (Kendall and Coplan, 2001). The strontium isotope ratios show ^{87}Sr/^{86}Sr range of 0.71201 to 0.71553. Boron isotopes (expressed as δ^{11}B values, normalized to SRM951) of the Catskill groundwater have a range of 13.1 to 28.1‰.

In contrast, integration of existing data on the chemical and water isotope compositions of the Marcellus Shale (Osborn and McIntosh, 2010) and new measurements of strontium and boron isotopes of the Marcellus brines and flowback water from a gas well in PA (Meadow #4, provided by the USGS) show that formation/ fracturing fluids waters from gas wells in PA have a significantly different composition relative to the local shallow groundwater in eastern PA. In addition to the large difference in the salinity of the water (TDS of 200-300 to mg/L in shallow groundwater relative to 250,000 mg/L in the Marcellus brines), the shallow groundwater has a Ca-HCO$_3$ composition relative to a Ca-chloride composition the produced water from the gas well. Given the multiple salinity sources (e.g., sewage and domestic waste water, road salt deicing, coal mining drainage, leachates from coal combustion products), the salinity factor cannot be a sole indicator for the contamination of groundwater by formation/ fracturing waters. Likewise, in spite of the fact that the stable water isotopes of the Marcellus shale are more enriched with ^{18}O and ^{2}H relative to the local groundwater with a significant lower δ^2H-δ^{18}O slope, this parameter cannot be used alone, as other salinity sources, particularly those that involved surface evaporation, would have similar isotopic composition.

A detailed analysis of the geochemical and isotopic variations of the flowback waters samples from Meadows #4 well in PA represents a mixture of fracturing fluids and the original Marcellus Shale brines shows that the concentrations of Ca, Ba, Sr, B, and Li, among others, increase in flowback fluids during the first twenty days sampling following fracturing. Our data also show that ^{87}Sr/^{86}Sr ratios increase from 0.71012 in the initial flow to 0.71122 on 20th flow day, as the isotopic shift occurred already on the first day of flow. Likewise, the δ^{11}B show a slight increase from 28.3‰ in the initial flow to 30.1‰ in the twentieth flow day. The Sr and B isotope ratios of the latest days are similar to those of the Marcellus Shale brines and thus indicating a blending of two end-members (1) fracturing fluids with lower salinity and concentrations of trace elements, lower ^{87}Sr/^{86}Sr ratios (<0.71012) and δ^{11}B (<28‰) values; and (2) the Marcellus Shale end-member with higher ^{87}Sr/^{86}Sr ratios (0.7115) and δ^{11}B values (32-33‰). This flow experiment also demonstrates that under operational conditions of continuous pumping, the composition of the Marcellus brines is expected to predominant the produced waters from gas wells.

Mixing modeling shows that the differences in both strontium concentrations and isotopic ratios between the Marcellus Shale brines and/or the mixed Marcellus-fracturing fluids with the local groundwater in eastern PA could be very useful in delineating even small contribution of formation water. Sensitivity tests show even a very small contribution of formation water (1/100) could be identified in a system that is controlled by mixing of the Marcellus Shale brines ($^{87}Sr/^{86}Sr$ =0.7115) and/or a mixture of the Marcellus Shale and fracturing fluids ($^{87}Sr/^{86}Sr$ <0.71012). Consequently, strontium isotopes could be a very sensitive tracer to track the possible contamination of shallow groundwater and surface water by formation/ fracturing waters from gas wells. While the boron concentrations of the flowback waters (17,000 to 63,000 μg/L) are higher by three orders of magnitude relative to the local groundwater (10 to 400 μg/L), the $\delta^{11}B$ values are only slightly higher (32-33‰ in the Marcellus brines relative to 13-28‰ in the Catskill groundwater). Nonetheless, this isotopic composition is different from other potential salinity sources (e.g., coal ash and acid mine drainage with elevated B concentrations and much lower $\delta^{11}B$ values of -15 to 0‰) and thus should be used, in conjunction with the other tracers as a critical tool to assess the possible interaction of formation/ fracturing waters with shallow groundwater or surface waters.

Overall, our study indicates that a detailed survey of the baseline chemical and isotopic compositions of shallow groundwater is crucial in evaluating possible contamination of flowback fracturing fluids and co-produced formation waters from gas wells. Our preliminary investigation of the Catskill formation groundwater from northeastern PA clearly shows significant chemical and isotopic differences between the shallow groundwater and the Marcellus brines and/or fracturing fluids mixed with the Marcellus brines. The ability to delineate trace levels of formation / fracturing waters in very early stages of water contamination depends on integration of multiple geochemical and isotopic tracers that could provide reliable and sensitive detections of contamination by effluents associated with hydro-fracturing and gas drilling.

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Summary and Abstracts from Theme 3: Field and Analytical Challenges

Summary of Presentations from Theme 3: Field and Analytical Challenges

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Technical Presentations

The first technical presentation in this theme addressed sampling issues such as representativeness, handling, and preservation.

Mark Engle, USGS, discussed the challenges of obtaining representative flowback fluid samples. Because fluids will undergo physical, chemical, and/or biological changes as they are moved from a geologic reservoir to the surface, sampling and preservation techniques affect the results. Dr. Engle also described modeling results indicating that composition of fluid varies non-linearly with flowback progress, which further emphasizes the need for time-series sampling.

The second set of technical presentations addressed practical quantitation and method reporting limits.

David Thal, Environmental Standards, Inc., discussed quality assurance (QA), quality control (QC), and method performance considerations for HF-related sampling. Mr. Thal discussed key quality parameters, including precision, accuracy, representativeness, completeness, comparability, sensitivity, and selectivity. He described a series of QA/QC best practices that can be applied to HF-related analyses and the interferences that could lead to QA/QC challenges.

Keith McLeroy, Texas A&M University, described a method for total organic carbon (TOC) determination utilizing a supercritical water oxidation (SCWO) procedure. The SCWO method allows for the effective analysis of TOC in samples where concentrations of inorganic species would usually inhibit oxidation.

Kesavalu M. Bagawandoss, Accutest Labs, discussed the challenges associated with practical quantitation limits, method detection limits, interferences, and dilution with respect to HF samples. Dr. Bagawandoss made a series of recommendations for dealing with highly viscous samples and emphasized the importance of establishing expectations and predefining analytical parameters.

The final set of technical presentations specifically addressed interference and dilution challenges associated with radionuclides.

Terry Romanko, TestAmerica Labs, described methods for radionuclide analysis (specifically radium-226/228) and provided suggestions for addressing interferences in different situations. He emphasized the importance of properly representing sample results.

Zoltan Szabo, USGS, discussed the need for high-precision radium analysis and described analytical methods and approaches that could be used to overcome the challenges of analysis in high brine matrices. He stressed the importance of yield monitoring in these analyses.

Summary of Discussions Following Theme 3: Field and Analytical Challenges Presentations

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The availability and capabilities of SCWO equipment. The equipment is available commercially, and Mr. McLeroy has developed specific methodologies and protocols for this application. The SCWO technique is the same as standard method 5310-D, though there is a difference in procedure. Mr. McLeroy stated that the SCWO method allows a user to focus on the organic carbons, which provide a food source for bacteria as well as act as potential tracers. Traditional TOC analyzers can only handle dilute samples, according to Mr. McLeroy.

Sample preservation and holding times. One participant recommended sub-sampling at the wellhead based on analyte; this way, samples can be treated individually based on their specific needs. For example, the participant explained that some samples can be immediately frozen while others can be filtered and preserved on site. A participant stated that holding times also vary depending on the type of sample. Speed is important for volatiles and reactive species, and these samples should be processed within 48 hours, according to this participant. However, the participant noted that less time-sensitive samples can be held for several days, or up to several weeks. Many analytes have prescribed holding times, and there is also guidance available from different sources. Participants emphasized that planning for holding times is an important part of the sampling and quality assurance planning process. Participants have found written plans and instructions for field personnel to be essential. In addition, participants suggested that operators and researchers should take into account the challenges of taking time-sensitive samples while in remote field locations. Participants also noted the importance of recording pressure checks and temperature for pressurized samples, as well as proper sample preparation and extraction.

