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Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Fate and Transport

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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 impacts of hydraulic fracturing on drinking water resources. EPA scientists are undertaking a study to better understand its potential impacts. The scope of the proposed research includes the full lifespan of water in HF, from acquisition of the water, through the mixing of chemicals and actual fracturing, to the post-fracturing stage, including the management of flowback and produced water and its ultimate treatment and disposal.

EPA has included stakeholder concerns in the planning process of the study from its inception. EPA engaged stakeholders in a dialogue about the study through a series of webinars and facilitated public meetings held May–September 2010. Four technical workshops were hosted by EPA during 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. EPA submitted a draft study plan to the Science Advisory Board (SAB) in February 2011 and the peer review of the draft study plan was held on March 7–8, 2011. (At the time the technical workshop proceedings were developed, the SAB had not given its official review of the study plan to EPA.)

The goal of the technical workshops was three-fold: (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 documents to inform research that effectively evaluates the relationship between HF and drinking water.

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

About the Proceedings

These proceedings provide an overview of the fifteen presentations and two posters given on fate and transport at the Technical Workshop for the U.S. EPA Hydraulic Fracturing Study held on March 28–29, 2011. This workshop consisted of three sessions or themes: Theme 1– Contaminant Identification, Transformation and Transport; Theme 2– Impacts of Hydraulic Fracturing on Natural Transport Systems; and Theme 3– Models to Predict Transport. 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 third of four technical workshops on topics relating to the EPA Hydraulic Fracturing Study. The other three workshops are: Chemical and Analytical Methods (Feb. 24–25), 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 Fate and Transport 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, JP Nicot of the University of Texas at Austin, assisted EPA in finalizing details for the workshop and served as the lead editor of the proceedings document. The theme leads—Angus McGrath of Stantec for Theme 1, Ahmad Ghassemi of Texas A&M University for Theme 2, and Andrew Havics of pH2, LLC/QEPA for Theme 3—served as editors for their respective themes.

Workshop Participants

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James	Farmerie	ITT Water & Wastewater
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Agenda

Technical Workshops for the Hydraulic Fracturing Study

Fate & Transport · March 28-29, 2011

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

March 28, 2011

8:30 am **Registration**

9:00 am **Welcome**

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

JP Nicot, Workshop Lead, University of Texas at Austin

Pat Field, Facilitator, Consensus Building Institute

Theme 1: Contaminant Identification, Transformation & Transport

9:15 am **Technical Presentation Session 1: Chemical Transformation and Identification**

A Simple Approach Identifying Contaminants of Most Concern to Underground Drinking Water Supplies from Hydraulic Fracturing Operations, Carl Palmer, Idaho National Laboratory

Contaminant Characterization of Effluent from Pennsylvania Brine Treatment, Inc., Josephine Facility Being Released into Blacklick Creek, Indiana County, Pennsylvania: Conceptual Models of Exposure Pathways to Recreationalists, Private Well Water Users and Municipal Water Systems, Conrad Volz, University of Pittsburgh

Fracing & Associated Media Composition in Colorado, Andrew Havics, pH2, LLC/QEPA

10:30 am **Break**

10:40 am **Technical Presentation Session 2: Chemical Mobility and Potential Pathways**

Comparison of Hydraulic Fracture Fluid Composition with Produced Formation Water Quality Following Fracturing: Implications for Fate and Transport, Debra McElreath, Chesapeake Energy Corporation

Fate and Transport of Select Hydraulic Fracturing Compounds of Potential Concern, Angus McGrath, Stantec

Fate and Transport Evaluation of Potential Release Scenarios during Hydraulic Fracturing Operations, George Deeley, Shell Exploration & Production

A Protocol to Characterize Flowback Water Contamination of Shallow Waters from Shale Gas Development, Donald Siegel, Syracuse University

12:10 pm **Lunch**

Theme 2: Impacts of Hydraulic Fracturing on Natural Transport Systems

1:00 pm **Technical Presentation Session 3: Fracture Propagation**

Rock Failure and Stimulated Volume in Hydraulic Fracturing, Ahmad Ghassemi, Texas A&M University

Fracture Growth in Layered and Discontinuous Media, Norman Warpinski, Pinnacle – A Halliburton Service

2:00 pm **Break**

2:10 pm **Technical Presentation Session 4: Fluid and Gas Flow in Fractured Formations**

Flow of Gas and Water in Hydraulically Fractured Shale Gas Reservoirs, Zhong He, Range Resources

Characterizing Mechanical and Flow Properties using Injection Falloff Tests, David Cramer, ConocoPhillips

Role of Induced and Natural Imbibition in Fracturing Fluid Transport and Fate in Gas Shales, Alan Byrnes, Chesapeake Energy Corporation

3:25 pm **Break**

3:35 pm **Revisit the Major Discussion Points of the Technical Presentation Sessions**

JP Nicot, Workshop Lead, University of Texas at Austin

Angus McGrath, Theme 1 Lead, Stantec

Ahmad Ghassemi, Theme 2 Lead, Texas A&M University

4:00 pm **Adjourn for the Day**

March 29, 2011

Theme 3: Models to Predict Transport

8:00 am	**Technical Presentation Session 5: Demonstration of Models and Determinations of Model Accuracy** *Modeling Versus the Real World of Hydraulic Fracturing*, Denise Tuck, Halliburton *Modeling Philosophies and Application*, Andrew Havics, pH2, LLC/QEPA *Modeling Drinking Water Related Human Health Risks from Hydraulic Fracturing Additives*, Manu Sharma, Gradient
9:15 am	**Revisit the Major Discussion Points of the Technical Presentation Session** JP Nicot, Workshop Lead, University of Texas at Austin Andrew Havics, Theme 3 Lead, pH2, LLC
9:45 am	**Closing Discussions** Jeanne Briskin, Hydraulic Fracturing Research Task Force Leader, EPA Office of Research and Development JP Nicot, Workshop Lead, University of Texas at Austin

Summary and Abstracts from Theme 1: Contaminant Identification, Transformation and Transport

Summary of Presentations for Theme 1: Contaminant Identification, Transformation and Transport

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Technical Presentations

The first set of technical presentations in this theme addressed chemical transformation and identification.

Carl Palmer, Idaho National Laboratory, described an approach for categorizing and ranking contaminants to determine which may be of most concern regarding impacts to ground water from hydraulic fracturing. This approach has been employed for in situ oil shale development to help identify contaminants that are likely to pose the greatest risk based on the contaminants' mobility, concentration, and toxicity. Mr. Palmer presented a graphical representation of mobility versus toxicity and identified contaminants of the greatest concern as those with both high mobility and high toxicity. Mr. Palmer also described the general methodology and limitations of this approach.

Conrad Volz, University of Pittsburgh, gave an overview of a field sampling and contaminant characterization study of the effluent from the Pennsylvania Brine Treatment facility (a public owned treatment works, or POTW) in Josephine, Pennsylvania. The POTW accepts only wastewater from the oil and gas industry, including flowback water from Marcellus Shale gas extraction operations. The study estimated the 24 hour mean concentration of a range of chemicals and compounds including barium (Ba), bromides (Br^-), strontium (Sr), benzene, 2-butoxyethanol (2-BE), chlorides (Cl^-), magnesium (Mg), total dissolved solids (TDS), sulfate (SO_4^{2-}), and pH. The concentrations found were compared to various drinking water, human exposure, and aquatic health guidelines and standards with many contaminants found at concentrations that exceeded standards and guidelines. Dr. Volz also discussed the implications of processing flowback fluids at numerous POTWs. Dr. Volz then provided environmental public health recommendations based on the results of the analysis.

Andrew Havics, pH2, LLC/QEPA, described results of a 2008 study on HF impact and estimated risk in four basins in Colorado. He conducted an assessment based on samples from pit solids and fluids, fracture fluids, drilling fluids, early and late flowback fluids/produced water, and soils (for background analyses). Potential chemicals of concern were identified and selected for risk assessment purposes. Mr. Havics emphasized the importance of determining background concentrations of potential contaminants. He described the limitations of classic risk assessments in this specific application and described his study methodology, including statistical assumptions and study limitations. Mr. Havics also noted the importance of establishing a process for addressing non-detects in the chemical analyses.

The second set of technical presentations addressed chemical mobility and potential pathways.

Debra McElreath, Chesapeake Energy Corporation, discussed implications of predicted fate and transport of HF chemicals, fate evaluation, and transport evaluation. Temperature and pressure affect the fate and transport of HF fluid components. Chesapeake compared vendor-supplied information on HF fluids, mixed HF fluids, and produced formation water following HF activities over the life of the well. The study demonstrated that produced water volumes vary based on location and tend to decrease over time. In addition, chemical concentrations can stabilize at different times in different shale plays and produced formation waters are highly variable in composition within and between shale formations. Ms. McElreath recommended that TDS, chloride, and divalent cations, which are present in high concentrations in formation waters, could be used as indicator chemicals.

Angus McGrath, Stantec, described a series of common and unconventional compounds of interest (COIs) in HF fluids. He discussed each compound's chemical properties and fate and transport characteristics, including mobility and persistence. In addition, he discussed the implications for each with respect to drinking water quality. Drawing on his fate and transport findings including the lack of persistence, Dr. McGrath noted that monitoring for any of these compounds may only be warranted if impacts from more concentrated reagents in fracturing fluids are detected in wells.

George Deeley, Shell Exploration and Production, described considerations for fate and transport evaluation of potential release scenarios during HF operations. Developing a conceptual site model (CSM) is the first step in the detection and prevention of potential problems. Appropriate CSMs consider all controls in the HF process as reflected in existing regulations and best management practices. Dr. Deeley emphasized the importance of focusing on realistic release scenarios, chemicals, pathways, and receptors, as well as the importance of establishing background concentrations and understanding the uncertainty of data and analytical methods.

Donald Siegel, Syracuse University, discussed a protocol to characterize flowback fluid contamination of drinking water and determine its source. Much of the concern over flowback fluids stems from elevated concentrations of trace elements, radium-226, and trace organic substances according to Dr. Siegel. However, these constituents geochemically react and naturally attenuate, stated Dr. Siegel, and thus elevated concentrations do not clearly identify the extent of flowback fluid contamination in drinking water. Dr. Siegel proposed that concentrations and ratios of dissolved halogens (hloride, bromide, and fluoride, and iodide) allow for identification of contamination from shale gas or oilfield brines. He described geochemical mixing models that allow for the identification of small amounts of flowback water, even when other salinity sources previously contaminated the water.

Summary of Discussions Following Theme 1: Contaminant Identification, Transformation and Transport Presentations

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The mobility/toxicity matrix. A participant asked if original fracture fluid concentrations were considered in the mobility/toxicity assessment. The presenter clarified that the provided example was from an oil shale and did not involve fracture fluids, but that the matrix approach is applicable to other scenarios. A participant asked why the two order of magnitude reduction in mobility was selected as a differentiation point in the mobility/toxicity matrix. The presenter explained that this was not a standard number but was selected based on travel times in the system.

Treating produced water at the Josephine facility. A participant asked whether the plots of decreasing barium and strontium concentrations over a 24-hour period represented conditions following cessation of waste disposal. The presenter clarified that surface disposal at the Josephine facility is a continuous operation and concentrations vary over time, and added that some POTWs discharge periodic pulses of effluent. The presenter indicated that the rate of discharge from the Josephine facility is approximately 150,000 gallons per day, and studies are currently investigating pore water and annual flow. He added that the facility uses settling ponds and sulfate (to remove barium) to treat the produced water and no techniques are applied to treat for salinity or chloride. Another participant asked if a person would be less affected by barium than by the high salinity of this water. The presenter agreed and noted that there are drinking water wells less than 100 yards downstream of the Josephine plant. He added that the capture curves of wells like these indicate that water can be pulled directly from the stream, which is a source of concern.

The presenter clarified that the Josephine facility has been in operation since the mid-1980s and currently takes only oil and gas fluids; it previously treated conventional brine from oil operations and now receives Marcellus Shale fluids instead. The presenter indicated that the Josephine facility processed 15 million gallons between July 2010 and December 2010. A participant asked if salinity had previously been a concern at the facility, and the presenter responded that the facility had not received much attention until it began processing Marcellus Shale flowback water. The presenter agreed with a participant's point that chloride levels have likely been high for years. He added that high levels of arsenic have also been found in ground water samples throughout Pennsylvania, though these are likely natural background concentrations.

A participant asked if the study considered influent to the plant or conditions upstream from the plant. The presenter clarified that his team did not have access to those potential sample locations and relied on information published by the Marcellus Shale Coalition, the Society of Petroleum Engineers, and other sources. However, the presenter mentioned that there are a number of ongoing projects addressing these issues including one study that is investigating impacted versus unimpacted drainages throughout Washington and Greene counties. The study is investigating Ba, Sr, several anions, 2-BE, thallates, and BTEX (benzene, toluene, ethylbenzene, and xylenes).

A participant asked how actual discharge values compare to permit limits at the Josephine facility. The presenter indicated that the permit allows for extremely high levels of total dissolved solids (TDS) and chloride. He compared this to the Dunkard Creek fish kill in 2009, noting that golden algae could grow at this site, especially in the summer, when flow decreases in the stream. A participant confirmed that the Josephine plant is grandfathered under Pennsylvania's new TDS regulations. Another participant asked if the sludge from the facility was analyzed. The researchers did not have access to the sludge, but have made observations regarding its volume and transport. The presenter expressed concern about leaching from landfills, though a participant described the result of leaching studies that indicated no risk from leaching.

2-butoxyethanol (2-BE). Participants noted that 2-BE is a common solvent present in household cleaners and other products and is expected to be found in effluent from wastewater treatment plants. They, therefore, suggested that it is important to quantify the background concentration, which is challenging. A participant added that the ATSDR (Agency for Toxic Substances and Disease Registry) reports that 2-BE was primarily tested on rats and mice, which are more prone to hematological reactions than people are. The participant noted that the difference in reactions between rodents and humans results in a great uncertainty factor built into 2-BE toxicology.

Safety of fish consumption. A participant asked whether studies have been done to determine the safety of fish consumption with regard to flowback contamination. The presenter clarified that no studies have been done; however, the same watersheds have been studied for a number of factors. For example, the presenter noted that Pittsburgh is also a center for coal-fired power plants, which contribute to mercury, selenium, and arsenic buildup in fish. Another presenter said that there are plans to study fish consumption during 2011 and that this analysis is essential because of the popularity of recreational fishing in Pennsylvania. The state issues fish advisories, but a participant noted the Pennsylvania Department of Environmental Protection (PA DEP) does not have the support to do much sampling although there are currently fish advisories for mercury and for a number of bioaccumulative contaminants, including some pesticides.

Concentration of flowback fluid versus injected fluid. A participant asked about the concentration of contaminants in fracturing fluids and pits in the Colorado study. The participant noted that operators have control over injected fluids. The presenter noted that there is a significant difference between concentrations in fracture fluids and early and late flowback, and he recommended that participants refer to the risk assessment document available on QEPA's Web site (http://www.qepa.com). The presenter also noted that data for pit fluids are also available but were not presented in this workshop.

Fingerprinting shale formations. A participant noted there are large differences in radionuclides in shale formations regionally, geographically, vertically, and horizontally. However, the participant added that there is likely not enough data available for fingerprinting.

Soil and degradation. A participant asked about microbial activity in soils compared to the deep subsurface, and the presenter agreed that biological activity is much lower in deeper formations and microbial degradation should be much slower. A participant asked about degradation of the biocide described by him as a microbially active compound that studies show that it degrades rapidly. The participant indicated that the biocide has toxic effects but that there is a dosing limit to the biocide below which it no longer functions as a biocide and can be degraded by microbes.