Sampling methods and challenges. Participants recommended using bombs (pressurized piston cylinders) for sampling at the well. However, not all environmental labs analyze these types of samples—participants recommended that a lab with a hydrocarbon division may be better equipped to address them. Decontamination of bomb samples can be an issue, according to some participants, depending on the level of TDS. Use of Gas Processors Association (GPA) method 2174-93 was recommended by one participant in order to preserve the samples under well conditions. Participants noted that collection of samples utilizing this method at the wellhead would also provide valuable information on the gases present in the sample stream.

Analysis methods and challenges. One participant noted that only a handful of labs have the capability to do isotope labeling analysis. Participants also expressed concern about the lack of reference standards for HF-related analyses. In addition, participants indicated that labs and states do not often have standard protocols for dealing with flowback samples. One participant mentioned additional methods for radionuclide analysis that are not yet EPA-certified, as well as the availability of specialized ion exchange resins for radium. The geothermal industry may be a source of relevant information on this topic, according to a participant.

Cost-control strategies. Participants stated that good process knowledge and screening processes can reduce cost of analysis. Participants also suggested that reducing the sample load and pooling method development efforts within the industry may be possible. A participant noted that some of the specialized protocols described in the presentations, such as TOC analysis, only need to be carried out on the “rich samples” that are high in salt and interferences, and analysis may not be necessary for every sample that is analyzed. One participant suggested using university labs instead of commercial labs, though other participants noted that results from academic labs may not be defendable in court. Many participants stated that academic labs are essential for method development, evaluation of procedures and methodologies, and analyses of specialized tracers.

Sources of chemical species and the disposal of solid waste. One participant suggested that barium and radium could be introduced into the HF waste stream through the drilling mud, and also raised the possibility of temperature-dependent precipitates could be removing barium and radium from samples that are taken after precipitation occurs. A participant noted that uranium is generally not a concern in the Marcellus Shale. Participants added that radioactivity does build up in treatment sludge, as dispersed radioactivity is concentrated into a smaller, solid form. A participant confirmed that well cuttings are sent to landfills. Radiation from reused materials may be a concern, according to some participants.

Fluid disposal and injection wells. A participant stated that a particular operator only uses tanks, not pits, for storing produced water. Another participant noted that a different company uses double-lined pits with leak detection capabilities to hold produced water, and the pits are designed, constructed, and overseen by a third-party engineering firm. The participant continued to explain that the pits are drained and inspected on an annual basis. There are very few Underground Injection Control (UIC) wells that accept brine from oil and gas production (Class II injection wells) in the Marcellus Shale and only eight in Pennsylvania.

Produced water in the Marcellus Shale and other formations. In most shale plays, participants noted that the majority of produced water is produced in the first months after HF. In the

Marcellus Shale, participants stated that approximately 15–20% of the injected volume is returned fairly quickly and then decreases to 1–3 barrels per million cubic feet of gas. This varies slightly geographically, according to participants: the Marcellus in West Virginia is somewhat wetter compared to northern Pennsylvania, though the Marcellus tends to be the driest U.S. shale play. The Haynesville returns 15–30% of injected water quickly, the Fayetteville returns about 30% quickly, and the Barnett, which is very wet, returns about 50–100%, according to participants. One participant noted that he has never seen a Marcellus Shale well that has returned the volume of water that had been injected. Other participants noted that Marcellus Shale wells do return some water, and the composition appears to represent formation water. Some participants explained that the salinity in produced water samples appears to be from paleo-evaporated seawater brines; this chemical signature is distinct from the fracture fluids and from salt dissolution.

Abstracts for Theme 3: Field and Analytical Challenges

Abstracts were submitted to U.S. EPA by the presenters for use in this proceedings document. Not all presenters submitted abstracts of their presentations.

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.

Quality Assurance, Quality Control and Method Performance Considerations for Chemical Testing of Environmental Samples Impacted by Hydraulic Fracturing Fluids

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A discussion of the traditional quality assurance and quality control (QA/QC) as practiced in environmental studies directed by the USEPA is presented, focused on the most common analyses provided for samples of hydraulic fracturing (HF) fluids, flowback waters and related samples. The types of analyses being applied most commonly are presented, based on interviews and correspondence with five commercial laboratory companies. The specific types of QA/QC studies and samples applied in a robust quality assurance program are presented for each type of analysis. A survey of interferences is presented, based on hundreds of samples of HF fluids and flowback waters, along with a cautionary summary, alerting the data user to the need for review of HF data by senior analytical chemists.

The USEPA requires that a systematic planning process be used to plan for data quality in environmental data operations that receive funding from the agency. To support this requirement, EPA developed a process called the Data Quality Objectives (DQO) Process. The DQO Process is a reasonable starting point to build a model for data quality planning in general. It identifies the data quality indicators (DQIs) that need to be measured to help assure that data of known quality will be obtained. The DQO process and DQIs are described in the publication *Guidance for the Data Quality Objectives Process* (QA/G-4).[1] Other agencies have also developed and have collaborated on guidance that define essential data quality parameters for Department of Defense and Federal Facilities in general.[2,3] A review of these documents reveals very close agreement between them on the list of DQI's.

The USEPA also provides instructions and specific requirements for the information needed in a QA Project Plan (QAPP) for environmental data operations funded by EPA. This document is titled EPA Requirements for Quality Assurance Project Plans (QA/R-5).[4] Conducting the DQO Process and developing a QAPP that covers all the requirements in the R-5 document is a very good foundation for quality planning. However, experience has shown that the traditional approaches can fall short in providing data for difficult matrices and cases in which the need for high confidence at low detection limits affects decision making. It is important to understand how the properties and composition of hydraulic fracturing fluids and flowback waters can impact data quality.

The G-4 lists principal DQIs as precision, bias, representativeness, completeness, comparability, and sensitivity. (PARCCS). In many derivative publications, and guidance documents these are referred to as the “PARCC” parameters, leaving sensitivity out of the mnemonic, and unfortunately, out of the data quality planning process. Additionally, the sensitivity of a method as practiced in laboratories is usually demonstrated on a reference matrix, with no chemical interferences present. In reality, interferences often result in dilutions, or reduced sample volumes being analyzed in the laboratory. In many (but by no means all) cases, the EPA methods themselves direct the use of dilutions and reduced sample volumes to overcome the impacts of matrix-borne interferences. Here again, and understanding of the types of interferences likely to be encountered.

A survey of commercial laboratories (5 companies) was conducted to determine the commonly applied testing technologies for samples impacted by or suspected of containing hydraulic fracturing fluids or flow back waters. The following types of testing method were common to almost all responses. The testing technologies applied were:

Classical Chemistry, often referred to as wet chemistry. This general category of testing usually involves wet chemical techniques and physical characterization, and may rely on more than one type of determinative technique (e.g., titrimetry, spectrometry, gravimetry, ion selective electrodes, ion chromatography, voltatmetry). Examples typical of classical chemistry techniques used fracturing fluid and flow back water studies include: Alkalinity, Ammonia, BTU Content, Carbonate, Chloride, Methylene Blue Active Substances, Oil and Grease, Potassium, Sodium, Specific Conductance, Sulfate, Sulfide, Total Dissolved Solids, Total Suspended Solids. Most interferences on anionic evaluations come from competing anions.

Gas Chromatography of Volatile Organic Compounds and Gasoline Range Organics, (GC-VOC &GRO). This type of testing involves the collection of samples which will be purged with nitrogen in the laboratory to bring volatile components into a gas chromatograph (GC). The GC which separates the components by physicochemical properties (polarity, molecular weight, electrostatic interactions), and ports them into a detector such as a flame ionization detector or mass spectrometer. Examples of HF analytes measured by this type of test include: 2-butoxyethanol, gasoline range organics, methane, ethane. Most interferences are from non target volatile organic compounds. Cross contamination can be a significant issue due the mobility of the analytes.