Principal component analysis. A participant asked whether Dr. Deeley had used principal component analysis for comparing two different sources. The presenter clarified that he has not used this technique.

Prior water contamination. A participant asked about the impacts of prior water contamination. The presenter stated that previous road salt contamination should not pose a problem because the bromide/chlorine ratio is tiny compared to formation brine, but there may be other parameters. The presenter also suggested that iodide is harder to analyze than bromide or chlorine. A participant added that water recycling is popular in Pennsylvania, and another participant asked if recycling flowback fluid would complicate analyses. In response, the presenter clarified that the composition of the new flowback can be incorporated into the mixing model.

Fracture fluid versus produced water. A participant asked Ms. McElreath whether she looked at the total mass of chemicals to determine how much fracture fluid returned when comparing fracture fluid and produced water. The presenter indicated that, in general, 20% to 40% of the fracture fluid is returned to the surface, while approximately 70% remains in the formation. However, she stated that this varies by play and within the formation. Another participant noted that toluene and benzene came back in produced water, and asked whether those contaminants could be byproducts or products from biological reactions. The presenter responded that these are not likely to be byproducts from biological reactions.

Conceptual models. A participant asked for a description of a model for fracture fluid that is injected at a depth of 6,000 feet and migrates into an aquifer. The presenter explained that one would need to consider how to produce a fracture reaching the surface. The presenter then noted that the basic energy balance must be considered, and it is important to determine whether there are natural controls. He suggested that other things to consider are whether there are man-made controls to contain those pressures, and if other potential pathways (such as abandoned wells) exist, how deep they extend, and whether they were completed or closed. The presenter added that it is essential to consider whether the models predict reasonable scenarios.

Availability of previous studies. A participant asked whether there have been previous efforts to study oil fields and noted that it would be useful for EPA's Office of Research and Development to access that work. In the late 1980's, there were EPA studies on produced water and drilling mud waste for RCRA considerations, and those studies are available on the EPA Web site.

Abstracts for Theme 1: Contaminant Identification, Transformation and Transport Presentations

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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A Simple Approach Identifying Contaminants of Most Concern to Underground Drinking Water Supplies from Hydraulic Fracturing Operations

Carl D. Palmer and Earl D. Mattson
Idaho National Laboratory

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.

There is concern that hydraulic fracturing operations for natural gas extraction could potentially contaminate groundwater supplies. We illustrate an approach we have employed for *in-situ* oil shale development to help identify contaminants that are likely to pose the greatest risk based on the contaminants' mobility, concentration, and toxicity. Mobility, addressed from the sorption characteristics of the compounds, is estimated under the expected subsurface geochemical conditions (pH, Eh, total organic carbon) using published experimental data and linear free energy relationships. We use the ratio of the concentration to some guideline concentration (e.g., an MCL) as a measure of the "toxicity" of that contaminant. A plot of mobility versus toxicity provides a simple graphical view of the relative risk for the transport of various contaminants from the near field to the far field. A Euclidean norm centered on a point of unit toxicity and low mobility can be used to order potential contaminants of concern. We illustrate the application of this approach using an oil shale retorting example and discuss limitations in the assumptions and available data. Applying an approach such as this to chemicals used in hydraulic fracturing fluids could help set research and development priorities for additional research.

Contaminant Characterization of Effluent from Pennsylvania Brine Treatment Inc., Josephine Facility Being Released into Blacklick Creek, Indiana County, Pennsylvania: Implications for Disposal of Oil and Gas Flowback Fluids from Brine Treatment Plants

Conrad D. Volz, DrPH, MPH; Kyle Ferrar, MPH; Drew Michanowicz, MPH, CPH; Charles Christen, DrPH, MEd; Shannon Kearney, MPH, CPH; Matt Kelso, BS; and Samantha Malone, MPH, CPH
University of Pittsburgh

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.

This report contains results from sampling and analysis of wastewater effluent entering Blacklick Creek, Indiana County Pennsylvania from the Pennsylvania Brine Treatment (PBT) Josephine Facility conducted by the Center for Healthy Environments and Communities (CHEC). The PBT-Josephine Facility accepts only wastewater from the oil and gas industry, including flowback water from Marcellus Shale gas extraction operations. This report describes the concentrations of selected analyzed contaminants in the effluent water and compares the contaminant effluent concentrations to standards, guidelines and criteria set by federal and state regulatory and investigative agencies for the protection of human and aquatic health.

Sampling Methodology and Concentrations of Contaminants in Effluent Water from Pennsylvania Brine Treatment Facility, Josephine Plant

CHEC conducted sampling of wastewater as it was discharged into Blacklick Creek, Indiana County, Pennsylvania from the PBT-Josephine Facility on December 10, 2010. Samples were taken at 3-hour intervals over the course of one 24-hour period. These samples were analyzed for listed inorganic and organic species by R. J. Lee Inc, a PA State Certified Laboratory (Certificate # 006).

The concentrations of analyzed contaminants in this effluent of primary environmental public health importance, which may also stress aquatic life, include: barium (Ba) [mean, 27.3 ppm; maximum, 37.0 ppm]; bromides (Br) [mean, 1068.8 ppm; maximum, 1100.0 ppm; strontium (Sr) [mean, 2983.1 ppm, maximum 3120.0 ppm]; benzene [mean 0.012 ppm; maximum 0.013 ppm] and 2 butoxyethanol (2-BE) [mean 59ppm; maximum 66 ppm]. Contaminant concentrations of ecological and secondary drinking water importance include: chlorides (Cl) [mean 117,625 ppm, maximum 125,000 ppm]; magnesium (Mg) [mean 1247.5 ppm; maximum 1300.0 ppm]; total dissolved solids (TDS) [mean 186,625 ppm; maximum 190,000 ppm]; sulfate (SO_4) [mean 560 ppm; maximum 585 ppm], and pH [mean 9.58 units; maximum 10 units].

Comparisons of Effluent Contaminant Concentrations to Standards, Guidelines and Criteria set by Federal and State Regulatory and Investigative Agencies for the Protection of Human and Aquatic Health

Levels of contaminants in effluent from the PBT- Josephine Facility were interpreted according to comparisons with applicable federal and state standards and recommended guidelines for both human and aquatic health. Barium had a mean concentration in effluent of 27.3 ppm (maximum of 37 ppm); this is approximately 14 times the United States Environmental Protection Agency (EPA) maximum concentration limit (MCL) of Ba in drinking water of 2 ppm. The EPA consumption concentrations 'water and organism' and 'organism alone' for barium are both 1 ppm. The levels of barium in the effluent are over 27 times these consumption concentrations. The U.S. EPA criteria maximum concentration (CMC) and the EPA criteria continuous concentration (CCC), both for protection of aquatic health, are 21 ppm and 4.1 ppm, respectively; the mean level of barium in effluent exceeds these criteria by 1.3 and 6.7 times, respectively. The mean level of barium in effluent water was 4, 4.73, and 9 times the derived drinking water minimum risk level (MRL) for intermediate and chronic exposures in adult men, adult women, and children, respectively.

The EPA recommended limit for strontium (Sr) in finished municipal drinking water is 4 ppm. The mean concentration of Sr in PBT-Josephine effluent water is 2981.1 ppm (over 745 times the recommended level). The MRL for Sr set by the Agency for Toxic Substances and Disease Registry (ATSDR) for intermediate length exposure is 2 mg/kg of body weight/day. The sampled mean level of strontium in PBT-Josephine effluent water was over 43, 51.7, and 97.9 times the derived drinking water MRL for intermediate exposures in adult men, adult women, and children, respectively.

Bromide in water is of concern because of its ability to form brominated analogs of drinking water disinfection by-products (DBP). Specifically, bromide can be involved in reactions between chlorine and naturally occurring organic matter in drinking-water, forming brominated and mixed chloro-bromo byproducts, such as trihalomethanes or halogenated acetic acids. There is general agreement that bromide levels in fresh-water sources be kept below about 100 ppb. The PBT- Josephine facility discharged effluent into Blacklick Creek with a measured mean concentration of bromide of 1068.8 ppm, which is 1,068,800 ppb. This is 10,688 times the 100 ppb level at which authorities become concerned.

The mean level of benzene, a known carcinogen, in outfall effluent from PBT-Josephine was 0.012 ppm or 12 ppb. The drinking water MCL for benzene is 5 ppb, thus effluent levels were above twice the drinking water MCL. The EPA consumption, water and organism risk level for benzene is 2.2 ppb in water; the mean level of benzene in PBT-Josephine effluent water is almost 6 times this criterion. The organism-only risk level for benzene is 50 ppb in water, and the mean level of benzene in effluent water is 24% of this guideline. The measured Benzene value was 0.6 times, 1.2 times, and 1.5 times the derived drinking water MRL for chronic exposures in adult men, women and children, respectively.

2-butoxyethanol (2-BE) is a glycol ether and is used as an anti-foaming and anti-corrosion agent, as well as an emulsifier in slick-water formulations for Marcellus Shale gas extraction. The mean concentration of 2-BE in the effluent exceeded derived drinking water MRL's for 2-BE for both acute and intermediate exposure for adult men and women and children.

Contaminants with secondary MCLs (SMCL) and aquatic receptor effects that were measured in the PBT-Josephine Facility effluent include magnesium, manganese, chlorides, sulfates, and total dissolved solids (TDS). Magnesium was found in the effluent with a mean concentration of 1,247.5 mg/L, which is 24,950 times the EPA Mg SMCL of .05 mg/L. The mean concentration of Manganese in the effluent was .08 mg/L, and the SMCL for Manganese concentration in drinking water is .05 mg/L. Therefore, the SMCL for manganese concentration is 62.5% lower than the concentration in the effluent. The mean concentration of chlorides in the sample analysis was 117,625 mg/L, which is 470.5 times the SMCL for chlorides in drinking water of 250 mg/L. To protect aquatic communities, the criteria maximum concentration (CMC) for chlorides in surface water is 860 mg/L, and the criteria continuous concentration (CCC) for chlorides in surface water is 230 mg/L. The mean concentration of chlorides measured in samples was 138 times the CMC and 511 times the CCC. The mean concentration of sulfates in the sample analysis was 560 mg/L , or 2.2 times the SMCL for sulfates in drinking water (250 mg/L). The SMCL for total dissolved solids (TDS) in drinking water is 500 mg/L, and the mean concentration of TDS measured in samples was 186,625 mg/L, or 373 times the SMCL.

Levels of strontium and 2-BE exceeded the NPDES reporting requirement set by the Pennsylvania DEP of 100 ppb and 500 ppb, respectively, for discharge of a toxic substance regularly or irregularly, respectively.

Masses of Contaminants Entering Blacklick Creek

CHEC has information from the Pennsylvania Department of Environmental Protection (PA DEP) that the PBT – Josephine Facility treated 15,728,241 gallons of oil and gas wastewater in the 6 month period from July 1, 2010 to December 31, 2010. Using this figure as the amount of effluent wastewater exiting the Josephine outfall and using the mean level of each contaminant found in the effluent over the sampling period of the study, the masses of contaminants with important human and ecological consequences discharged from the PBT, Josephine Facility into Blacklick Creek in the last 6 months of 2010 are projected to be: barium - 1627 kg (3588 pounds); strontium - 177,712 kg (391,856 pounds; 196 tons); bromides -63,708 kg (140,476 pounds; 70.2 tons); chloride – 7,011,631 kg (15, 460,646 pounds; 7,730 tons); sulfate – 33,382 kg (73,607 pounds; 36.8 tons); 2-BE – 3517 kg (7,755 pounds; 3.88 tons); and TDS – 11,124,733 kg (24,530,036 pounds; 12,265 tons).

Potentially Exposed Populations

Recreationalists are at high risk of being exposed to outfall contaminants through ingestion, inhalation and through dermal exposure. The outfall of the Josephine Facility is easily accessible to users of nearby rails-to-trails pathways, and there are indications that anglers frequent the area.[1] Additionally, children wade and swim in the creek during warmer weather, and regional watershed websites indicate that paddlers use the creek for canoeing and kayaking. 2-BE released into Blacklick Creek may be ingested by swimmers in the creek, as this pollutant can become airborne and present an inhalation hazard to anglers, swimmers and boaters. It is also taken in to the body via dermal absorption. Anglers catching and eating fish from upstream or downstream of the effluent outfall are at risk for exposure to multiple contaminants that were sampled in this study.

CHEC has developed maps showing numerous private water wells in the immediate vicinity of Blacklick Creek downstream from the effluent discharge. Private well water users are at risk of exposure to contaminants in effluent being released into Blacklick Creek because these private wells may capture water from the creek when the well pump rate is sufficiently high. High pump rates can occur especially during peak usage by residents.

The first identified municipal drinking water intake downstream of this discharge is at Freeport, Pennsylvania on the Allegheny River. Populations served by the Freeport authority and water authorities downstream of Freeport are at potential risk for exposure to contaminants identified in effluent, as well as other contaminants in Marcellus Shale flowback water that were not sampled for in this study.

Implications of Effluent Discharge from the PBT – Josephine Facility Discharge for Exposures to Other Contaminants Known to be Present in Marcellus Shale Flowback Fluids and a Regional Appreciation of These Results

Of particular environmental public health significance is that Marcellus Shale flowback water contains other contaminants, in addition to those analyzed for in this study, which have health consequences if ingested, inhaled, and/or absorbed through the skin. While we make no statements regarding the presence of other contaminants in this effluent water being discharged into Blacklick Creek, it is imperative that additional testing be conducted immediately by federal and state health and enforcement agencies to determine if other contaminants of public health significance are entering this watershed.

Oil and gas wastewater and Marcellus shale flowback fluids are being disposed of in “brine treatment” facilities and at Publicly Owned Treatment Works (POTW’s) throughout the Commonwealth of Pennsylvania and in Ohio, West Virginia, and New York. Therefore, the ramifications of disposal of large quantities of oil and gas wastewater through ineffectual brine treatment plants and POTW’s needs further evaluation throughout the region to determine its impact on stream and river systems and public drinking water supplies, as well as to recreationalists and private well water users.

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[1] Blacklick Creek has been classified as a ‘trout stocking” stream.

[2] US EPA. 2004. "Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs (Final)." Office of Water, June.

[3] New York State Department of Environmental Conservation (NYSDEC). 2009. "Draft Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program—Well Permit Issuance for Horizontal Drilling and

Recommendations

- Operations at this plant should be halted until all contaminants of human and aquatic health concern in accepted oil and gas fluids are known and it can be determined that the treatment processes used at the plant effectively remove these contaminants from the fluids being treated.
- All approaches to the effluent discharge area and a reasonable distance downstream (at least 100 meters) from streamside and landside should be posted with warning signs. These signs should discourage any use of and/or contact with stream water.
- An advisory to all anglers should be issued stating that fish taken from this stream, both upstream and downstream may be contaminated in order to discourage fish take and consumption.
- Studies to determine the levels of all potential Marcellus Shale flowback fluid contaminants in downstream water, sediments and pore water should be undertaken immediately.
- Residential and other private well water users downstream of the effluent outfall of the PBT-Josephine Facility should be advised that there may be contaminants in their well water and discouraged from using it for drinking, cooking or bathing until such water is tested for continuous safe use.
- Municipal water authorities downstream of this outfall should be notified of the contaminants found in effluent from the PBT- Josephine Facility, of other possible contaminants in Marcellus Shale flowback fluids and oil and gas wastewater, and that there are other treatment facilities and POTW's in the Blacklick, Conemaugh, and Kiskiminetas drainages that accept and discharge oil and gas waste fluids into surface water.
- All municipal water authorities at reasonable distances downstream of "brine treatment" and POTW's accepting Marcellus Shale flowback fluids and other oil and gas wastewater in the region extending eastward across Ohio, Pennsylvania and West Virginia and New York should be notified of these results.
- The PA DEP and other state and federal regulatory authorities should immediately review all surface water discharge permits granted to brine treatment facilities and POTW's that accept Marcellus Shale flowback fluids and oil and gas wastewater, to ensure that 2-BE concentrations being discharged are below all applicable standards, guidelines and criteria. This review should be informed by results of this report but should be extended to all known contaminants in flowback and other oil and gas wastewater.

Fracing & Associated Media Composition in Colorado

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The fracing process begins with wellpad siting, proceeds through completion and ends with production (and the eventual decommissioning or abandonment). The steps in the process include: site selection, well pad development, drilling, fracing, and production. The chemical composition of media during the fracing as well as naturally occurring constituents present in the natural resources all add to the constraints and characteristics of fate, transport, exposure and projected risk. The classical risk assessment process can be divided roughly into: 1) Hazard Identification, 2) Dose-Response Determination, 3) Exposure Assessment, and 4) Risk Characterization, followed by Risk Management (including policy development) and preceded as well as intermingled with research (NRC, 1983, 1994). Within the Exposure Assessment aspect is the fate and transport of chemicals and subsequent exposure. In terms of this risk framework, chemical composition plays a strong initial role in Hazard Identification but is also relevant in terms of dose-response, exposure pathway determination, fate and transport property selection, and risk assessment. The process and consideration of chemical selection are presented with regard to the investigation of fracing impact in four energy basins in Colorado completed in the spring of 2008. The focus will be on three media, flowback material, frac fluids, and produced waters, although other media and subsequent pathways were considered and are discussed in part here.

Risk Assessment in Regards to the Identification of Constituents for Analytical Evaluation

As just mentioned, the identification and eventual selection of chemicals for consideration in risk assessment is part of the classic risk assessment (RA) process (NRC 1983, 1994). Although the identification and selection of chemicals seems limited in scope and limited in interaction to hazard identification, it can be driven by regulatory requirements or public concerns. It can also impact the cost, eventual selection of exposure pathways, and bring to light underlying issues in the RA process and the interweaving of policy with the science.

The steps in the process of drilling and fracing produce a variety of media (frac fluids, produced water, waste pit solids, etc.), all of which should be considered in a holistic approach to both understanding and managing risk in the Oil & Gas (O&G) Industry.

Selection of Chemicals for Analysis

In 2008, in a project funding by the Colorado Oil and Gas Association (COGA), QEPA, pH2 through QEPA, and URS were contracted to devise a sampling and analytical plan as part of a risk assessment for proposed changes in the O&G regulations in Colorado (COGCC, 2008). This first necessitated the identification of chemicals for analytical evaluation (CAE) and eventual selection of the chemicals (URS, 2008). The Material Safety Data Sheets (MSDS) were gathered by requesting input from 7 of the COGA member companies and reviewing the submissions. More than 100 products were looked at and broken into reported relative sub-quantities (%) by Chemical Abstract Service (CAS) number. MSDS are required to report any standard listed chemicals that make up more than 1% of the chemical composition, or >0.01% if the chemical is carcinogenic (OSHA, 2008). From this, the beginnings of a CAE list was produced, which included glycols and pH as a surrogate for acids and bases. A list of standard chemicals of interest in the O&G industry (BTEX, PAHs, Boron, Chloride, etc.) were also added (CDPHE, 2007; COGCC, 2008). Because of a lack of clarity with regard to total extractable petroleum hydrocarbons (TEPH), these were analyzed for both Diesel Range Organics (DRO) and Motor Oil Range Organics (MRO) to allow relative hydrocarbon grouping if desired. Primary metals (and metalloid) included were the eight Resource Conservation and Recovery Act (RCRA) metals consisting of arsenic, barium, cadmium, chromium, lead, mercury, silver, and selenium. An additional fifteen target analyte list (TAL) metals were also added from the EPA Method 6020A Method list and included Aluminum, Antimony, Beryllium, Calcium, Cobalt, Copper, Iron, Magnesium, Manganese, Nickel, Potassium, Sodium, Thallium, Vanadium & Zinc. Based on a review of potential agents associated with raw material derived from subsurface deposits, gross alpha and gross beta were selected. Analysis for specific isotopes at this phase was considered unwarranted by the risk assessor. Consideration for chemicals recommended by local environmental groups was also undertaken; this was also accounted for post-sampling in terms of reviewing tentatively identified compounds (TICs) for relevance and comparing to groups of chemicals used, and the MSDS product list. Basin usage for the products was also recorded in the event that significant findings relevant to geologic formation(s) was(were) discovered. A small subset of samples was analyzed by EPA's Toxic Characteristic Leaching Procedure (TCLP) for eight RCRA metals, plus pH, reactive sulfides, and reactive cyanides to evaluate waste disposal considerations.

Statistical Considerations

In any sampling plan, several consideration with regard to chemicals should be made, including, but not limited to: a) number of samples for the intended use, b) minimum limit of detection (LOD) and limit of quantification (LOQ) for a constituent, c) background levels, d) level of quality of sampling and analysis, e) statistical application, and f) appropriate selection of a method. One should never take a sample before knowing what one will communicate once the results are in. The desire would be to collect multiple samples from each media and ones that are representative of a typical media by energy basin and type of drilling or fracing operation. For example, one should collect both early and late flowback samples and one should consider the regulatory impact of required oil-water separation in certain basins, etc. In terms of return on statistical data, five to six samples (base on a normal distribution) place the mean as reasonably estimated. However, to reasonably estimate the standard deviation more than twenty samples would be necessary. In the case of RA, much of the decision making is driven in orders of magnitude (QEPA, 2008). Therefore, five to six samples per media setting provides a good basis to work from, even in consideration of right-skewed distribution (e.g., lognormal). The subsequent quasi-policy and quasi-science decision of selecting an appropriate estimator (mean, max, upper confidence limit one sided at 95% [UCL1,95]) can then be utilized by a risk manager. In terms of LOD and LOQ for analytical method selection, regulatory levels in Colorado (COGCC, 2008; CDPHE, 2007) were reviewed along with risk assessor pre-estimates of effective dilution-attenuation factors to determine relevant methodologies. Thus, by recognizing end risk calculation relevancy, PAH detection levels were set at standard levels, which are higher than that achievable by more sophisticated (and costly) methods.

Media and Sample Collection

Sample quality is important, particularly if the analysis has broader policy implications. In the 2008 project in Colorado, URS personnel collected the samples independent from the risk assessors (QEPA & pH2) and independent from the labs used for analysis. Statistical analyses were performed by both URS and pH2/QEPA with pH2 directing the parameters. Samples were collected at a variety of sites--55 in all--to represent four energy basins in Colorado; these basins are the Denver-Julesburg (DJ), Piceance, Raton, and San Juan. The media types selected were in consideration of the RA and included: pit solids, pit fluids, drill fluids, frac fluids, flowback fluids, produced water and background soils. It should be noted that some of the materials are co-mingled with other fluids and moved between pits as multiple-pads or sites are developed. Sample analysis for both solids and liquids were separated, and sets of dissolved and total constituent analyses were performed in most cases. Decisions for sample media categorization (fluid/solid) were ultimately determined by the risk assessor after input from URS and the lab.

Samples were collected at points representative of current drilling and fracing operations, both near and away from residences and within differing hydrogeologic and geologic conditions. Multi-point composite samples were collected to achieve better representation (except for VOCs due to potential constituent loss). There was a high frequency of co-located field duplicates (45%) and MS/MSDs (30%) QC samples collected. In addition, rigorous paper, photo, and video documentation were also performed to incorporate with the Level IV Quality Control (QC) data packages and analysis by an NELAC certified laboratory. Also, samples were analyzed for >170 constituents using EPA-approved methods (e.g., VOCs by 8260, SVOCs by 8270, Glycols by 8015). Thorough data validation was performed resulting in >99% data usability. Other Precision, Accuracy, Representativeness, Completeness, and Comparability (PARCC) parameters were satisfactory (URS, 2008).

Analytical Results for Flowback Materials, Frac Fluids, and Produced Waters

Analytical sampling results from the COGA study completed in 2008 represented more than 52,000 data points for pit solids, liquids, fracing fluid, flowback, and drilling fluids. Analytical data included BTEX, PAHs, metals (primary eight RCRA plus secondary), gross alpha, gross beta, boron, and glycols.

Chemicals not Detected

For the solid media, 43 VOCs were reported as Not Detected (ND) in every solid sample, as were 57 semivolatile compounds (SVOCs). In addition, reactive cyanide and reactive sulfide were not detected for reactivity, corrosivity, and ignitability (RCI) analyses performed on solid samples.

The list of non-detect (ND) constituents for liquid media was not as extensive as the list for solids. A total of 39 VOCs and 48 SVOCs were reported as ND in every sample that was analyzed as a liquid. Although the liquids list is shorter, not every constituent that was reported as ND for liquid samples was also reported as ND for solids. In total, the two lists share 81 common constituents, including 35 VOCs and 46 SVOCs. Reactive sulfide and cyanide are not included in this figure because RCI analyses were not performed for liquid samples.

Flowback

A total of twenty four base samples (plus duplicates) of flowback fluids were collected and analyzed throughout the four basins. One of the flowback fluid samples collected in the DJ Basin was analyzed as a solid due to the high amount of suspended sediment present in the sample. The following constituents were detected in 100 percent of the flowback fluid samples: barium, benzene, boron, chloride, ethylbenzene, naphthalene, nickel, toluene, total xylenes, trimethylbenzene (TMB), and TEPH. A few constituents of significance were often below detectable levels, for example: 37% of gross beta, 69% of gross alpha, and 84% of anthracene were ND, whereas ones like BTEX, 1,2,4-TMB, and 1,3,5-TMB, boron, and chloride were always detected. Although the max concentrations for flowback fluids were 270 and 4,030 pCi/L for gross alpha and beta, respectively, the comparable pit fluids were only 17 and 174 pCi/L, respectively

Frac Fluids

Two frac fluid samples (plus a duplicate) were collected and analyzed in the Piceance Basin. One of the frac fluid samples collected was analyzed as a solid due to the high amount of suspended sediment present in the sample. The following constituents were detected in 100 percent of the frac fluid samples: barium, benzene, boron, chloride, ethylbenzene, gross beta, naphthalene, nickel, sulfate, toluene, total xylenes, TMB, and TEPH.

Produced Water

Produced water samples were collected in the Raton and San Juan Basins. Altogether, 10 produced water samples (plus duplicates) were collected between the two basins. The following constituents were detected in 100 percent of produced water samples: barium, boron, chloride, and nickel. These constituents occur naturally in formation waters, and at least a portion of the detected concentration for each constituent is likely due to natural background.

In regard to other PCOCs, benzene was detected in 5 produced water samples; ethyl benzene was detected in 3 produced water samples; naphthalene, toluene, total xylenes, TMB, and

TEPH were detected in 4 produced water samples. In general, the PCOCs were detected at a higher frequency in produced water from the San Juan Basin than from the Raton Basin.

Chemicals Matching MSDS Constituents

Only 8 constituents out of more than 100 found to be present in MSDS reviewed. The constituents found include: propanol, 2-butoxyethanol, ethylene glycol, n-heptane, isopropanol, naphthalene, 1,2,4-TMB, and ethanol. The constituents detected in most of the media are 1,2,4-TMB and naphthalene. Solvents and fracing agents were the most common use of these 8 constituents in the O&G industry in CO.

As a caveat, the detection of a chemical listed in an MSDS for a product in a particular media does not necessarily mean that it came from that product. It only means it could have come from it, but for some it just as easily could have come from a natural occurring deposit. Also, a chemical's presence does not mean that it is a significant risk either.

Narrowing the Selection for Risk Assessment Purposes

From the CAE, a select group of those chemicals meeting one of the following characteristics were selected for assessment of risk: a) present in either significant amounts (near the proposed COGCC Table 910-1 values for instance), b) or those with a significant frequency of presence (e.g, TMBs, BTEX, most metals), or c) those with a concern because of significant usage (e.g., glycols, barium, chloride) , or those thought to be of concern but having little prior test data (e.g., PAHs, gross alpha and gross beta).

These were then considered as constituents in the following media scenarios:

Solids placed in Pits
Liquids in Subsurface Pits
Fracing Fluid placed in pits
Fracing Fluid placed in containers
Produced Water placed in containers
Produced Water placed in pits
Drilling fluids in drilling
Drilling fluids in pits

Details of the RA are provided in QEPA, 2008.

Limitations

As with any assessment there are a number of gaps or limitations imposed or resulting from the manner in which this RA was commissioned. The first is that groundwater as a resource was the prime focus, thus air was not considered in as great as detail; nor is it relevant for the scope this workshop. Secondly, samples were from operations in place in Spring of 2008, not prior, nor post. Other seasons may result in different concentrations, e.g., VOCs. Some practices from the past (diesel fuel in the drilling) or more common today (treatment or recycling of produced waters) were not accounted for. Also, only produced water data from 3 energy basins was collected and there was limited drilling fluid & frac fluid samples compared to that desired by the risk assessor.

In terms of other RA fate & transport aspects, there was no verification of actual depth to groundwater on-site, no verification of actual hydrogeologic properties (hydraulic conductivity, head difference), although neighboring data was gathered and evaluated. All estimated exposure doses for base risk were therefore modeled using conservative parameters for the potential chemicals of concern (PCOCs), i.e, maximum or $UCL_{1,95\%}$.

There are other limitations created by classical risk assessment guidance (ASTM, 2002; EPA 1989a, 1989b, 1991a, 1991b), which includes failure to consider background concentrations (e.g., arsenic), basic solubility under site-specific situations, and toxicological constraints. One of the toxicology constraints is that barium sulfate, normally used as a drilling fluid, is expected as the primary source of the barium, yet it is neither very soluble in many instances, nor very toxic compared the $BaCl_2$ upon which the Reference Dose (RfD) for the element is based (EPA, 2005). In RA it is also important to gauge the general level of influence of one parameter versus another in a RA. For chemicals, the RfDs, Reference Concentrations (RfCs), Benchmark Dose Levels (BMDL), Minimal Risk Levels (MRLs), and Slope Factors (SFs) drive the primary order of magnitude of risk, and generally use safety-uncertainty margins in the range of 10-100 already. For instance $BaCl_2$ uses a safety-uncertainty factor of 300 (EPA, 2005). If is useful to consider this in ranking the value of chemicals and their health hazards in scenarios like the one presented here. In the cases where there is no relevant acceptable value for toxicity, other means, such as a control banding approach, could be applied (Nelson, et al., 2011).

Acknowledgments

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References

ASTM: E1739-95(2002), Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites. ASTM, Conshohocken, PA. 2002.

Colorado Department of Public Health and Environment, Hazardous Materials and Waste Management Division, Table 1 Colorado Soil Evaluation Values (CSEV) – December 2007

Colorado Oil and Gas Conservation Commission, Draft Rules for Oil and Gas Development in Colorado, (HB 1298 & HB 1341), March 31, 2008.

EPA: Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part A, Interim Final. EPA 540/1-89/002. USEPA: Washington, DC. 1989a.

EPA: Risk Assessment Guidance for Superfund, Volume II, Environmental Evaluation Manual, Interim Final. EPA 540-1-89-001. USEPA: Washington, DC. March, 1989b.

EPA: Risk Assessment Guidance for Superfund, Volume I, Human Health
Evaluation Manual, Part B: Development of Risk-Based Preliminary Remediation Goals, Interim. EPA 540/R-92/003. USEPA: Washington, DC. December, 1991a.

EPA: Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part C: Risk Evaluation of Remediation Alternatives. USEPA: Washington, DC. December, 1991b.

EPA: Toxicological Review of Barium and Compounds (CASRN 7440-39-3), EPA-635-R-05-001, June, 2005.