Gas Chromatography of Semivolatile Organic Compounds, Diesel and Oil Range Organics,GC-SVOC, DRO, ORO). This type of testing involves the collection of samples which will be extracted with solvents in the laboratory to bring semivolatile components into a gas chromatograph (GC). The GC which separates the components by physicochemical properties (polarity, molecular weight, electrostatic interactions), and ports them into a detector such as a flame ionization detector or mass spectrometer. Examples of HF analytes measured by this type of test include: Diesel Range Organics, Oil Range Organics, Ethylene Glycol, Formaldehyde and many other analytes. Most interferences are from non-target organic compounds including fats, oils, organic acids and sulfur in the extracts.

Inductively Coupled Plasma – Atomic Emission Spectrometry. (ICP-AES) The sample is typically digested with acids under heated conditions and the liquid digestate is aspirated into an inductively coupled plasma. Light focused on the excited metals further excites the electon states, and they emit spectral light that is passed through a gradient filter and detected by wavelength and intensity. Examples of analytes that are detected by this technique include. Calcium, Barium, Iron, Potassium and Sodium and many others.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) The sample is typically digested with acids under heated conditions and the liquid digestate is aspirated into an inductively coupled plasma. The analytes are then passed into a quadupole mass analyzer, where they are separated by their mass-to-charge ratio. Some instruments pass the analytes through a collision cell prior to the quadrupole to reduce polyatomic interferences. The analytes then strike an electron multiplier and are detected by the current generated. Examples of analytes of interest in HF studies that are detected by this technique include: aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium selenium, silver, sodium, zinc.

Naturally Occuring Radioactive Materials. (NORM). Several radiochemical methods can be applied to this general field of testing. In each case the fundamental analytical technique involves carefully arranging the sample into a reproducible geometry and measuring the radioactive emissions using gross alpha, gross beta or gamma spectrometry when information on specific radionuclides is needed. Examples of nuclides of interest would include radium 226, radium 228.

Specialized Gas Chromatography or Liquid Chromatography – Mass Spectrometry. (GC/LC-MS SVOC). Liquid chromatography is well suited to highly polar, or ionic compounds, such as some phenols, glycols and organic acids. Specialized GC-MS can be used for alkylphenols, and some glycols and alcohols. For analytes that are easily fragmented, or in need of highly specific analyses, specialized mass spectrometry, such as ms/ms, ms^n, negative ion chemical ionization and high resolution mass spectrometry may be of use. The suite of QA/QC measures for these tests should be the same as those indicated for routine GC/MS, as long as the methods of sample preparation are analogous.

The commonly practiced types of QA Study or QC sample are defined and briefly described below.

Initial demonstration of proficiency or capability. (IDOC) This QA measure is typically comprised of a series of tests on positive controls (spiked reference samples) analyzed as a part of staff training or method capability testing. Precision and percent recovery are evaluated. This may be set up as four consecutive, or four simultaneously prepared samples.

Laboratory control sample (LCS). The LCS is a sample comprised of a reference matrix spiked with analytes of concern and taken through all steps of preparation and analysis within the laboratory. Recovery is compared to control limits established in the method, QAPP, or laboratory (based on historical data). It is prepared and analyzed with each batch of (20 or fewer) samples, and may be prepared in duplicate (LCSD) if insufficient sample material is available to perform the matrix spike/matrix spike duplicate or sample duplicate.

Matrix Spike (MS). An aliquot of the field sample is analyzed as received, and another aliquot is analyzed with a known quantity of analyte added prior to sample preparation and analysis. This measures recovery in the presence of matrix interferences.

Matrix Spike Duplicate (MSD). A separate aliquot of the field sample used for the MS is spiked and prepared in the same manner as the MS. The results are compared and are measures of both precision and recovery in the presence of the sample matrix.
For metals analyses, If the MS/MSD recoveries are unacceptable, the same sample from which the
MS/MSD aliquots were prepared should also be spiked with a post digestion spike.

Post digestion spike. For metals analyses, this step involves adding the metals directly to the prepared sample to determine whether the recovery problem is related to the original matrix, or the analytical technique.

Unspiked Duplicate, also termed Laboratory Duplicate. This is useful when the parameter being studies is always present, or when the parameter is difficult to add. It is simply a separate aliquot of sample analyzed alongside the original, and compared to the original sample as a measure of precision.

Dilution test. For metals analyses. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ±
10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

Method Blank (Sample Preparation Blank). A reference matrix is taken through all the steps of sample preparation and analysis, alongside the field samples, to determine whether contamination may be present in the laboratory environment or materials. This is a measure that helps evaluate the accuracy of the data, particularly at low levels.

Instrument Blank. A pure aliquot of the sample carrier (e.g.,gas, aqueous acid, solvents depending on the type of method) is introduced to the instrument in the same manner as a sample. This checks for sample-to-sample carryover potential in the analysis.

Trip Blank (Volatile Organic Compounds). A sample of analyte-free water is placed in a sample shipment cooler and travels with the sampling materials to the sampling location, and then travels with the samples back to the laboratory. This sample is analyzed to identify the potential for contamination of samples or sample bottles in the field or under shipping conditions.

The types of QA/QC that may reasonably be expected and required in a robust QA/QC program are presented in Table 7.

Table 7. Types of QC Samples Expected in Mature QA Programs

Quality Check	Classical Chemistry	GC-VOC (&GRO) & GC/MS-VOC	GC-SVOC	ICP-AES /ICP-MS	NORM	GC/LC-MS SVOC
Initial Demonstration of Capability	Yes	Yes	Yes	Yes	Yes	Yes
Method Detection Limit Studies	Most methods	Yes	Yes	Yes	Note 1	Yes
Standard Reference Materials (NIST traceable if available.)	Yes	Yes	Yes	Yes	Yes	Yes
Blind PE Samples	Yes	Yes	Yes	Yes		Yes
Trip Blanks (VOCs)		Yes				
Equipment Blanks	Rare	Yes	Yes	Yes	Yes	Yes
Instrument Blanks	Some	Yes	Yes	Yes	Yes	Yes
Field Duplicates	Yes	Yes	Yes	Yes	Rare	Yes
Method Blanks	Yes	Yes	Yes	Yes	Yes	Yes
Laboratory Control Samples	Yes	Yes	Yes	Yes	Yes	Yes
Matrix Spikes/ Matrix Spike Duplicates	Some	Yes	Yes	Yes	Yes	Yes
Laboratory Duplicates	Yes	Yes	Yes	Yes	Yes	Yes
Dilution Check				Yes		
Post Dilution Spike				Yes		

Notes

1. For NORM Minimum detectable activities are calculated using instrument backgrounds and sample characteristics.

Matrix Interferences Typical of HF Fluids, Flowback Waters and Related Samples

A series of chemical testing results from hydraulic fracturing fluid and flowback waters (within the first 5 days post-fracturing) from various Marcellus sites was examined for potential matrix-borne interferences. The results were provided by a commercial laboratory providing analytical services to many sites across the Marcellus formation. (TestAmerica Nashville). Ranges of observed levels of interferences were also taken from literature sources.[5, 6] Known interferences for the test methods are described below, along with an evaluation of the potential impact from matrix-borne interferences in this data set. Many of the known interferences are described *verbatim* as they appear in the USEPA Methods being applied.

Total Dissolved Solids (Gravimetric Method 160.1). Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing. Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate. Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg. (On a 100 mL sample this would be 2000 mg/L, 3.4% of the sample

Alkalinity (Titrimetric Method 310.1): Oil and grease may coat the electrode causing sluggish response for both alkalinity and pH. Salts of weak organic and inorganic acids may cause interference in the electrometric pH measurements. For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, method modifications are needed (i.e., the laboratory is to titrate to an electrometric endpoint of pH 3.9,using ASTM Standard, D- 067, Method D or superseding methods).

Anions (Chloride, Fluoride, Bromide, Nitrite, Nitrate, Phosphate, Sulfate): Any species with a retention time similar to that of the desired anion will interfere. Large quantities of ions eluting close to the anion of interest will also result in an interference. For example, high levels of organic acids that may interfere with inorganic anion analysis may be present. Two common species, formate and acetate, elute between fluoride and chloride. (Several organic acid homopolymers, polymers and telomers are used in fracturing fluids.

Total Kjeldahl Nitrogen (Methods 350.1,2,3,4 -Automated Colorimetry, Titrimetry, Potentiometry, Ion Selective Electrode): High nitrate concentrations (10X or more than the TKN level) result in low TKN values. If interference is suspected, samples should be diluted and reanalyzed. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

Barium (ICP-AED or MS, e.g. 200.7, 6010, 6020): The total recoverable sample digestion procedure will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

Metals by ICP-AED (e.g., 200.7, 6010): Flow variation due to physical interferences with the sample nebulization and transport processes can results from changes in viscosity and surface tension. This in turn can result in significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. The use of a high-solids nebulizer or sample dilution is often necessary. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. Here again, use of a high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample may help alleviate the difficulty. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. The QA/QC program should provide for matrix matching, and standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element. The Spectral Interference Check addresses most interferences at 50 mg/L. (300 mg/L Fe; 200 mg/L Al: 50 mg/L Ba; 50 mg/L Be; 50 mg/L Cd; 50 mg/L Ce; 50 mg/L Co; 50 mg/L Cr; (i) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO2; 50 mg/L Ti; 50 mg/L Tl and 50 mg/L
Of all these limits, barium was exceeded for one sample.

For ICP-MS (6020A)
The interference check standards for this method check for interferences at the following levels: Ca (300 mg/L); Fe (250 mg/L); Mg (100.0 mg/L); Na (250 mg/L) 250.0; K (100 mg/L); Cl (2000 mg/L).

- Of these, 10 percent of the samples exceeded the Na check standard level.
- Four percent (4%) exceeded the K check standard level.
- One percent (1.3%) of the 381 samples exceeded the Mg check standard level. Higher values reported in the literature exceed 25 times the interference check standard level.
- One of 74 samples exceeded the Fe check standard level.
- Two percent (1.8%) of the 542 samples exceeded the Cl check standard level.
- Three percent (3.0%) of the 439 samples exceeded the Ca check standard level. Higher literature values exceed the check standard concentration 100-fold.

Both metals methods note that dissolved solids should not exceed 0.2 % (True for 4% of 462 samples.) Literature values range up to 2.5%.

Finally, memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber.

Summary

Many standard analytical methods apply to the analysis of HF fluids and flowback water samples. However, they will perform poorly in some cases involving high levels of interferents. The interferences are well characterized, but a careful evaluation of the entire data set is needed to understand the potential biases.

For Metals, ICP-MS method alone is not a good fit for this matrix. ICP-Atomic Emission Spectrometry is needed to help overcome the many interferences well above the interference check standard.

Total Dissolved Solids data should be scrutinized for potential impacts on the metals data, and classical chemistry parameters.

Field duplicates should be used and evaluated carefully. If the anion data set does not make sense, consider using the method of standard additions.

Watch barium levels closely. If they are not consistent, or if they are high, engage a senior analytical chemist to help evaluate the data set.
It is important to evaluate the sulfate levels.

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Determination of Total Organic Carbons in Difficult Sample Matrices Utilizing the Supercritical Water-Oxidation TOC Procedure

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Abstract

The requirement for monitoring Total Organic Carbon (TOC) in oil/gas produced waters is inevitable. Most often, organics in these types of waters are volatiles, petroleum distillates, and natural organic acids or purposely added organic chemical compounds. These are generally difficult to analyze due to the presence of several interfering factors such as high turbidity, increased alkalinity, drilling mud additives and very high concentrations of various salts/minerals. Additionally, inorganic compounds in the waters (i.e.: brines, alkalinity) can give false high readings in traditional total organic analyses if not accounted for. The methodology of Supercritical Water Oxidation (SCWO) for monitoring TOC in oil/gas produced waters is being utilized and evaluated. The SCWO method has shown to be a robust procedure for analyzing TOC in otherwise difficult water matrices.

Introduction

An inherent issue with TOC analyses of oil/gas production water is the problem with difficult sample matrices. Produced waters contain a variety of organic and inorganic compounds which may be capable of exacerbating the chemistry mechanisms of analytical testing. Additionally, environmental monitoring of oil and gas produced wastewaters is dependent upon protocols that are robust enough to be of reliability. The work presented here is the evaluation of the modified wet-oxidation method described as Supercritical Water Oxidation (SCWO) for the analysis of TOC in very difficult oil/gas produced water sample matrices.

TOC Methodologies

TOC analysis is carried out through a choice of methodologies. Given that all TOC analyzers only actually measure total carbon, TOC analysis always requires some accounting for the IC that is always present. One analysis technique involves a two-stage process commonly referred to as TC-IC. It measures the amount of IC evolved from an acidified aliquot of a sample and also the amount of TC present in the sample. TOC is calculated by subtraction of the IC value from the TC the sample. Another variant employs acidification of the sample to evolve carbon dioxide and measuring it as IC, then oxidizing and measuring the remaining non-purgeable organic carbon (NPOC). This is called TIC-NPOC analysis.

A more common method directly measures TOC in the sample by again acidifying the sample to a pH value of two or less to release the IC gas to the atmosphere. Any remaining NPOC-CO_2 dissolved in the liquid aliquot is then oxidized releasing the gases. These gases are then transmitted to the detector for quantification.

TOC analysis does have intrinsic problems with difficult sample matrices. Turbidity, salinity, oils and other high mineral content samples can be problematic to adjust for and calibrate for in most traditional TOC methodologies. Concerns are environmentally controlled waters and oil/gas production wastewaters may not be monitored for TOCs' due to those issues.

If laboratories do have the capability to analyze difficult samples, they generally require more frequent maintenance, and weekly or daily recalibrations. To eliminate those issues, the SCWO was developed by GE Analytical Instruments (Boulder, CO.) to provide complete oxidation of organic carbons in complex sample matrices.

Supercritical Water Oxidation

By convention, there are three phases of matter; solid, liquid, and gas**.** Science has since shown that there are fifteen (15) states of matter, including super critical. When describing supercritical water, it is fundamental to understand the different phases of water. When liquid water is sitting in an open container at room temperature and ambient atmospheric pressure and then cooled to below 0 °C, the water transitions from liquid phase to solid phase. If the temperature of the liquid water in the same open container is raised above 100 °C, the water boils and transitions from liquid phase to gas phase. This is normal behavior when atmospheric pressure is kept constant at ambient conditions. At the same weight, or mass, solid water and liquid water occupy about the same volume at atmospheric pressure. The equivalent weight of gaseous water occupies about 1,600 times the volume at atmospheric pressure. However, if a gas-tight lid was attached on a container and the temperature rose to 130 °C, the liquid water would transition into the gas phase. Given that the volume needed for expansion is limited, the pressure in the headspace of the sealed container would begin to increase as more gas is formed. As shown in the phase diagram of water (Figure 1), an increase in head pressure raises the temperature at which all the liquid water would transition into the gas phase. As a result, the liquid water can be heated to a higher temperature without boiling. In this example, the resulting pressure inside the container increases to nearly twice atmospheric pressure.

At a specific point, pressure can no longer be increased to maintain the liquid phase. Beyond 374 °C and 218 atm (3200 psi), the gas and liquid phases merge to form another phase of matter. This phase is called Supercritical Water (SCW). When in a supercritical state, water exhibits the characteristics and benefits of both a liquid and a gas. The SCW has a density closer to that of a liquid, but can still diffuse similar to a gas. Organic material and gases become highly soluble in SCW and, conversely, inorganic salts become insoluble. These conditions are ideal for SCWO reaction. The GE InnovOx (InO) TOC Analyzer employed in the study uses the wet chemical oxidation technique. This process seeds the solution with an oxygen donating reagent. The InO employs a 30% weight/volume solution of sodium persulphate as the oxidizer. It then heats the sample and oxidizer in a sealed reactor past the critical point and SCWO is achieved. The increased pressure within the reaction cell noticeably enhanced the efficiency of the oxidation process, thus offering better recovery of CO_2 from difficult sample matrices. The CO_2 is then analyzed through a highly stable, non-dispersive infrared (NDIR) detector.