National Research Council (NRC): Risk Assessment in the Federal Government: Managing the Process. NAP, Washington, DC. 1983.

National Research Council (NRC): Science and Judgment in Risk Assessment. NAP, Washington, DC. 1994.

Nelson, Deborah Imel, Stephen Chiusano, Anne Bracker, Lance Erickson, Charles Geraci, Martin Harper, Carolyn Harvey, Andrew Havics, Mark Hoover, Thomas Lentz, Richard Niemeier, Susan Ripple, Erica Stewart, Ernest Sullivan, and David Zalk: Guidance for Conducting Control Banding Analyses. AIHA, Fairfax, VA. 2007.

OSHA: 29 CFR 1910.1200 (Hazard Communication Standard). July 1, 2008.

QEPA: Pathway Analysis and Risk assessment (PARA) For Solids and Fluids Used In Oil and Gas Exploration and Production in Colorado, pp. 1-930, June 2008.

URS: Field Activities Report for Characterization of Exploration and Production Pit Solids and Fluids in Colorado Energy Basins, June 4, 2008.

Comparison of Hydraulic Fracturing Fluid Composition with Produced Formation Water following Fracturing – Implications for Fate and Transport

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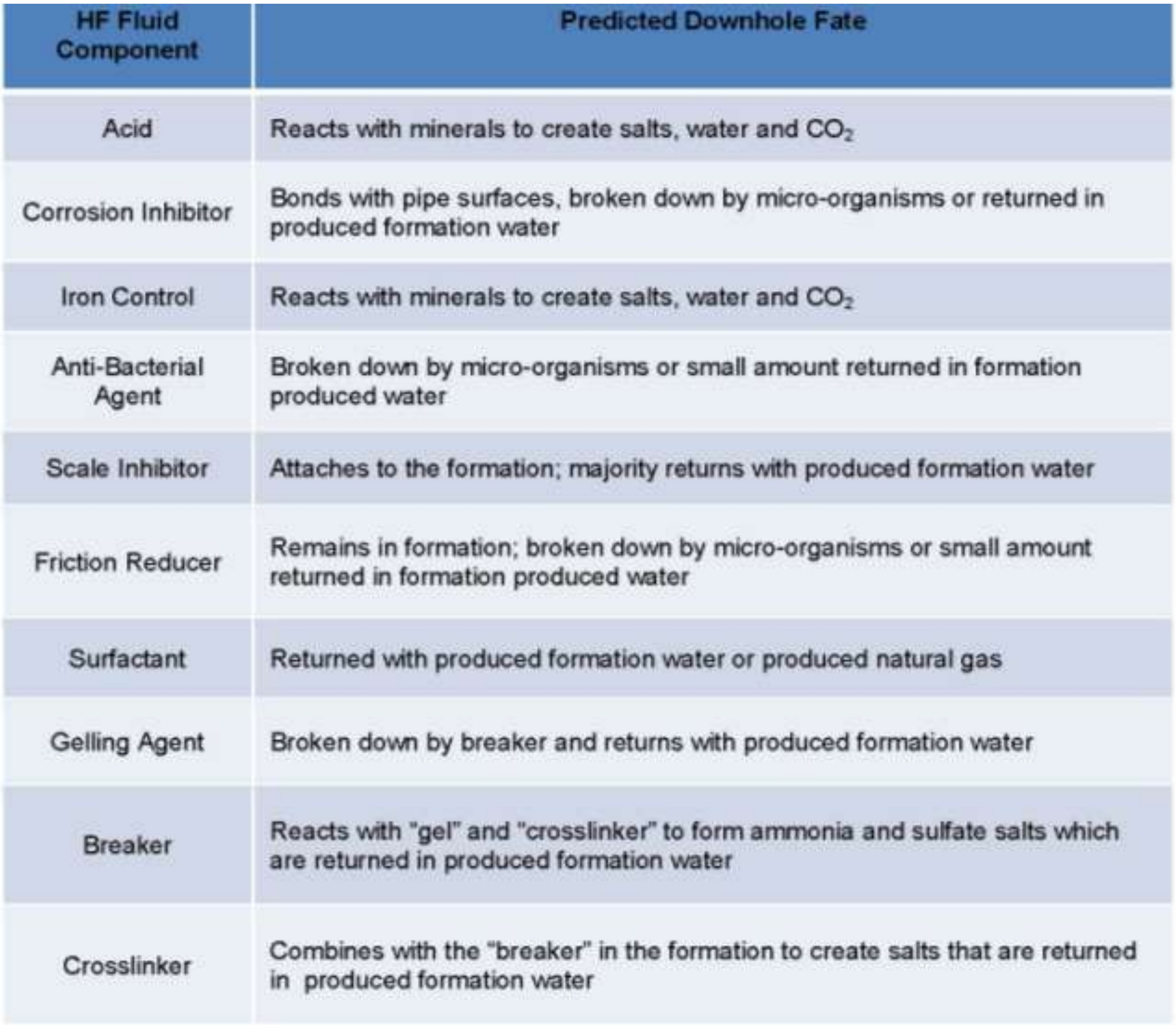
The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Chesapeake Energy Corporation (Chesapeake) as a part of an evaluation of produced formation water had examined the composition of hydraulic fracturing chemicals used in natural gas production wells. Samples of the hydraulic fracturing fluid prior to the addition of proppant had been analyzed as well as time series samples of produced formation water for a natural gas well located in a shale formation west of the Mississippi River (Location 1) and another well in the eastern U.S. (Location 2). Some of the data evaluated is subject to attorney-client privilege (hereinafter “privileged data”). The major conclusions from Chesapeake’s evaluation of produced formation water data are:

- Produced formation water is highly variable within and between shale plays.
- The elevated temperature and pressure affect the fate and transport of hydraulic fracturing fluid components and can create safety issues for sampling.
- 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.
- The most reliable sentinel compounds appear to be total dissolved solids, chloride and divalent cations. The concentrations of these components are related to each other and are also related to the formation water volume.
- The concentration of total dissolved solids is predictive of the concentration of other species.
- The concentration of indicator parameters for hydraulic fracturing mixtures, such as chloride, sulfate, and boron, are overshadowed by the naturally-occurring concentrations of these parameters in formation water.
- The presence of NORM is delayed and associated with higher percentages of formation water in the produced water with increasing time.

Based on the predicted downhole behavior of the hydraulic fracturing fluid, Chesapeake designed a sampling program for hydraulic fracturing fluid and produced formation water in order to understand the fate of hydraulic fracture chemicals in the produced formation water. The sampling design incorporated a review of chemicals used in two Chesapeake wells during hydraulic fracturing. Produced formation water samples were taken in a time series, hours to days, following hydraulic fracturing. The analyte list Chesapeake utilized was the complete list found at 40 CFR Part 264, Appendix IX, and commonly associated with groundwater monitoring supplemented with three glycols. All of the analyses were conducted using EPA analytical methods and were performed by a single NELAC-certified laboratory.

Table 1. Predicted Downhole Fate for Hydraulic Fracturing Fluid Components



HF Fluid Component	Predicted Downhole Fate
Acid	Reacts with minerals to create salts, water and CO_2
Corrosion Inhibitor	Bonds with pipe surfaces, broken down by micro-organisms or returned in produced formation water
Iron Control	Reacts with minerals to create salts, water and CO_2
Anti-Bacterial Agent	Broken down by micro-organisms or small amount returned in formation produced water
Scale Inhibitor	Attaches to the formation; majority returns with produced formation water
Friction Reducer	Remains in formation; broken down by micro-organisms or small amount returned in formation produced water
Surfactant	Returned with produced formation water or produced natural gas
Gelling Agent	Broken down by breaker and returns with produced formation water
Breaker	Reacts with "gel" and "crosslinker" to form ammonia and sulfate salts which are returned in produced formation water
Crosslinker	Combines with the "breaker" in the formation to create salts that are returned in produced formation water

Source: Chesapeake, 2010. Marcellus Shale Hydraulic Fracturing Fact Sheet, July.

Since it was predicted that many of the hydraulic fracture fluid chemicals would undergo transformation, the focus of this paper is indicator parameters, such as total Kjeldahl nitrogen, ammonia, sulfate, and sodium, which are used as surrogates for the presence of breakdown products of the hydraulic fracturing chemicals. In many cases, analytical methods are not available to analyze a compound but instead the analysis is conducted on a compound's predicted components since these results can be combined to provide an estimate of the compound’s concentration. Focusing on indicator or sentinel parameters is also cost effective and does not require use of exotic or yet-to-be developed methodology.

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. 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. It does not appear that the glycol methods can provide meaningful results for samples with these matrix issues. 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. Radiochemistry methods are particularly affected by the elevated concentrations of barium and total dissolved solids. Since hydraulic fracture fluid is a product rather than an environmental sample, certain standard requirements for environmental samples, such as holding time, are not applicable.

Hydraulic fracturing service vendor-supplied data was available to compile the water volume, proppant volume, and specific hydraulic fracturing products and related volumes used for fracturing of the individual well. Component information for each of the hydraulic fracturing products was drawn from the Material Safety Data Sheets. These data were utilized to calculate the concentrations of the individual chemicals used in the hydraulic fracture fluid for each of the two subject wells. For some, surrogate chemical species, e.g. sodium or chloride, were calculated for comparative purposes.

Produced formation water volumes have been estimated for the Location 1 well. Typically, produced water volumes decrease markedly with time once a natural gas well is in production. In the first ten days of production, about 600,000 gallons or 60,000 gallons per day are produced; between days 11 and 365, the volume drops to approximately 8,400 gallons per day. In subsequent years of production, the well would be expected to produce about 4,200 gallons per million standard feet of gas (MMCF) of gas produced average for the life of the well. Chesapeake used approximately 4 million gallons of water for drilling and fracture stimulation.

For the Location 1 well, a hydraulic fracture fluid containing the following compounds was utilized: biocide (gluteraldehyde and an alcohol); beaker (ammonium persulfate); iron control (sodium compound); friction reducer (polymer and a hydrocarbon); crosslinker (polyol and borax); corrosion and scale inhibitors (alcohols, organic acids, and sodium salt of a polymer); and acid (hydrochloric acid). Therefore, boron, sodium, sulfate, and total Kjeldahl nitrogen were expected to be useful as surrogate analytes.

Analytical results were available for the hydraulic fracture fluid (pre-injection) and produced formation water samples in time series for 6 hours, 1 day, 2 days, 9 days, and 30 days following fracturing. The results for several surrogate/indicator species, total Kjeldahl nitrogen, ammonia, chloride, total dissolved solids, sodium, boron and glycols, were summarized. Data were also available for two radium isotopes (Ra-226 and Ra-228). Since the hydraulic fracture fluid did contain a hydrocarbon carrier, benzene and toluene were also evaluated (most other volatile organic compounds and semi-volatile organics were below detection limits).

In general, the concentrations for the analytes of interest increased, especially the total dissolved solids, chloride and sodium, with time following hydraulic stimulation. These increases reflect increasing percentages of formation water entering the produced water volume. It should be noted that the sodium, chloride and boron concentrations in hydraulic fracture fluids were rapidly overshadowed by the naturally-occurring concentrations of these compounds on formation water. The increasing concentrations of the nitrogenous compounds probably reflect degradation of the nitrogen compounds in the hydraulic fracture fluid and microbial activity.

The results for the divalent cations, barium and strontium concentrations were examined for relationship with total dissolved solids concentrations. The correlation coefficient for barium and total dissolved solids was 0.998 and that for strontium and total dissolved solids was 0.935. The correlation between chloride and total dissolved solids was 0.943. The relationship between total dissolved solids and radium-226 and radium-228 appear to be similar to that of the other divalent cations. It is evident that the presence of total dissolved solids can be used as a sentinel parameter.

The calculated concentration of glycols was 55,000 µg/L; however, the analytical result for the hydraulic fracture fluid was 35,800 µg/L. As the total dissolved solids increased in the 12 hour and day 2 samples, the detection limit for EPA Method 8015 increased to <10,000 µg/L. These results point to the limitations of Method 8015 for glycol analyses in produced formation water.

Produced formation water volumes have been estimated for the Location 2 well located in the eastern U.S. Typical produced water volumes decrease markedly with time a natural gas well is in production. In the first ten days of production, about 600,000 gallons or 60,000 gallons per day are produced; between days 11 and 365, the volume dropped to approximately 8,400 gallons per day. In subsequent years of production, the well would be expected to produce less than 200 gallons per MMCF average for the life of the well. Chesapeake used approximately 3.4 million gallons for fracture stimulation.

For the Location 2 well, the hydraulic fracture fluid contained the following: biocide (sodium salt, sodium hydroxide, and a bromide salt); breaker (sodium and potassium salts); iron control (citric acid); friction reducer (water soluble nitrogenous-based polymer); gel (guar gum, a hydrocarbon, and polymer); corrosion and scale inhibitors (alcohol, glycol and an amide); surfactant (alcohol, glycol and a hydrocarbon); and acid (hydrochloric acid). Sodium, chloride, total Kjeldahl nitrogen, and sulfate were expected to serve as surrogates for the components of the fracture fluid.

Analytical results were available for the hydraulic fracture fluid (pre-injection) as well as for the subsequent produced formation waters at 6 hours, 12 hours, 5 days, 10 days and 30 days following fracture stimulation. The results for surrogate and indicator parameters were evaluated. These included sulfate, total Kjeldahl nitrogen, ammonia, total dissolved solids, sodium, glycol and 2-butoxyethanol. Examination of the glycol and 2-butyoxyethanol results reveals the difficulty in accurately quantitating glycol using the available EPA approved method. Benzene and toluene results were found to increase within 12 hours to concentrations well above that in the original hydraulic fracture fluid. The occurrence of these compounds is attributed to natural occurrence within the natural gas production zone.

The results for the divalent cations, barium and strontium concentrations were examined for relationship with total dissolved solids concentrations. The correlation coefficient for barium and total dissolved solids was 0.966 and that for strontium and total dissolved solids was 0.988. The correlation between chloride and total dissolved solids was 0.933. There appears to be a similar relationship between total dissolved solids and radium-226 and radium-228 as well. It is evident that the presence of total dissolved solids can be used as a sentinel parameter.

The appearance of gross alpha, gross beta, two radium isotopes and uranium-238 in produced formation water following hydraulic fracturing represents an example of transport of naturally-occurring materials from the shale formation into these waters and the time at which concentrations appear to stabilize varies considerably from shale play to shale play. For locations in the western U.S., the measured activity for these radiochemistry parameters varies considerably. The range of gross alpha and gross beta is from 620 to 4,000 pCi/L (mean value 1,750 pCi/L) and 250 to 1,200 pCi/L (mean value 760 pCi/L), respectively. Radium 226 and 228 appear together with the radium 228 being the lesser in terms of activity. No uranium-238 was detected. The activities encountered in the well samples from the eastern U.S. covered a wider range of activity levels and exhibited higher maximum values. When results for a single location are examined, there does appear to be a relationship with increasing total dissolved solids. This appears to be true for results for both Location 1 and Location 2.

The major conclusions from the review of produced formation water data are:

- Produced formation water is highly variable within and between shale plays.
- The elevated temperature and pressure affect the fate and transport of hydraulic fracturing fluid components and can create safety issues for sampling.
- 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.
- The most reliable sentinel compounds appear to be total dissolved solids, chloride and divalent cations. The concentrations of these components are related to each other and are also related to the formation water volume.

- The concentration of total dissolved solids is predictive of the concentration of other species.
- The concentration of indicator parameters for hydraulic fracturing mixtures, such as chloride, sulfate, and boron, are overshadowed by the naturally-occurring concentrations of these parameters in formation water.
- The presence of NORM is delayed and associated with higher percentages of formation water in the produced water with increasing time

Fate and Transport of Select Compounds of Potential Concern (COPC) in Fracing 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.