Noted in the current evaluation was the difference from the traditional Standard Methods for The Examination of Water and Wastewater (SM) 5310-D. Wet-Oxidation Combustion procedure, was that the SCWO process completely removed all by-products from the sample flow path between sample runs. This allowed for no carry over contamination from sample to sample. Analysis data from organic-free water blanks between sample runs, demonstrated this. Additionally noted was that as discussed previously, when water reaches a supercritical state, organic material and gases become highly soluble in SCW, while inorganic salts become insoluble. This concept is of importance, since salts will typically scavenge the oxidizer, resulting in an incomplete organic C to CO_2 conversion. This was of significance when analyzing the oil and gas produced wastewaters which were excessive in chlorides.

Evaluation of SCWO

The evaluation of the SCWO method employed the GE Analytical InO TOC Analyzer.

Water samples described in Table 8, were obtained from various sources that represented a spectrum of industries that may make use of the TOC results for organic loading monitoring into the environment, experimental TOC removal technology in the oil/gas industry, frac-water studies and raw water characteristics.

For this assessment, oil/gas produced and source waters that were to be treated by various membrane or chemical treatment systems were collected. The Global Petroleum Research Institute (GPRI) and the Membrane Separations Laboratory (MSL) at Texas A&M University (TAMU), College Station, Texas provided the samples and treatment technology. Samples were analyzed at The Texas Engineering Extension Service (TEEX) Water and Environmental Laboratory, College Station, Texas.

Table 8. Samples evaluated for SCWO-TOC

Sample Type	Industry
Brazos River	Source Water
Fractured Pond Waste	Gas Fracing Drilling
Brine Pond	Crude Oil Production
Glycol Condensate	Natural Gas Drying
Mixed Oil/Gas Wastewater	Environmental Monitoring

Table 9. Results of SCWO-TOC analyses

Raw Sample	TOC PPM	Dup. PPM	Blank PPM	%RSD	Cal. Range
Brazos	180.3	181.4	0.32	0.30	1000.0 PPM
Frac-Pond	83.2	82.5	1.90	.42	1000.0 PPM
Gly. Cond.	44.3	39.5	0.14	5.72	1000.0 PPM
Mixed WW	91.0	92.7	0.05	0.92	10000.0 PPM
Brine Pond	15.3	17.3	0.11	6.13	1000.0 PPM

Post Treated	TOC PPM	Dup. PPM	Blank PPM	%RSD	Cal. Range
Brazos	15.7	21.0	0.09	14.4	1000.0 PPM
Frac-Pond	22.3	19.2	0.12	7.4	1000.0 PPM
Gly. Cond.	40.0	33.1	0.11	9.58	1000.0 PPM
Mixed WW	15.7	19.2	0.01	10.0	10000.0 PPM
Brine Pond	16.0	19.1	0.94	8.83	1000.0 PPM

Raw Sample	Chloride PPM	Alkalinity PPM	Sulfate PPM	pH S.U.	Turbidity NTU
Brazos	33.4	162.9	3.1	7.44	775
Frac-Pond	25,492	427.0	67.8	8.01	360
Gly. Cond	10,041	34.7	273.8	9.05	12
Mixed WW	125	79.1	157.4	8.02	152
Brine Pond	31,202	519.0	6.81	7.73	88
Concentrate	**TOC PPM**	**Dup. PPM**	**Blank PPM**	**%RSD**	**Cal. Range**
Frac-Pond	59.3	58.2	0.32	0.94	1000.0 PPM
Brine Pond	2.44	2.42	1.01	0.41	1000.0 PPM

Observations

The InO and SCWO had performed well above expectations for this Phase I evaluation. The Brazos River sample containing the heavy silt was duplicated within a RSD of 0.30%. This was unexpected due to the high levels of solids. The brine pond water required no dilution, filtration or adjustments to the persulfate feed on the InO and primary standards ran after the analysis showed very good accuracy and no carry-over of contamination from the samples previously analyzed. Repeat samples of the frac-water had a precision of 7.4 %RSD, despite having a heavy black colored turbidity and strong sulfide odor. The glycol condensate water was clear but high in chloride. Organic-free water blanks ran between each sample repeat batch showed that the InO rinse cycles performed efficiently and no carry-over had occurred. The membrane concentrate wastes contained a heavy brine level and effectively, the SCWO method was able to compensate for those levels and still maintain RSDs' of 0.94 and 0.41 respectively.

The InO can determine Total Inorganic Carbon (TIC), NPOC, and TOC by difference (TC-IC). This allows for any combination of these modes in a single sample run or multiple duplicates on the same sample**.**

Conclusions

The Phase I evaluation of the SCWO-TOC Method had proved to be a robust and accurate method on otherwise difficult sample matrices. The SCWO methodology had demonstrated that at specific calibration levels, readings were analyzed without needed dilutions. Despite heavy solids loading and color in some samples, the InO was able to analyze the samples and provide proper line flushing and rinse cycles to prevent carry over. The analyst friendly software guided the technician through the step-by-step sample set-up and provided printer friendly reports. Calibration curves were not difficult to develop and the certified primary standards were delivered in a ready to analyze kit and there was no need to make-up laboratory standards. The portability of the analyzer was also a convenience as some samples were analyzed in different laboratory locations and outdoors during field trials. The InO required no carry gas cylinders making it an ideal analyzer for field analysis.

The SCWO methodology demonstrated to be a very robust method and had the ability to handle very difficult matrices and still provide accurate and precise results.

Practical Quantitation, Method Detection Limits, Interferences and Dilution Challenges

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Introduction

The matrices of fracturing fluids vary significantly in consistency and viscosity prior to fracturing. Hence, the analytical challenges increase with the viscosity of the samples provided for analyses. The samples on their own merits are generally representative. The flow back water samples are representative and uniform in nature unless the amount of sediment collected is a significant quantity.

Samples should be collected before fracturing and after fracturing to understand the contaminants present before fracturing and after fracturing. This would yield valuable information in terms of the transformations occurring during the fracturing process and comingling of components from the host materials or the extracted materials. Another suggested step would be collection of a sample of the host material if available or possible, to assess the material balance or source of components detected. One recommendation is that gas samples be collected at the point of exposure as the flow back water is discharged to determine if gaseous components are being emitted and account for any emissions. A suggested method for determining gaseous components in backflow water samples flowing from the wells would be the use of GPA 2174-93. (GPA=Gas Processors Association)(Constant pressure sampling method) This method allows for the samples to be captured at the same conditions as the stream of water.

Sample Preservation

Preservation of the samples of fracturing fluids for the various analytical processes does not pose any issues. Preservation of the Backflow waters generally does not pose issues. Volatile components in both the fracturing fluids and the backflow waters need not be preserved with acid and analyzed within 7 days of collection of samples thus satisfying the regulatory guidelines on holding times prescribed in the various methodologies.

Practical Quantitation Limits (PQLs) and Method Detection Limits (MDLs)

Methods employed for the analyses of the fracturing fluids include US EPA 500 and 600 series methods and Standard Methods for Water and Wastewater in combination with SW846 methods. The typical methods utilized are listed in Table 10. The components of the analytical suite are presented in Table 11 through Table 14. The practical quantitation limits are also listed in the aforementioned tables. However, depending on the viscosity of the frac fluids and the interferences present in the various samples, the PQLs may be affected. The MDLs utilized are those determined for liquid samples. The MDLs are statistically derived, as outlined in the method requirements for each of the analytes.

Interferences and Dilution Challenges

The PQLs are affected when dilutions are performed due to the matrix interferences. Dilutions are generally performed to alleviate the viscosity issues or the interferences. Based on analyses performed, flow back waters do not pose the same challenges as the fracturing fluid matrices. Matrix interferences, specially, with respect to samples which are highly viscous are handled by dilutions. Surrogates and internal standards and its behavior in the matrix vary based on the samples. In some cases matrix spike compounds behave differently. For example, in a VOA analysis the gases may recover fine yet the rest of the compounds may not recover at the same level as the gaseous components. In a semi volatile analysis the acid surrogates may not recover where as in the same sample the base surrogate recoveries may be adequately recovered. Based on our experience, approximately 10 % of the fracturing fluid matrices pose analytical challenges for the parameters analyzed.

Table 10. Typical Methods

- Acrylamide – SW846 – 8316
- Metals – Method 200.8 / 245.1
- Cyanide/ Weak and dissociable, Total – SM 4500 CN E & I
- Fecal and Total Coliform – SM 9222D & B
- Total Phenolics – EPA Method 420.1
- Herbicides – SW846 – 8151
- Ion Chromatography – EPA Method 300
- Residual Chlorine – SM 4500 CL G
- VOA's – EPA Method 624
- SVOA's – EPA Method 625
- Pesticides/ PCB's – EPA Method 608
- 2,3,7,8 – TCDD – EPA Method 1613B
- Halo Acetic Acids – EPA Method 552.3
- 1, 2 – Dibromoethane – EPA Method 504.1

Table 11. 500 Series Methods

Method	Analyte	PQL, ug/L
EPA 552.3	Dibromoacetic Acid	0.8
EPA 552.3	Dichloroacetic Acid	0.8
EPA 552.3	Monobromoacetic Acid	1.6
EPA 552.3	Monochloroacetic Acid	0.8
EPA 552.3	Trichloroacetic Acid	0.8
EPA 552.3	Haloacetic Acid	0.8
EPA 504.1	1,2-Dibromoethane	0.025

Table 12. 600 Series Methods

Method	Analyte	PQL,ug/L
EPA 608	4,4´-DDD	0.05
EPA 608	4,4´-DDE	0.05
EPA 608	4,4´-DDT	0.05
EPA 608	Aldrin	0.05
EPA 608	alpha-BHC	0.05
EPA 608	Aroclor 1016	1
EPA 608	Aroclor 1221	1
EPA 608	Aroclor 1232	1
EPA 608	Aroclor 1242	1
EPA 608	Aroclor 1248	1
EPA 608	Aroclor 1254	1
EPA 608	Aroclor 1260	1
EPA 608	beta-BHC	0.05
EPA 608	Chlordane	0.5
EPA 608	delta-BHC	0.05
EPA 608	Dieldrin	0.05
EPA 608	Endosulfan I	0.05
EPA 608	Endosulfan II	0.05
EPA 608	Endosulfan sulfate	0.05
EPA 608	Endrin	0.05
EPA 608	Endrin aldehyde	0.05
EPA 608	gamma-BHC	0.05
EPA 608	Heptachlor	0.05
EPA 608	Heptachlor epoxide	0.05
EPA 608	Methoxychlor	0.05
EPA 608	Toxaphene	1
EPA 624	1,1,1-Trichloroethane	1
EPA 624	1,1,2,2-Tetrachloroethane	1
EPA 624	1,1,2-Trichloroethane	1
EPA 624	1,1-Dichloroethane	1
EPA 624	1,1-Dichloroethene	1
EPA 624	1,2,4-Trichlorobenzene	1
EPA 624	1,2-Dibromo-3-chloropropane	5
EPA 624	1,2-Dichlorobenzene	1
EPA 624	1,2-Dichloroethane	1
EPA 624	1,2-Dichloropropane	1
EPA 624	1,3-Dichlorobenzene	1
EPA 624	1,4-Dichlorobenzene	1
EPA 624	2-Chloroethyl vinyl ether	5
EPA 624	Acrolein	50
EPA 624	Acrylonitrile	5

Method	Analyte	PQL,ug/L
EPA 624	Benzene	1
EPA 624	Bromodichloromethane	1
EPA 624	Bromoform	1
EPA 624	Bromomethane	1
EPA 624	Carbon tetrachloride	1
EPA 624	Chlorobenzene	1
EPA 624	Chloroethane	1
EPA 624	Chloroform	1
EPA 624	Chloromethane	1
EPA 624	Dibromochloromethane	1
EPA 624	Dibromomethane	1
EPA 624	Epichlorohydrin	10
EPA 624	Ethylbenzene	1
EPA 624	Methylene chloride	1
EPA 624	Styrene	1
EPA 624	Tetrachloroethene	1
EPA 624	Toluene	1
EPA 624	Trichloroethene	1
EPA 624	Vinyl chloride	1
EPA 624	cis-1,2-Dichloroethene	1
EPA 624	cis-1,3-Dichloropropene	1
EPA 624	m,p-Xylene	2
EPA 624	o-Xylene	1
EPA 624	trans-1,2-Dichloroethene	1
EPA 624	trans-1,3-Dichloropropene	1
EPA 624	1,3-Dichloropropylene	1
EPA 624	Trihalomethane, Total	1
EPA 624	Xylenes,Total	1
EPA 624	Epichlorohydrin	25
EPA 625	1,2,4-Trichlorobenzene	5
EPA 625	1,2-Diphenylhydrazine	5
EPA 625	2,4,6-Trichlorophenol	5
EPA 625	2,4-Dichlorophenol	5
EPA 625	2,4-Dimethylphenol	5
EPA 625	2,4-Dinitrophenol	25
EPA 625	2,4-Dinitrotoluene	5
EPA 625	2,6-Dinitrotoluene	5
EPA 625	2-Chloronaphthalene	5
EPA 625	2-Chlorophenol	5
EPA 625	2-Nitrophenol	5
EPA 625	3,3´-Dichlorobenzidine	10
EPA 625	4,6-Dinitro-2-methylphenol	25

Method		PQL,ug/L
EPA 625	4-Bromophenyl phenyl ether	5
EPA 625	4-Chlorophenyl phenyl ether	5
EPA 625	4-Nitrophenol	25
EPA 625	Acenaphthene	5
EPA 625	Acenaphthylene	5
EPA 625	Anthracene	5
EPA 625	Atrazine	5
EPA 625	Benz(a)anthracene	5
EPA 625	Benzidine	20
EPA 625	Benzo(a)pyrene	5
EPA 625	Benzo(b)fluoranthene	5
EPA 625	Benzo(g,h,i)perylene	5
EPA 625	Benzo(k)fluoranthene	5
EPA 625	Bis(2-chloroethoxy)methane	5
EPA 625	Bis(2-chloroethyl)ether	5
EPA 625	Bis(2-chloroisopropyl)ether	5
EPA 625	Bis(2-ethylhexyl)phthalate	5
EPA 625	Butyl benzyl phthalate	5
EPA 625	Chrysene	5
EPA 625	Di-n-butyl phthalate	5
EPA 625	Di-n-octyl phthalate	5
EPA 625	Dibenz(a,h)anthracene	5
EPA 625	Diethyl phthalate	5
EPA 625	Dimethyl phthalate	5
EPA 625	Fluoranthene	5
EPA 625	Fluorene	5
EPA 625	Hexachlorobenzene	5
EPA 625	Hexachlorobutadiene	5
EPA 625	Hexachlorocyclopentadiene	10
EPA 625	Hexachloroethane	5
EPA 625	Indeno(1,2,3-cd)pyrene	5
EPA 625	Isophorone	5
EPA 625	N-Nitrosodi-n-propylamine	5
EPA 625	N-Nitrosodimethylamine	5
EPA 625	N-Nitrosodiphenylamine	5
EPA 625	Naphthalene	5
EPA 625	Nitrobenzene	5
EPA 625	Pentachlorobenzene	5
EPA 625	Pentachlorophenol	25
EPA 625	Phenanthrene	5
EPA 625	Phenol	5
EPA 625	Pyrene	5