Use of proprietary mixtures of reagents in fracing fluids injected in deep (>1,000 feet) zones, in an effort to liberate natural gas, has led to considerable controversy regarding the potential contamination of shallower (<500 feet) drinking water aquifers. This paper focuses on the different classes of compounds identified in fracing fluids, and discusses:

1. their properties in soil/sediment and groundwater,
2. their potential fate in the environment, and
3. the potential problems analyzing for them.

The Canadian Society for Unconventional Gas (Understanding Hydraulic Fracturing, 2011) identifies the following as the typical composition of fracing fluid (citing All Consulting, based on data from a fracing operation in the Fayetteville Shale, 2008):

- Water and Sand = 99.51%
- Other 0.49% =
    - Acid = 0.123%
    - Friction Reducer = 0.088%
    - Surfactant = 0.085%
    - KCl = 0.06%
    - Gelling Agent = 0.056%
    - Scale Inhibitor = 0.043%
    - pH Adusting Agent = 0.011%
    - Breaker = 0.01%
    - Crosslinker = 0.007%
    - Iron Control = 0.004%
    - Corrosion Inhibitor = 0.002%
    - Biocide = 0.001%

Table 2 (Adapted from the EPA, 2004) provides examples of typical compounds used in each class of chemicals listed above. This paper will focus on the less common compounds included in the list. The transport and fate of the compounds listed below is well understood and treatment options have been identified where warranted, so they will not be evaluated:

- Muriatic acid or hydrochloric acid;
- Guar gum;

- Diesel (BTEX);
- Ethanol and isopropanol;
- Sodium chloride;
- Formic acid;
- Fumaric and adipic acids; and
- Boric acid.

This paper will focus on the compounds below which are not commonly encountered in the environment and/or whose fate and transport is not clearly understood:

- Ethylene glycol;
- Mono or di-ethanol amine;
- 2,2 Dibromo-3-nitrilopropionamide, a
- biocide;
- 2-Butoxy ethanol; and
- Diammonium peroxosulfate (ammonium persulfate).

Compounds of Potential Concern (COPCs)

Ethylene glycol (EG) is a chemical commonly used in a variety of applications such as airplane deicing and radiator fluid. It is used in analytical laboratories and found as an impurity in alcohols and other compounds. It is a polar liquid that is miscible in water and due to its low Henry's constant and octanol-water partitioning coefficient (K_{ow}), is unlikely to volatilize or adsorb onto carbon or soil organic matter. One of the main reasons EG is not a common analyte for environmental investigations is because it is not considered very toxic (not regulated by the EPA although states, such as Pennsylvania, have set a regulatory goal of 14 milligrams per liter, mg/L) and it is a common laboratory contaminant leading to false positive detections in environmental samples at concentrations as high as 3 to 5 mg/L. With respect to its environmental fate, although it is quite mobile in soil and groundwater, EG also biodegrades readily under aerobic and anaerobic conditions which are common in areas with methane contamination through the following reaction pathway (Dwyer, 1983, Huang, 2005):

ethylene glycol → acetaldehyde → ethanol → acetate → methane + CO_2

Nitrate can serve as the electron acceptor in anaerobic biodegradation of EG (Schramm and Schink, 1991), and nitrate is a common contaminant in rural groundwater as a result of agricultural practices and/or septic field contamination of drinking water.

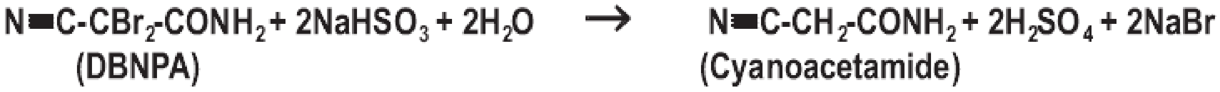
EG is unlikely to be significantly retarded by adsorption and therefore maybe a potential concern for groundwater transport. Because it degrades readily and is not considered to be persistent in the environment, it is not likely to be a significant problem for groundwater migration.

Mono- or di-ethanol amine is a polar, colorless liquid that, like most amines, is weakly basic. It is commonly used as a foaming agent and used in shampoo and cosmetics. The amine group allows it to be a surface active compound that can adsorb onto mineral surfaces although it has a low K_{ow} (estimate of its adsorption onto soil organic matter) and Henry's constant limiting its adsorption onto carbon and its potential to be stripped from water. As a result, diethanolamine will be difficult to treat in groundwater using conventional water treatment technologies such as granular activated carbon and air-stripping.

It undergoes moderate to rapid biodegradation and is not considered persistent. Knapp et al. (1996) isolated an anaerobe that uses diethanolamine as a carbon source and found that it grew better under reducing conditions in the presence of nitrate than under aerobic conditions. Therefore, due to its lack of persistence in the environment, diethanolamine should not pose a significant risk of migration.

2,2 Dibromo-3-nitrilopropionamide (DBNPA) is a water soluble (15 g/L) solid that is categorized as a "quick-kill" biocide marketed by Dow for protecting reverse osmosis membranes, paper mills, and offshore oil flooding operations. The definition of quick-kill comes from the relatively effective biocidal properties of the compound. Dow (2006) sells a formulation of DBNPA as a biocide, that includes EG to increase DBNPA solubility. Their marketing material promotes the short persistence of DBNPA in the environment.

Dow (2006) and Exner et al. (1973) explain that DBNPA reacts with nucleophiles (or reducing agents, I^-, HS^-, HSO_3^-, $S_2O_3^{2-}$, and SO_3^{2-}) in aqueous systems to form cyanoacetamide and bromide as shown in the reaction below:



$$\underset{\text{(DBNPA)}}{N{\equiv}C\text{-}CBr_2\text{-}CONH_2} + 2NaHSO_3 + 2H_2O \rightarrow \underset{\text{(Cyanoacetamide)}}{N{\equiv}C\text{-}CH_2\text{-}CONH_2} + 2H_2SO_4 + 2NaBr$$

Cyanoacetamide is subsequently hydrolyzed to cyanoacetic acid, its amide, and malonic acid. Exner et al. (1973) evaluated the degradation of DBNPA in soil/groundwater and surface water assessing the half-life for hydrolysis, nucleophilic substitution (as described above) and exposure to sunlight. They found that hydrolysis is rapid at pH 7.4 with a half-life of approximately 21 hours. The half-life of hydrolysis increases to 155 hours at a pH below 6. When they evaluated degradation rates in soil, they found that biodegradation under aerobic conditions occurred with a half-life of 6 to 15 hours and formed no measurable degradation byproducts besides ammonia and bromide. In order to assess the role of adsorption versus biodegradation, they washed the soil with deionized water, filtered it and added DBNPA to the extracted water. No byproducts were observed besides ammonia and bromide. The reaction was observed at a pH of 5.8, therefore the reaction was believed to be biologically mediated since hydrolysis was determined to be negligible below a pH of 6.

An evaluation of DBNA toxicity after reaction with activated sludge (simulating wastewater treatment) indicated that the DBNPA was deactivated by the reaction (Gartiser and Ulrich, 2003). The study did not evaluate for the presence degradation products, and attributed the change to adsorption onto the activated sludge. The results of the Exner et al. (1973) appear to indicate that the deactivation was likely due to biodegradation, enhanced by the microbial enriched activated sewage sludge.

The available data appears to confirm that DBNPA has a short half-life in soil and sediments and should biodegrade rapidly in the environment. Under reducing conditions and above a pH of 7.4 the toxicity of the compound should be rapidly deactivated. Therefore, due to its short half-life, DBNPA is unlikely to pose a significant risk of migration.

2-Butoxy ethanol is a colorless liquid that is miscible in water and most organic solvents. It is used as a solvent in many surface coatings and fast drying paints and lacquers. It is also found in many cleaning agents and is therefore a common contaminant in domestic households, businesses and their wastes. Beihoffer and Ferguson (1994) reported that concentrations of 2-butoxyethanol were observed in aqueous samples from a municipal and an industrial landfill in the USA at concentrations ranging from <0.4 to 84 mg/l.

Given the common structure of its functional groups, it is relatively easily biodegraded. Howard et al. (1991) determined an aerobic surface water half-life of 1 to 4 weeks and a soil half-life of 2 to 8 weeks in soil.

The WHO reports that 2-butoxy ethanol has a low K_{ow} and Henry's law constant making it both poorly adsorbed by organic matter in soil and not likely to volatilize into the gas phase once dissolved in water. Therefore it will be difficult to treat in solution using either adsorption or air-stripping.

Groundwater monitoring for 2-butoxy ethanol as a trace constituent in fracing fluids will be complicated by the fact that it is commonly found in house hold cleaning products and paints which maybe spilled at residential sites impacting shallow groundwater. Many domestic wells exhibit contamination from both septic and other domestic sources which could include 2-butoxy ethanol.

Although it is unlikely to be significantly retarded by adsorption, because 2-butoxy ethanol is not considered to be persistent in the environment, it is unlikely to pose a significant risk for contaminant migration. Household cleaning products and paints may pose a greater risk for exposure.

Diammonium peroxosulfate or ammonium persulfate is a salt comprised of two common ions, ammonium and persulfate. Persulfate is commonly used in the environmental remediation field to oxidize petroleum hydrocarbons, chlorinated solvents and other organic contaminants. It degrades into sulfate and can form strong sulfate and hydroxyl radicals when activated by ferrous iron or heat. Because it is a reactive oxidant, it is not persistent in soil or groundwater and will react to form sulfate within a few weeks depending on how reducing groundwater conditions are. As an oxidant, persulfate is one of the more slow reacting oxidants under standard temperature and pressure and in the absence of a catalyst such as ferrous iron or heat.

Once reacted to form sulfate and ammonium ions, the main concern with this compound is that it increases the total dissolved solids (TDS) in groundwater and may create algal blooms in surface waters because it may increase the nitrogen concentration in surface waters. Both ions are easily removed from impacted groundwater through ion exchange or reverse osmosis treatment. It is not anticipated to pose a significant risk for migration because it will react with organic carbon and reduced materials in the aquifer.

Priorities for Groundwater Monitoring and Treatment

Based on the findings of this evaluation, none of the compounds identified appear to pose a significant risk of migration due to lack of persistence. Their chemical structure, reactivity and/or biodegradability lower their persistence in the environment and limit their potential to impact drinking water wells. That is not to say that screening and monitoring for these compounds is not warranted if there is a reason to believe, based on hydrogeologic data and other evaluations, that the fracing fluids have the potential to reach a drinking water well.

References

Beihoffer J, C. Ferguson. 1994. Determination of selected carboxylic acids and alcohols in groundwater by GC-MS. Journal of Chromatographic Science, 32, p102–106.

Dow. 2003. Antimicrobial 7287 Water Treatment Microbiocide. Product Information Sheet.

Dwyer, D.E. and J.M. Tiedje. 1983. Degradation of Polyethylene Glycols by Methanogenic Consortia. Applied and Environmental Microbiology, July, p 185-190.

EPA Report. 2004. Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic

Fracturing of Coalbed Methane Reservoirs. Chap. 4: Hydraulic fracturing fluids. EPA 816-R-04-003.

Exner, J.H., G.A. Burk, and D. Kyriacou. 1973. Rates and products of decomposition of 2,2-dibromo-3-nitrilopropionamide. J. Agr. Food Chem., 21(5), p 838-842.

Gartiser, S. and E. Urich. 2003. Elimination of cooling water biocides in batch tests at different inoculumconcentrations. SETAC Conference. Poster.

Howard ,PH, R.S. Boethling, W.F. Jarvis, W.M. Meylan, E.M. Michalenko. 1991. Handbook of environmental degradation rates. Chelsea, MI, Lewis Publishers Inc.

Huang, Yi-Li. 2005. Anaerobic Biodegradation of Polyethylene Glycols Using Sludge Microbes. Process Biochemistry 40, p 207-211.

Knapp, J. S., N. D. Jenkey, C. C. Townsley. 1996. The anaerobic biodegradation of diethanolamine by a nitrate reducing bacterium. Biodegradation, 7 (3), p 183-189

Schramm, E. and B. Schink. 1991. Ether-Cleaving Enzyme and Diol Dehydratase Involved in Anaerobic Polyethylene Glycol Degradation by a New Acetobacterium sp. Biodegradation, 2, p 71-79.

Table 1: Characteristics of Undiluted Chemicals Found in Hydraulic Fracturing Fluids (Based on MSDSs)

Product	**Chemical Composition Information**	**Hazards Information**[1]	**Toxicological Information**[2]	Ecological information
Linear gel delivery system	1) Guar gum derivative 2) Diesel	• Harmful if swallowed • Combustible	• Chronic effects/Carcinogenicity – contains diesel, a petroleum distillate and known carcinogen • Causes eye, skin, respiratory irritation • Can cause skin disorders • Can be fatal if ingested	Slowly biodegradable
Water gelling agent	1) Guar gum 2) Water 3) Fumaric acid	None	May be mildly irritating to eyes	Biodegradable
Linear gel polymer	1) Fumaric acid 2) Adipic acid	Flammable vapors	Can cause eye, skin, and respiratory tract irritation	Not determined
Linear gel polymer slurry	1) Diesel oil #2	• Causes irritation if swallowed • Flammable	• Carcinogenicity – Possible cancer hazard based on animal data; diesel is listed as a category 3 carcinogen in EC Annex 1 • May cause pain, redness, dermatitis	Partially biodegradable
Cross-linker	1) Boric acid 2) Ethylene Glycol 3) Monoethanolamine	• Causes irritation if swallowed • Combustible	• Chronic effects/carcinogenicity DS may cause liver, heart, brain, reproductive system, and kidney damage, birth defects (embryo and fetus toxicity) • Cause eye, skin, respiratory irritation • Can cause skin disorders and eye ailments	Not determined
Cross-linker	1) Sodium tetraborate decahydrate	May be mildly irritating: • to eyes and skin • If swallowed	May be mildly irritating	• Partially biodegradable • Low fish toxicity
Foaming agent	1) Isopropanol 2) Salt of alkylamines 3) Diethanolamine	• Harmful if swallowed • Highly flammable	• Chronic effects/carcinogenicity – may cause liver and kidney effects • Causes eye, skin, respiratory irritation • Can cause skin disorders and eye ailments	Not determined
Foaming agent	1) Ethanol 2) 2-Butoxyethanol 3) Ester salt 4) Polyglycol ether 5) Water	Harmful if swallowed or absorbed through skin	• May cause nausea, headache, narcosis • May be mildly irritating	Harmful to aquatic organisms
Acid treatment-hydrochloric acid	1) Hydrochloric acid	• May cause eye, skin and respiratory burns • Harmful if swallowed	• Chronic effects/carcinogenicity – prolonged exposure cause erosion of teeth • Causes severe burns and skin disorders	Not determined
Acid treatment-hydrochloric acid	1) Formic acid	• May cause mouth, throat, stomach, skin, and respiratory tract burns • May cause genetic changes	• May cause heritable genetic damage in humans • Cause severe burns • Causes tissue damage	Not determined
Breaker fluid	1) Diammonium peroxodisulphate	• May cause respiratory tract, eye or skin irritation • Harmful if swallowed	May cause redness, discomfort, pain, coughing, dermatitis	Not determine
Biocide*	1) 2,2-Dibromo-3-nitrilopropionamide			

Table 2. Adapted from Table 4-1, Chapter 4, EPA Report 816-R-04-003. Hazard and toxicological information sources from MSDS according to EPA. Biocide not included in original table. Identified by multiple sources as a biocide for hydraulic fracturing.