Method	Analyte	PQL,ug/L
EPA 625	2-Methylphenol	5
EPA 625	3 & 4-Methylphenol	5

Table 13. SW846 Series

Method	Analyte	PQL, ug/L
EPA 8316	Acrylamide	80
EPA 8270	Atrazine	50
EPA 8151A	2,4,5-TP (Silvex)	1
EPA 8151A	2,4-D	0.94
EPA 8151A	Dinoseb	0.47
EPA 8151A	Dalapon	1.1

Table 14. Inorganic Parameters

Method	Analyte	PQL,mg/L
EPA 200.8	Antimony	0.005
EPA 200.8	Arsenic	0.005
EPA 200.8	Barium	0.005
EPA 200.8	Beryllium	0.004
EPA 200.8	Cadmium	0.005
EPA 200.8	Chromium	0.005
EPA 200.8	Copper	0.005
EPA 200.8	Lead	0.005
EPA 200.8	Nickel	0.005
EPA 200.8	Selenium	0.005
EPA 200.8	Silver	0.005
EPA 200.8	Thallium	0.005
EPA 200.8	Zinc	0.005
EPA 245.1	Mercury	0.005
SM4500 CN E	Cyanide	0.005
SM45000 CN I	Cyanide, Weak and dissociable	0.005
Method	Analyte	PQL,colonies/100 mL
SM9222 D	Coliform,Fecal	1
SM9222 B	Coliform, Total	1
Method	Analyte	PQL,mg/L
EPA 300.0	Nitrogen,Nitrate (As N)	0.5
EPA 300.0	Nitrogen,Nitrite (As N)	0.5
EPA 300.0	Fluoride	0.5
EPA 420.1	Phenolics,Total Recoverable	0.005
SM 4500 Cl G	Residual Chlorine,Total	0.1

Challenges for Precise Radium Analysis in Brine

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For detailed evaluation of changes in radionuclide concentrations and isotopic ratios for studying waste-products generation during the fracturing process, analyses require high precision and accuracy to study progressive changes. For high precision determinations of the concentrations of Ra-226 with low minimum critical detection levels (MDLs), the most commonly used technique is the USEPA-approved (Method 903.1) radon (Rn) de-emanation technique, with scintillation counting of the Rn-222 progeny after cold-trapping on charcoal. Alpha spectrometry has become increasingly commonly used to determine concentrations of Ra-226 and Ra-224. A 100-minute count for a 1 L (liter) sample is typically long enough to achieve detection of 1 pCi/L or less for aliquots with simple matrices. Spectral analysis can also explicitly include short-lived progeny for verification and improved quantification (example, polonium-216 progeny for Ra-224). The gamma-spectrometric analytical technique (Standard Method 7500-E of the American Public Health Association, 2005) has become more commonly used, though it has a precision and MDL that is higher by factors of 2 to 5 times that of the alpha-spectrometry technique using reasonable operating parameters. The strong benefit of the technique is that it can determine all four of the naturally occurring Ra isotopes, but the background gamma count cannot be maintained at levels as low as those achievable for measurements of alpha particles, thus is also more imprecise under comparable optimal operating conditions. The counting time required for alpha-spectrometric or Rn de-emanation technique is shorter (60 or 100 minutes as opposed to 1000 minutes), the sample volume required for achieving low MDL is smaller (1 L as opposed to 4 to 20 L), and the instrumentation is less bulky and expensive than that required for gamma-spectrometric determination. Delayed coincidence counting has also allowed for an increase in precision and level of detection for multiple isotopes at once.

Multiple-counting inductively coupled plasma mass spectrometry (MC-ICP-MS) and thermal ionization mass spectrometry (TIMS) for U and Th isotopes and for Ra-226 have increased the level of available precision and detection substantially. The limitation to these atom-counting techniques remains the ability to effectively extract and purify the isotopes from brine. One option in using TIMS is once the Ra-226 is precisely quantified, other techniques such as gamma spectroscopy that define the ratios of Ra isotopes relative to each other can be used on remaining sample aliquots to provide a reasonable estimation of the other Ra isotope levels.

Extraction, purification, and pre-concentration along with successful yield monitoring are critical steps in achieving low detection levels and high precision. Chemical separation by forming a Ba-Ra-sulfate precipitate is most commonly used to extract Ra isotopes from sample aliquots for Ra-226 and Ra-224 analyses by the Rn de-emanation technique, by alpha spectrometry, and by gamma spectroscopy. Cation-exchange chromatography (Bio-Rad AG 50W-X8 resin) is typically used to first separate the Ra and Ba, which are then eluted with 8-molar HNO_3, and are co-precipitated with barite using a seeding suspension. The seeding suspension is needed to ensure the formation of uniform fine-grained crystals of the barite that is required for efficient counting by alpha spectrometry, which is most sensitive of the techniques to variable geometry of the Ra-bearing precipitate crystals. Experimentation is ongoing with forming the precipitate on Sr-specific resin filter plates. Using a bed of previously precipitated microcrystalline barite as the seeding agent has also been tried to improve the precipitate formation. A widely used approach is to improve barium-specific precipitation performance by using ethylenediaminetetraacetic acid **(**EDTA) as a complexing agent to limit co-precipitation of impurities. The Ra isotopes can also be extracted using Mn-coated fibers (prepared in various forms: in tubes, filters, or disks). Oxic and alkaline waters are optimal for use with the Mn-coated fibers, however, in acidic and especially in reducing waters such as might be encountered in deep brines extraction efficiency is limited by the properties of manganese oxide. Numerous element-specific resins have been developed for Ra, Pb, U, Th that may allow for efficient extraction of the target radionuclide from briney solution. The issue is cost, as the more specialized extraction resins are expensive.

A radioactive tracer (Ba-133) is added to the samples during precipitation of the Ra-bearing barium sulfate to determine yield. The Ba-133 is analyzed by gamma spectroscopy after sample purification. The Ba-133 tracer on occasion exhibits variable and low recoveries in Ca- and Sr-rich waters, and in these cases, may not match Ra recovery quantitatively; thereby, cation-exchange removal or EDTA-complexing of the competing divalent cations is helpful. For atom counting techniques, a mixture containing Ra-228 and Th-229 can be added to monitor recovery of Ra-226 and Th-228. The use of these tracers more precisely quantify Ra yield, which is appropriate for the more precise measurements possible with atom counting as opposed to activity counting techniques. Organic compounds provide interference for TIMS analysis, Ba for MC-ICP-MS analysis, and Th-228 interferes with yield tracing with Ra-228; of these, limiting Ba poses the greatest challenge. The MDLs and precision for all analysis types are influenced by dilution, interference effects, temperature or pressure that need to be understood and minimized.

Revisiting the Major Discussion Points of the Technical Presentation Sessions

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The workshop lead and theme leads addressed the workshop participants and EPA at the conclusion of presentations for each theme and at the end of the workshop. Leads summarized the major discussion points and commented on research needs and data gaps.

Wilma Subra of Subra Company, the workshop lead, thanked the participants for their questions and summarized the main points of the presentations and discussions. She said several presenters emphasized the need for baseline/background sampling, whether required by state regulations or by industry initiative. According to participants, salinity or chloride alone is not sufficient as a tracer; many other important parameters should be considered. Ms. Subra noted an important knowledge gap related to tracers and changing chemistry of recycled produced water and flowback water. Reuse/recycling is clearly an important topic, but the effects on tracers and chemicals deserve more study. Other key points included the difference between sanitizing and sterilizing (with regard to biocide) and air quality. Air quality is not addressed in the current study plan, but it is an important issue. The need for method and procedure development was reiterated by Ms. Subra. While this is somewhat outside of the scope of the EPA study, it forms the basis of investigating potential instances of ground water, shallow subsurface, and surface contamination. She noted that there are many issues that need to be addressed by industry, EPA, and academia. Ms. Subra described a few key issues, including disclosure, wastewater recycling, and tracer selection.