Fate and Transport Evaluation of Potential Release Scenarios during Hydraulic Fracturing Operations

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Introduction

Fate and transport includes the processes that control the behavior of chemicals if they are released from some source by escaping existing natural or manmade barriers. Therefore, the mechanism and chance of release must be determined before prioritizing any potential release scenarios. Determination of potential receptors must then be determined for the realistic potential release scenarios. With realistic sources and receptors identified, fate and transport analysis may proceed. Fate and transport analysis will then require input data on appropriate chemicals, hydrogeological data, and geochemical data within a proper modeling framework. Fate and transport results are used to determine appropriate collection of data to fill gaps, validate models, or eliminate pathway from further consideration.

Scope

While focusing on fate and transport of chemicals (exposure pathways) and processes related to potential impacts of hydraulic fracturing on drinking water, there will also be some description of the selection of reasonable release scenarios and receptors. The fate and transport processes will, in general, be similar to those found with other potential chemical releases to soil and groundwater such as surface spills, impoundment leaks, and leaks from underground storage tanks. The major differences will be in some potential release scenarios such as cement jobs, pipe strings, and fractures, which are normally prevented with engineered and natural controls. This process demands the evaluation of these controls before proceeding to further evaluation steps. Also, the chemical nature of potentially released material in upstream operations has been characterized as high volume and low toxicity.[1] Therefore, upstream materials such as produced water are of low potential risk when managed appropriately.

Conceptual Model

A conceptual site model (CSM) is a "…written or pictorial representation of an environmental system and the biological, physical, and chemical processes that determine the transport of contaminants from sources through environmental media to environmental receptors with the system."[2] Barriers (controls or defenses) may also be part of the system (Figure 1). Whatever the form used, a CSM is critical for determining prioritizing reasonable release scenarios for fate and transport evaluation.

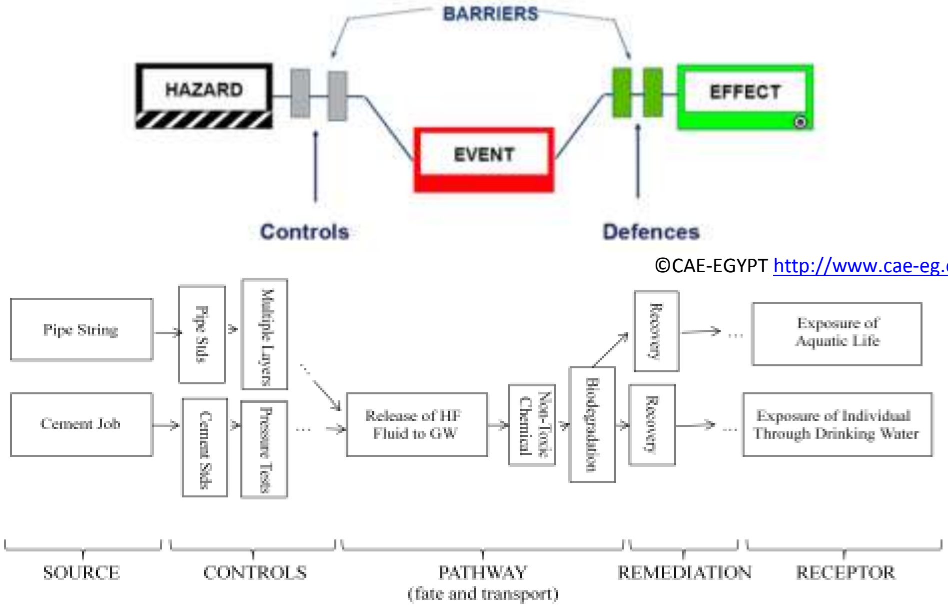

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Figure 1. A generalized and a specific form of conceptual site model.

Realistic Potential Release Scenarios

The example CSM in Figure 1Figure 1 shows a potential pathway from a cement job. There would be no need to evaluate further if the controls for the cement job are adequate to prevent release. Controls may include cement standards, and pressure tests. However, proceeding with development of a potential release scenario may be necessary if controls were considered weak and simple modifications are not sufficient to provide confidence in the controls.

Identify the potential release scenarios by examining the hydraulic fracturing processes that could potentially release material in a manner that could impact drinking water resources. Gather information critical to this potential scenario. These data might include process information and controls, identification of volume and type of additives used in the process, and total volumes of hydraulic fracturing fluids that might be released if controls could fail.

Returning to the potential for a failed cement job, there are numerous standards through regulation or guidance in the industry to prevent such an occurrence.[3.4] In this case then, it may be determined that existing standards and regulations mitigate cement jobs as a reasonable release scenario. No further analysis is required in this case.

For the sake of discussion, assume that there is found to be potential for a release to surface soil somewhere in hydraulic fracturing process from a control failure. Also assume that it was not due to noncompliance to any applicable regulations. If about 50,000 gallons of hydraulic fracturing fluids[5] were released, this would represent a maximum volume from one hydraulic fracturing treatment substage.

As much information as possible on the release liquid is now required. With a hydraulic fracturing fluid this would include its make-up. It is primarily water, sand, and about 0.5% (5,000 ppm) of up to about 8 additives.[6] These additives may include a gellant (guar), buffer (sodium hydroxide), breaker (NaCl), friction reducer (mineral oil), antimicrobial (gluteraldehyde), acid (HCl), and surfactant (citrus terpenes and isopropanol). If this were flowback solution, there might be salt (NaCl), hydrocarbons, and ions from formation water. Composition of the hydraulic fracturing fluid and formation water may vary greatly depending upon reservoir requirements and properties.

At this point, the source release scenario, release volume, and release composition will be known to some extent. In this case: A surface release of 50,000 gallons of hydraulic fracturing fluid containing 50% original hydraulic fracturing fluid and 50% formation water to surface soil. There would of course be changes to the original hydraulic fracturing fluid such as a loss of proppant to the producing formation.

Assume a roughly estimated composition of spilled material (fluid and formation water) as shown in Table 3.

Table 3. Hypothetical release concentrations (my rough estimates)

Water (from fluid and formation water)	97.8%	
Guar (from fluid)	0.02%	200 ppm
Sodium Hydroxide (from fluid)	0.005%	50 ppm
Sodium Chloride (from fluid and formation water)	2.0%	20,000 ppm
Mineral Oil (from fluid)	0.04%	400 ppm
Gluteraldyhyde (from fluid)	0.0005%	5 ppm
Hydrochloric Acid (from fluid)	0.06%	600 ppm
Hydrocarbon (from formation water)	0.05%	500 ppm
Citrus Terpenes (from fluid)	0.005%	50 ppm
Isopropanol (from fluid)	0.005%	50 ppm
NORM (from formation water)	Managed if present	

Fate and Transport

Data are now required on hydrogeology, geochemistry, and chemical properties. This also must include background chemical information (naturally occurring or anthropogenic) for potentially impacted drinking water sources that might interfere with fate and transport evaluation. Typical background chemical constituents and parameters are salts, pH, metals, naturally occurring hydrocarbons, and anthropogenic hydrocarbons.

For each component, available chemical and physical property data are required for subsequent evaluation. These data may include dissolution, precipitation, degradation rates, volatility, sorption, and dispersivity data.

At this point modeling may be performed based on site parameters. In the absence of the detail required for sophisticated modeling, screening models may be used to conservatively estimate fate and transport. For reactive inorganic compounds, a mineral equilibrium model such as minteqa2 may provide information on the behavior of chemicals such as barium, strontium, etc.[7] Most of these metals will fall out of solution due to solid precipitation or adsorption at the levels found in the source material. Soluble salts can be conservatively treated as remaining in solution. All chemicals in solution will be subject to potential transport through the unsaturated zone and movement with groundwater. Concentrations in Groundwater will tend to decrease with distance downgradient from the source due to mechanical mixing (dispersion) and biodegradation. This decrease over distance can be defined as a dilution attenuation factor for the saturated zone. This dilution factor is site specific and dependent on horizontal distance to the point of extraction, biodegradation rate, retardation, groundwater flow velocity, dispersivity, and source size. This relation between groundwater concentration in the source area and downgradient from the source can be described by the following steady-state solution for groundwater[8]:

$$\frac{C_s}{C_x} = DF_{sat} = \left(\exp \left\{ \frac{x}{2\alpha_x}\left[1-\sqrt{1+\frac{4\lambda\alpha_x R}{v}}\right]\right\} \times \left(erf \left[\frac{S_w}{4\sqrt{\alpha_y x}}\right]\right)\left(erf\left[\frac{S_d}{2\sqrt{\alpha_z x}}\right]\right)\right)$$

where:

C_x = dissolved salt at a distance x from the source (mg/L)
x = horizontal distance to point of extraction (cm)
λ = first-order degradation constant – salt does not degrade (day^{-1})
R = constituent retardation factor (dimensionless)
v = specific discharge (cm/day)
α_x = longitudinal dispersivity (cm)
α_y = transverse dispersivity (cm)
α_z = vertical dispersivity (cm)
S_w = source width (cm)
S_d = source depth (cm)

Validation

Once any modeling is completed, it cannot be considered representative of a system until it is validated, especially where there is uncertainty on any model factors. Uncertainly has to be addressed through data gap analysis and appropriate data gathering to fill those gaps. Also, field sampling and analysis will be required to test the model.

Chemicals must be selected for analysis based on their predicted ability to reach sampling points. Chemicals that are biodegraded readily (benzene, citrus terpenes, isopropanol), precipitated out of solution (barium), adsorbed to soils (polymers), or reacted (HCl) will not move a significant distance. Therefore, they may not be measureable downgradient. Upstream fate and transport modeling and monitoring exercises have been most successful when performed on salts and divalent ions. Potential impacts may also be evaluated using ion ratios, isotopic methods, and trilinear diagrams.

Remember that any spill from a hydraulic fracturing operation will be of limited mass and volume so one cannot assume an infinite source, i.e., the source is finite and will disappear with time. Immobile chemicals will stay near the release area to be left in place or readily removed.

Risk Assessment

Knowing the distance to a receptor, an exposure rate can be determined. This can be evaluated with accepted risk exposure models for various drinking water receptors.

Conclusions

Processes are available for evaluating the fate and transport of selected reasonable release scenarios in hydraulic fracturing operations. These methodologies consider all controls in the hydraulic fracturing process as reflected in existing regulations and best management practices before selecting scenarios. Background chemicals, both anthropogenic and natural, must be considered in any analysis. Tools must be used that are appropriate for uncertainty in available data and analytical techniques.

References

[1] USEPA, October 2002, Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations, United States Environmental Protection Agency, Washington, D.C., accessed at: http://www.epa.gov/osw/nonhaz/industrial/special/oil/oil-gas.pdf

[2] ASTM International, 2008, Standard Guide for Developing Conceptual Site Models for Contaminated Sites, E 1689-95 (Reapproved 2008), ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959.

[3] DOE, May 2009, State Oil and Natural Gas Regulations Designed to Protect Water Resources, prepared by Ground Water Protection Council for U.S. Department of Energy, accessed at: http://www.gwpc.org/home/GWPC_Home.dwt.

[4] API, October 2009, Hydraulic Fracturing Operations – Well Construction and Integrity Guidelines, Guidance Document HF1, First Edition, American Petroleum Institute, Washington, D.C., accessed at: http://www.api.org/.

[5] DOE, April 2009, Modern Shale Gas Development in the United States – A Primer, prepared by Ground Water Protection Council for U.S. Department of Energy, accessed at: http://fossil.energy.gov/news/techlines/2009/09024-Shale_Gas_Primer_Released.html.

[6] Energy in Depth, 2009, A Fluid Situation: Typical Solution Used in Hydraulic Fracturing, accessed at: http://www.energyindepth.org/frac-fluid.pdf.

[7] USEPA, March 1991, Minteqa2/Prodefa2 – A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, United States Environmental Protection Agency, Athens, GA, accessed at: http://www.epa.gov/ceampubl/mmedia/minteq/USERMANU.PDF

[8] Domenico, P. A., 1987, An analytical model for the multidimensional transport of a decaying contaminant species, J. of Hydrology, 91, 49-58.

A Protocol to Characterize Flowback Fluid Contamination of Drinking Water

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The Appalachian Basin of New York, Pennsylvania and West Virginia contains one of the largest gas plays in the world in the organic-rich Paleozoic-age Marcellus and Utica Shales. The hydrocarbon-extraction industry has begun drilling and hydrofracturing (fracking) to produce methane sorbed in the shale lamina. One concern relates to the potential for flowback fluids and methane from the producing formation to contaminated drinking waters because of improper grouting of vertical well casings and/or surface disposal.

Much of the concern over flowback fluids stems from elevated concentrations of trace elements, radium-226, and trace organic substances. But, these constituents geochemically react and naturally attenuate. For example, reactive iron and manganese in the anoxic flowback fluid precipitate upon contact with oxygen. Also, barium in solution precipitates upon contact with dissolved sulfate. Small concentrations of dissolved organic carbon in flowback fluid, including possible aromatic hydrocarbons and glycols, biodegrade once discharged to fresh waters -- analogous to natural attenuation associated with UST spills with orders of magnitude greater concentrations of dissolved organic substances. Finally, rock formations can provide many trace substances common to that found in flowback fluid. For example, the Marcellus Shale in Appalachia contains barium and strontium mineralization that seals fractures (Siegel et al., 1987; Chamberlain et al., 1986). In short, elevated concentrations of trace metals and many dissolved organic compounds do not provide the means to unequivocally identify the extent of flowback fluid contamination of drinking waters.

Formation waters mixing with shale bed methane flowback fluids have high salinities associated with formation brines. But, in the Northeastern United States, road salt and septic discharge of salts associated with water softeners also contribute salinity to surface waters (Mullaney et al., 2009). Seawater intrusion can occur near coastal areas. Also, the surface disposal of acid mine drainage from coal mines can elevate the salinity of drinking water by the addition of calcium and sulfate, among other solutes (Tetra Tech, 2009).

Fortunately, the dissolved halogen elements associated with salinity: chloride, bromide, and fluoride, and iodide, can provide the means to unequivocally identify where flowback fluids or oilfield brines have contaminated drinking waters. Mineral-water reactions minimally affect these solutes, the ratios of which can distinguish among salinity sources (e.g. Panno et al., 2006;

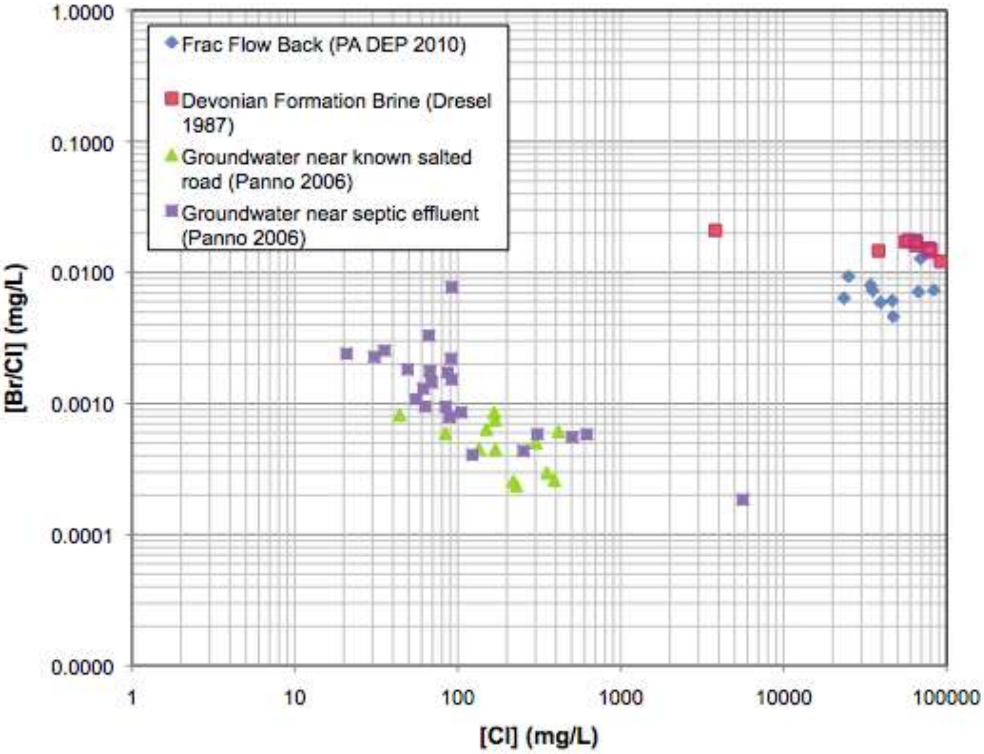

Figure 2. Bivariate plot of Br/Cl versus Cl concentrations for Marcellus frac fluids, Pennsylvanian Devonian sedimentary basin brines, and representative road salt contamination and septic effluent. Note the clear separation between the flowback fluid, brines and other sources of contamination (Kight and Siegel, 2011)

Townsend, and Whittemore, 2005). Therefore, any contaminants associated with flowback water that do not naturally attenuate must move with flowback fluid halogen salinity.
We have heuristically investigated using halogen and major solute ratios and chemical mixing models to develop a protocol to characterize potential flowback water contamination of drinking waters in the Appalachian Basin. Our preliminary results (Kight and Siegel, 2011) show that plotting Br/Cl ratio versus Cl concentrations distinguishes the presence of flowback fluid contamination from other salinity sources (Figure 2).

The Br/Cl ratio of Marcellus flowback fluids also show that Appalachian Basin brine probably provides the source for flowback salinity, not dissolving rock salt as previously proposed (Blauch et al., 2009). The Br/Cl ratio of flowback fluid would have to be at least an order of magnitude smaller to reflect halite dissolution because bromide is excluded from halite when it precipitates. Either hydrofracking-induced vertical fractures beyond the contacts of the formation with more permeable and brine-filled formations, or the Marcellus contains disseminated brine, yet unrecognized.

Our geochemical mixing models enable us to identify extraordinarily small amounts of flowback water in mixtures, even when other salinity sources previously contaminated drinking waters.

Our protocol using halogen concentrations coupled to mixing models needs to be applied on a site-by-site basis. That is, the background chemical composition of potential drinking-water receptors must be obtained as well as representative analyses of flowback waters produced near them. Every shale gas methane basin has its own geochemical halogen fingerprint. However, once we have identified flowback from halogen ratios, the presence of solutes and substances that could potentially compromise drinking waters can be addressed without the fear of false positives.

We are continuing our work by addressing additional combinations of halogens and major solutes and characterizing the most plausible source for methane in drinking waters by using a combination of mixing models, coupled to methane isotopes and trace gases.

References Cited

Blauch, M.E., Myers, R.R., Moore. T.R., Lipinski, B.A., 2009, Marcellus Shale Post-frac Flowback Waters--Where is All the Salt Coming From and What are the Implications?, In Proceedings: Eastern Regional Meeting of Society of Petroleum Engineers, Paper SPE 125740, Charlestown, West Virgina, 23-25 September 2009.

Chamberlain, S.C., Dossert, W.P. and Siegel, D.I., 1986, A new paragenesis and new localities for the barium carbonate, witherite, Canadian Mineralogist, vol. 24, p. 79-90.

Dresel P.E., 1985. The geochemistry of oilfield brines from western Pennsylvania. Master's thesis, Pennsylvania State Univ.

Kight, M. and Siegel, D.I., 2011, A protocol for characterize flowback water contamination to shallow waters from shale gas development. Abstracts and Program, NE Geological Society of America Meeting, Pittsburgh, PA, p. 76.

Panno, S.V., K.C. Hackley, H.H. Hwang, S.E. Greenberg, I.G. Krapac, S. Landsberger, and D.J. O'Kelly, 2006, Characterization and Identification of Na-Cl Sources in Ground Water, Ground Water, Vol. 44, p. 176–187.

Rose, A.W. and Dresel, P.E., 1989, Deep brines in Pennsylvania: in Water Resources in Pennsylvania, Availability, Quality, and Management, S.K. Majumdar, E.W. Miller, and R.R. Parizek (eds.), The Pennsylvania Academy of Science, pp. 421-431.

Siegel, D.I., Chamberlain, S.C. and Dossert, W.P., 1987, The isotopic and chemical evolution of mineralization in septarian concretions: Evidence for episodic paleohydrogeologic methanogenesis, Geological Society of America, vol. 99, p. 385-394.

Davis, S.N., Whittemore, D.O.; and Fabryka-Martin, J, 1998, Uses of chloride/bromide ratios in studies of potable water, Ground Water, Vol. 36, p. 338-350.

Mullaney, J.R., Lorenz, D.L. and Arntson, A. D., 2009, Chloride in Groundwater and Surface Water in Areas Underlain by the Glacial Aquifer System, Northern United States, U.S. Geological Survey, National Water-Quality Assessment Program, Scientific Investigations Report 2009–5086, 54p.

Tetra Tech NUS, Inc., 2009, Evaluation of High TDS Concentrations in the Monongahela River, 126p.

Townsend, M.A. and Whittemore, D.O., 2005, Identification of nitrate and chloride souces affecting municipal wells waters of the city of McPherson, Kansas, Kansas Geological Survey Open File Report 2005-34, 24p.

Summary and Abstracts from Theme 2: Impacts of Hydraulic Fracturing on Natural Transport Systems

Summary of Presentations from Theme 2: Impacts of Hydraulic Fracturing on Natural Transport Systems

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Technical Presentations

The first set of technical presentations in this theme addressed fracture propagation.

Ahmad Ghassemi, Texas A&M University, discussed rock failure and stimulated volume with regard to HF. He described the stress and pressure changes resulting from HF treatments, the variables that affect rock failure, and how this information is used to predict stimulated rock volume (SRV), the volume of rock with fracture-induced enhanced permeability. Dr. Ghassemi explained that stimulation often results in the formation of a complex fracture structure, which is important to consider. He explained the assumption that Mode I fracture propagation dominates; however, microseismic monitoring shows that shear fracture also does occur and at times is the dominant mode. Therefore, Dr. Ghassemi recommended that mixed-mode fractures and slip and shear dilation should be incorporated into models. Dr. Ghassemi added that the large volume of failed rock tends to redistribute the stresses in the rock mass and can modify the nearby rock permeability. The rock mass heterogeneity and the time-dependent behavior of intact rock and fractures are important in the permeability evolution of the stimulated volume, according to Dr. Ghassemi.

Norman Warpinski, Pinnacle – A Halliburton Service, discussed vertical fracture growth and the effect of heterogeneities in layered and discontinuous media. He indicated that fracture patterns are not simple to model; fractures are complex with many complex individual strands. Mr. Warpinski stated that vertical fracture growth is influenced by many factors that vary between and within reservoirs, and that in situ stress distribution is the dominant influence, according to Mr. Warpinski, but sedimentary interfaces, natural fractures, and other heterogeneities can also affect fracture behavior, and layering and interfaces resulting in inefficient growth.

The second set of technical presentations addressed fluid and gas flow in fractured formations.

Zhong He, Range Resources, discussed the flow of gas and water in hydraulically fractured shale gas reservoirs, focusing mainly on flow taking place after the fracture treatment. Pressure gradients are the driving factor for fluid flow: a pressure sink in the depleted zone drives gas through the fractures and into the wellbore. While a portion of the injected fluid is returned to the surface through the wellbore, the presenter stated the majority of the fluid is trapped by the shale formation and becomes immobile. Mr. He emphasized that physical principles preclude the migration of gas and water away from the stimulated zone.

David Cramer, ConocoPhillips, discussed the use of injection fall-off tests for characterizing mechanical and flow properties. He described the procedure for fall-off testing and provided details on two specific types of analysis: (1) fracture closure analysis for determining in situ stress and identifying non-ideal fracture closure mechanisms, and (2) after-closure analysis for determining reservoir flow behavior, reservoir flow capacity or transmissibility, and initial reservoir pressure. He stated that the information gathered from these analyses can be used to predict the results of the HF treatment (fracture geometry, proppant placement, fracture conductivity, etc.) and to inform modifications of the treatment design.

Alan Byrnes, Chesapeake Energy, described the role of induced and natural imbibition in fracturing fluid fate and transport. He described calculations for estimating stimulated reservoir volume and presented data from experiments and models demonstrating that a majority of the injected fluid leaks off into the fracture face, resulting in an "invaded zone" of elevated HF fluid concentrations 2-6 inches thick. As pressure in the reservoir drops, Mr. Byrnes indicated that strong capillary pressures hold these imbibed fluids in place.

Summary of Discussions Following Theme 2: Impacts of Hydraulic Fracturing on Natural Transport Systems Presentations

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Horizontal and vertical fractures. The presenters clarified that heterogeneity in the vertical direction influences stresses, and other rock mechanical properties like ductility or brittleness will also affect hydraulic conductivity. They stated that above a depth of approximately 1,500 feet, the dominant component of fractures will shift from vertical to horizontal. The presenters indicated that differences in overburden pressure are unlikely to affect fracture orientation. They noted that controlling fracture orientation would require controlling the in-situ stress since, at depth, almost every fracture is vertical. A participant asked whether the operator would know if horizontal activity were occurring, and the presenters responded that the operator would know if overburden stress were exceeded and would be aware of changes in pressure.

Shallow fracture depths. A participant asked about the shallowest depths for HF. While most operators' shallowest fracture jobs have been 1,000–1,200 feet, a participant indicated that HF is performed for some ground water cleanup work and other applications at depths of only a few meters.

Distance of perforation clusters. A participant asked about the spacing of perforation clusters on horizontal wells. A presenter responded that the optimum spacing is determined empirically.

Fracture fluids and different formation types. A participant asked if different types of fracture fluids are used for deep shale gas and shallow coalbed methane (CBM) jobs. The presenters explained that water-based fluids and crosslinked gels are both used in shales. The presenters stated that, in general, viscous fluids do not create the desired level of complexity, though in certain situations, denser fluids are used to encourage downward fracture growth. They stated that borate systems are more popular for CBM, and higher-viscosity fluids tend to perform better in coal formations. Participants noted that tight sands are treated similarly to shales, though tight sands do have more complexities.

Propagation rates. A participant asked about the rate of the propagation across lamina. The presenter responded that while laboratory experiments have been performed in layered rock, there is no way to directly measure these propagation rates in the field. Participants suggested that microseismic techniques or pressure profiles might be used to calculate them. Other participants noted that, due to the small scale and complexity of the layered systems, this would be very difficult to model.

Models simulating fracture growth. A participant noted that most of the complexities introduced into fracture growth models result in predictions of less fracture growth than the models would otherwise predict. A participant asked if any uncertainties would lead to a higher fracture growth than predicted. The presenters clarified that models are used much less than empirical knowledge when designing fracture jobs. In addition, they noted that less complexity does not necessarily equate to less fracture propagation, but simply indicates a more complex geometry and higher levels of uncertainty. They also stated that information on permeability can be related to flowback performance to gain understanding of the properties of the fracture network.

Conceptual models for fluid migration. A participant asked for more information on conceptual models that would involve fractures propagating from deep reservoirs to shallow aquifers. The presenters emphasized the importance of understanding the in situ stress profile and lithologic variations. In the field, the presenters noted that diagnostic microseismic techniques provide data on fracture height. In general, presenters indicated that stress conditions controls fracture height, and fluid pressure within the formation is also important to understand. The presenters indicated that extreme vertical fracture growth is very unlikely.

Electromagnetic (EM) methods. A participant mentioned magnetotellurics and asked whether electromagnetic methods are used to monitor fracture propagation. A presenter indicated that EM methods are frequently used for geothermal applications and are also sometimes used in the oil and gas industry.

Production termination. A participant asked when a shale gas system would become a pressure sink. A presenter explained that this is based on permeability; if most of the pressure is in microfractures, a depressurized zone will be created when that pressure is dissipated. The presenter noted that the production decline curve provides information on dissipating pressures within fractures, and matrix depletion is a function of the permeability of the matrix.

Imbibition. A participant asked about collecting post-injection core samples to confirm that water is held immobile in the rock. Another participant noted that because shale formation production is fairly new, this has not been done. However, data from lab-tested core samples do indicate that water is trapped in the matrix. Another participant asked about the six-inch invasion zone. The presenter clarified that the six-inch area is the induced imbibition zone, and that after this point, natural imbibition factors go into effect. A participant asked if imbibition causes changes in the rock, damaging the shale. The presenters answered that operators try to produce water from the well as quickly as possible following a HF job so that the water in the formation is not working against gas production since water in the near-fracture face environment slows down the production rate. In addition, the presenters indicated that the imbibition process is not static; it does not stop when pumping stops. Other participants added that the more successful wells are generally the ones where the least amount of injected water is returned, meaning that the formation is porous and permeable enough to hold the water.

Pressure fall-off tests. A participant asked about the effect of viscosity changes on pressure test curves. The presenter stated that the viscosity of the reservoir fluid is an important parameter to know or estimate (it is the μ in kh/μ, the expression for rock transmissibility). However, changes in the viscosity of the injected fluid (due to pressure changes) do not impact the pressure test curve. A participant noted that, in his experience, relative permeability curves are more asymmetric than the one included in the presentation. The presenter clarified that the curves in the presentation are generic curves, not specific to gas shales. The presenter explained further that relative permeability curves for gas shales are not inconsistent with those for tight sands; the curves are generally asymmetric, and the shape of the curve varies depending on the formation. The presenter indicated that water relative permeability curves are not very well defined for gas shales because the permeability of the rock to water is very low (in the range of a few nD or less).

Pressure buildup in plugged wells. A participant noted that, in Upstate New York, some people are concerned that pressure will increase in a plugged well and cause a blowout. The presenters were not aware of any instances of this. One participant noted that pressure can build up over long periods of time; however, he suggested that with good engineering practices, the most extreme pressure experienced by the well occurs during the initial completion. In addition, he noted that multiple plugs set at different depths would protect against this kind of event. Another participant added that layers above the cement plug would be at hydrostatic pressure, in contrast to the underpressured, depleted reservoir. The participant indicated that this would prevent a dangerous pressure buildup.

Potassium chloride (KCl) substitutes. A participant asked about potassium chloride (KCl) substitutes. The presenters clarified that KCl is expensive in large quantities and that other chemicals, such as tetramethylammonium chloride, can be used instead. However, they indicated that KCl and KCl substitutes are often not necessary at all, depending on the properties of the formation. Participants noted that they do not use KCl substitutes in the Marcellus and the Eagle Ford.

Microseismic data and vertical fracture heights. The presenters clarified that, in the slides showing microseismic data, aquifer depth corresponds to the depth of the deepest water wells per county, based on U.S. Geological Survey (USGS) data. A participant asked if vertical fracture heights could reach 1,000–1,500 feet. The presenters suggested that fracture height growth will vary as a function of the formation and the properties of the vertical stress profile. However, participants indicated that, fundamentally, pressure and energy constraints would prevent the creation of induced fractures that large.

Fluid migration through abandoned wells. A participant asked if native brine could travel up an unplugged abandoned well and reach sources of drinking water, in a case where the gas reservoir was overpressurized. A participant noted that this would require gas lift or another drive mechanism. Another participant described a situation where an operator fractured into offset wells and saw water at the surface. However, the presenters noted that moving proppant from the injection well to the offset well would require a continuous string of proppant from one well to the other, which is difficult to achieve. Participants emphasized the need for monitoring and coordination when there are nearby wells. One participant noted that, while well communication does occur, operators are not aware of any resulting environmental problems.