Cal Cooper of Apache Corporation, the Fracture Fluid Chemistry theme co-lead**,** emphasized that fracture fluid composition is quite variable, depending on many geologic and operational factors. However, fracture fluids for individual wells are not composed of large numbers of chemicals. Industry has changed fluid composition over time to address technical, economic, and environmental factors. The gas industry produces from formations with a very wide range of pressure, temperature, and salinity characteristics, but industry works to solve any challenges posed by these geologic differences. Dr. Cooper noted the movement toward using more environmentally-friendly chemicals in fracture fluids. In addition, Dr. Cooper said that industry understands that surface contamination is a key concern that needs to be addressed; at the same time, the public confuses surface and subsurface issues, which causes perception problems. Dr. Cooper also mentioned that more information is needed on fate and transport of deep subsurface flow and on how pressure dissipates at these HF sites.

Tracy Bank of University at Buffalo, the Fracture Fluid Chemistry theme co-lead, speaking from the academic perspective, said she feels encouraged by the presentation of data from the industry participants. She asked industry to share data and samples with academia. Dr. Bank also invited workshop participants to submit results to an upcoming Geological Society of America session related to HF that she is co-chairing with Dr. Kirby.

Jennifer McIntosh of University of Arizona, the Fingerprinting theme lead, described the need for collecting baseline water chemistry data before and during HF operations, as well as for continued time-series sampling after HF operations are completed. Data are needed regarding water quality from ground water (including shallow aquifers) and native formation waters from the target shales, as well as data on the chemistry of the injected fluids. She noted that an understanding of inherent variability is a key component of baseline studies. An understanding of local (shallow) methane sources is also important. Dr. McIntosh also described the power of combining multiple tracers, including water chemistry, stable and radiogenic isotopes, and gas components. The combination of tracers is especially important as some chemical constituents (e.g., pH, metals) are not conservative and can change as conditions (physical, chemical, biological) change within the formation, within the well bore, inside storage tanks, etc. Dr. McIntosh also emphasized the importance of understanding the basic source of solutes in shale formation waters to distinguish them from injected HF fluids.

Kesavalu Bagawandoss of Accutest Labs, the Field and Analytical Challenges theme lead, thanked the speakers for an interesting discussion on analytical techniques and sampling. He described the major points of the discussion, including the need for the development of additional analytical methods and the need for defining expectations for analytical techniques. He also noted the need for good data on the chemical components that are used in HF, as well as the natural chemical characteristics of the subsurface. He emphasized the importance of sample collection; an analytical method is only as good as the sample collected. Because of the pressures and temperatures involved, sampling for HF purposes is a sophisticated process and requires trained personnel following established protocols. The radionuclides analysis methods must be updated to account for the interferences due to the presence of barium, strontium, and calcium in the matrix, as outlined in the presentations.

Summary of Discussions Following Workshop and Theme Lead Summaries

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The importance of surface water. A participant stated that in EPA Region 3 (Pennsylvania, Maryland, West Virginia, Virginia, Delaware, and Washington, DC), 80% of the population is served by surface water. One participant noted that surface water issues will be addressed at the fourth workshop on Water Resource Management.

The transport, storage, and use of HCl. A participant explained that HCl for HF is brought to the site in its own tank and is not stored on location. The HCl reacts rapidly downhole, usually with common salts, and is completely spent, claimed the participant, and it is not returned to the surface. The participant indicated that the concentration used is usually 15% HCl by weight, and the maximum concentration that can be held by the tanks is 28% by weight. One industry participant noted that his company recently began testing an acid reduction program and subsequently eliminated acid use from 80% of their HF jobs in southwestern Pennsylvania. He noted that using acid is a site-specific decision.

The possibility of a test site. A participant suggested that a test site be established where industry, academia, and EPA could all have access for sampling. One participant pointed out that there is no such thing as a “typical” HF site, due to geographic variations in the shales. Several participants raised potential safety concerns. One participant recommended that EPA participate in a short course on the basics of HF.

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 (http://www.spe.org/glossary/wiki/doku.php/)
Schlumberger	Schlumberger Oilfield Glossary (http://www.glossary.oilfield.slb.com/default.cfm)

ABBREVIATIONS

BTEX benzene, toluene, ethyl benzene and xylene
CMC critical micelle concentration
DBNPA 2,2-dibromo,3 nitriloproprionamide
DIC dissolved inorganic carbon
DQI data quality indicator
DRH diesel range hydrocarbons
EDTA ethylenediaminetetraacetic acid
EXAFS extended x-ray absorption fine structure
FIFRA Federal Insecticide, Fungicide and Rodenticide Act
FR friction reducer
GMWL global meteoric water line
GPA Gas Processors Association
HF hydraulic fracturing
HPG hydroxypropyl guar; a chemically modified guar (SPE)
IC inorganic carbon
ICPMS inductively coupled plasma mass spectrometry
INAA instrumental neutron activation analysis
InO GE InnovOx TOC Analyzer
LPG liquified petroleum gas
MC-ICP-MS multiple-counting inductively coupled plasma mass spectrometry
MCL maximum contaminant level
mD millidarcy
MDL method detection limit
MIT mechanical integrity test
MSI Marcellus Shale Initiative
NDIR non-dispersive infrared
NORM naturally occurring radioactive material
NPOC non-purgeable organic carbon
NSLS National Synchrotron Radiation Lightsource
PQL practical quantitation limit
QA quality assurance
QAPjP quality assurance project plan
QC quality control
SCW supercritical water
SCWO supercritical water oxidation
SEM/EDX scanning electron microscopy energy dispersive x-ray
SRB sulfate reducing bacteria

SRV stimulated rock volume
STP surface treating pressure
SVOCs semivolatile organic compounds
TDS total dissolved solids
THPS tetrakis hydroxymethyl phosphonium sulfate
TIC total inorganic carbon
TIMS thermal ionization mass spectrometry
TMAC tetramethylammonium chloride
TOC total organic carbon
TOF SIMS time-of-flight secondary ion mass spectrometry
UIC Underground Injection Control
ULWP ultra-lightweight proppants
USGS United States Geological Survey
VES viscoelastic surface-based system
VOCs volatile organic compounds
VSMOW Vienna Standard Mean Ocean Water
XANES x-ray absorption near edge spectroscopy. Also called µXANES.
µ-SXRF micro-x-ray fluorescence

GLOSSARY

baseline water quality water quality data collected prior to the beginning of an activity

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)

imbibition absorption and adsorption of fluids into the pores of the rock (SPE)

interfacial tension a measurement of the difficulty of moving a fluid past another fluid (SPE)

irreducible water saturation the fraction of the pore space occupied by water when the hydrocarbon content is at maximum. This level of water can only be reduced by flow of very dry gas that evaporates the water. (SPE)

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

leak off The magnitude of pressure exerted on a formation that causes fluid to be forced into the formation. The fluid may be flowing into the pore spaces of the rock or into cracks opened and propagated into the formation by the fluid pressure. (Schlumberger)

retrograde condensate condensate that precipitates in the pore space of the rock in a previously dry gas (single phase) reservoir as the pressure drops below the dew point. The building condensate severely reduces the permeability to gas (SPE)

shut-in pressure The surface force per unit area exerted at the top of a wellbore when it is closed at either the Christmas tree or the BOP stack. The pressure may be from the formation or an external and intentional source. The SIP may be zero, indicating that any open formations are effectively balanced by the hydrostatic column of fluid in the well. If the pressure is zero, the well is considered to be dead, and can normally be opened safely to the atmosphere. (Schlumberger)

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

tight formation non specific term meaning lower permeability (SPE)

type-II kerogen Exinite; has an intermediate hydrogen to carbon and oxygen to carbon ratio. Oil and gas prone with yields of 40 to 60%. From plant sources. (SPE) See also *kerogen*.

type-III kerogen Vitrinite; has a low hydrogen to carbon and high oxygen to carbon ratio.Low quality gas prone with low yields. Source is wood and high order plant debris. Coal precursor. (SPE) See also *kerogen*.

workover repairing a well. Usually implies opening the well and running in with a tubing string. May or may not involve killing the well and may or may not involve a conventional rig (SPE)

SC
IEN
CE

EPA
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Environmental Protection
Agency

Office of Research and Development (8101R)
Washington, DC 20460