Buoyantly rising fluids. Participants discussed the possibility of fluids rising in a slug, similar to magma rising buoyantly through layers of rock. Some participants argued that this type of movement would require a complete absence of leakoff, which seems extremely unlikely, even in crystalline rock. In addition, they said that the horizontal stresses that act to close the fracture would have to be counteracted. One participant described a situation where this may have happened in the Gulf of Mexico. Another participant referenced studies showing a correlation between the thickness of the Marcellus Shale and the amount of radon in residents' basements. However, another participant noted that this is diffusive transport. One participant suggested modeling the buoyant rise, and another participant noted that an abandoned well conduit would be a situation with zero leakoff.

Alternative fracturing fluid systems. A participant asked about using gas for HF instead of water. Another participant stated that one operator has been using gas in HF for years, mostly in subpressurized reservoirs. The participant gave an example of the use of nitrogen or carbon dioxide in foam fracturing. A participant added that nitrogen is used in shale reservoirs with very low underpressures, and another participant asked about HF with liquid carbon dioxide ("dry frac"). The presenter responded that dry frac systems are primarily used in Canada, because that is where the few blenders of this fluid system are located. He noted that liquid carbon dioxide is used in super-depleted, very low permeability formations where any water in the wellbore would create a problem, and these systems are very expensive and rarely economically viable. In addition, he indicated that proppant transport is not very good. The presenter noted that it is more likely that an operator would use foam instead, which has most of the benefits of the dry fracture with better proppant placement and a lower price.

Participants noted that thinner fracture fluids would, in general, lead to more complexity in fracture growth.

Abstracts for Theme 2: Impacts of Hydraulic Fracturing on Natural Transport Systems

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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Rock Failure and Permeability Enhancement in Tight Gas Hydraulic Fracturing

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Introduction

Generally, a tight gas reservoir is defined by its low permeability, however, it has been suggested (Holditch, 2007) to define a tight gas reservoir as one that "cannot be produced at economic flow rates or recover economic volumes of natural gas unless a special technique is used to stimulate production." Large hydraulic fracture treatments, often from a horizontal wellbore or multilaterals must be used to increase the recovery efficiency in the reservoir. Fracture conductivities of 10 mD/ft or higher appear to be necessary for economic gas production.

Shale gas reservoirs have heterogeneous geological and geomechanical characteristics that pose challenges to accurate prediction of their response to hydraulic fracturing. Experience in shale gas formations shows that stimulation often results in formation of a complex fracture structure, rather than the planar fracture aligned with the maximum principal stress. The fracture complexity arises from intact rock and rock mass textural characteristic and the in-situ stress and their interaction with applied loads. Open and mineralized joints and interfaces, and contact between rock units play an important role in fracture network complexity which affects the rock mass permeability and its evolution with time. Currently, the mechanisms that generate these fracture systems are not completely understood, and can generally be attributed to lack of in-situ stress contrast, rock brittleness, shear reactivation of mineralized fractures, and textural heterogeneity.

Stimulated Volume and Permeability Enhancement

The idea of stimulation by hydraulic fracturing is to create a large volume of fractured rock with enhanced permeability. Many tight gas reservoirs are characterized by high deviatoric stresses and hard, naturally fractured rock. Stimulation treatments in such reservoirs may result from slip on pre-existing critically stressed fracture systems and or creation of new fractures. It is generally believed that fracturing is caused by both shear and tensile failure. Shear slippage is induced by altered stresses near the tip of the fractures as well as by increased pore pressure in response to leakoff through the fracture "walls". In view of this, it has been suggested that increased viscosity promotes tensile failure and can lower complexity (Cipolla *et al.* 2008). Accordingly, water fracs are used where shear failure is anticipated to dominate (Chipperfield, S.T., Wong, J.R., Warner, D.S. *et al*. 2007). According to Cramer (2008), water is used as a base fluid in most unconventional reservoir treatments.

To determine intact rock failure and joint slippage, a failure criterion is employed. There are many failure criteria for the sliding of jointed rock masses but often the Mohr-Coulomb failure criterion is used. By combining a stress analysis with a criterion, one can assess the effects of increasing pore pressure on rock by generating a structural permeability diagram. This map that shows the *ΔP* required to reactivate joints of different orientations (e.g., Nygren and Ghassemi, 2005; Nelson *et al*. 2007) during fracture stimulation treatments at high treating pressures. One such map is shown in Figure 3 for the New Albany Shale.

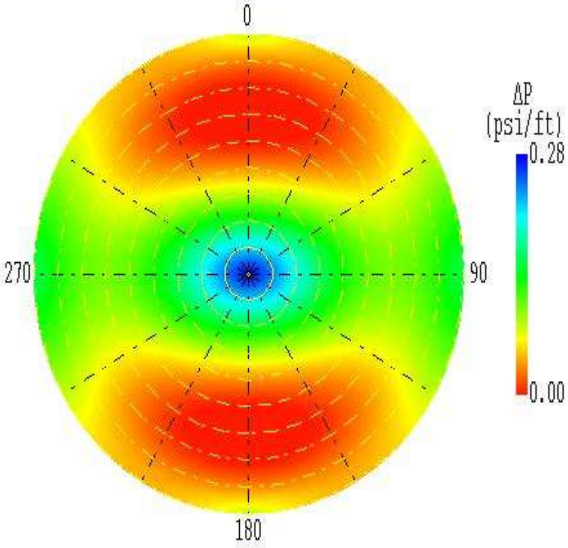

Figure 3. Structural Permeability Diagram for New Albany Shale (μ=0.6).

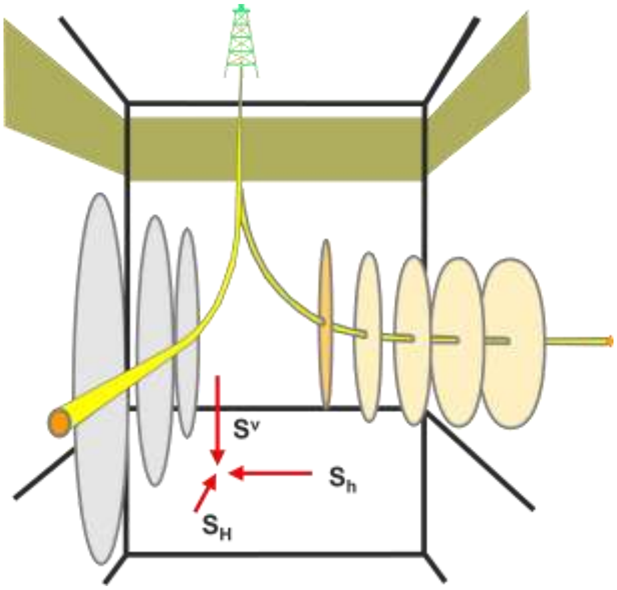

Figure 4. Fracture orientation in horizontal wells.

Most field implementation of stimulation involves creation of multiple hydraulic fractures and stimulation of the neighboring rock volume by compression and pore pressure increase.

Normally hydraulic fracturing is performed in horizontally-drilled wells. The geometry and propagation direction of a hydraulic fracture will mostly depend on the drilling direction of horizontal well and the in situ conditions as shown in Figure 4.

It is generally accepted that hydraulic fractures propagate perpendicular to the least principal stress. In shallower environments where the least principal stress is vertical, a fracture will grow horizontally. At some depth where the increase in overburden causes the least principal stress to be horizontal, the predominant fracture growth geometry will be vertical. Variations in stresses between different lithology in vertical sequences of rocks can cause fracture growth in a contained manner and generate length, or allow it grow vertically upwards or downwards. In addition to the in-situ stress, fracture growth will depend on many factors such as natural fractures, bed laminations, and other characteristics of a reservoir including the formation pore pressure in the reservoir. The pore pressure will affect the effective in situ stresses, and can further affect the post-fracturing deformation of rock and its natural fractures which will, in turn, influence the path of the hydraulic fracture (Koshelev and Ghassemi, 2001).

Fracture interaction

Multiple stage hydraulic fracturing is popular in the stimulations of tight gas reservoirs.

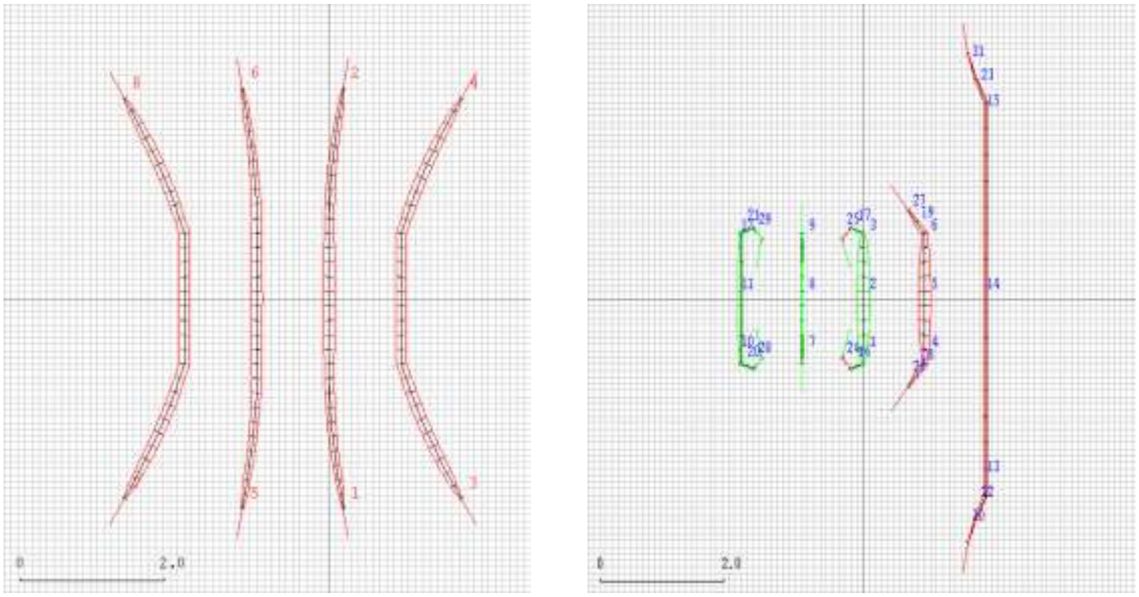

Figure 5. Interaction of multiple fractures in a horizontal well. Green represents closed fractures. Note the fractures turning away from each other to follow the path of least resistance.

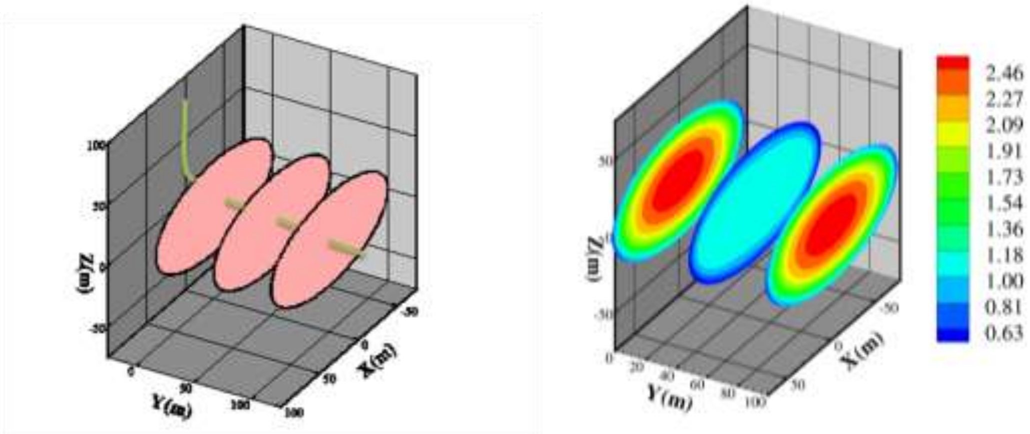

Figure 6. Fracture aperture distribution (in cm) after 3 hours of pumping in Barnett shale.

Estimating Stimulated Volume

It is believed that microseismic events (Figure 8) are mainly created as a result of shear slippages around the hydraulic fractures (Albright and Pearson (1982); Warpinski *et al*. (2001); Rutledge *et al*. (2003)). Shear slippage is induced by altered stresses near the tip of the fractures as well as shear slippages related to leakoff induced pore pressure changes.

Accepting that failure of the formation around a hydraulic fracture is caused by pore-pressure and stress perturbations, the stimulated reservoir volume (volume of "failed" rock in the reservoir) can be assessed using the areal extent of the micro-seismic cloud (Plamer *et al*. 2005; Jun and Ghassemi, 2005). However, it should be this procedure for evaluation of stimulated volume and fracture surface area is based on the assumption that energy release is exclusively related to fluid penetration, which may not always hold true. The micro-seismic record may also be used to detect hydraulic connection with the outside zone.

Prediction of enhanced permeability

The methodology of predicting the permeability in the failed region around a fracture is based on a trial and error procedure: (i) use the pressure profile at shut-in, and guesses a value for permeability, K; (ii) for a selected net fracture pressure, predict the failed rock volume (FRV) using the stress analysis; (iii) vary K until the FRV matches the particular trend-line of the stimulated reservoir volume from induced seismicity at the given net fracturing pressures. This method is based on the equivalent permeability for the failed rock and does not consider the time dependent behavior of rock and the fractures that are created. Furthermore, it is assumed that the MEQ's are related to local pore pressure perturbations.

The interaction of the multiple hydraulic fracture stimulation on the larger scale flow regime is not clearly understood. The large stimulated volume that is generated tends to redistribute the stresses within the crust and can cause changes in nearby rock permeability. In this context, the presence of faults (active and inactive) need be considered.

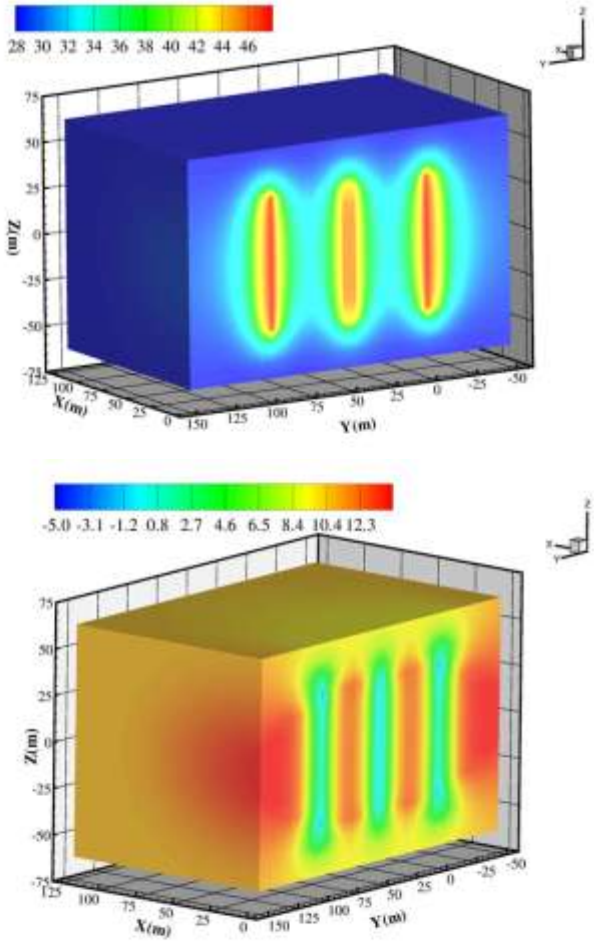

Figure 7. Distribution of pore pressures (MPa) in the formation; minimum principal effective stress (Barnett shale, 0.09 m^3/s per fracture; 3 hrs) (Rawal & Ghassemi, 2011).

Fracture Mapping Results
DPI-2485-21
3. Discussion

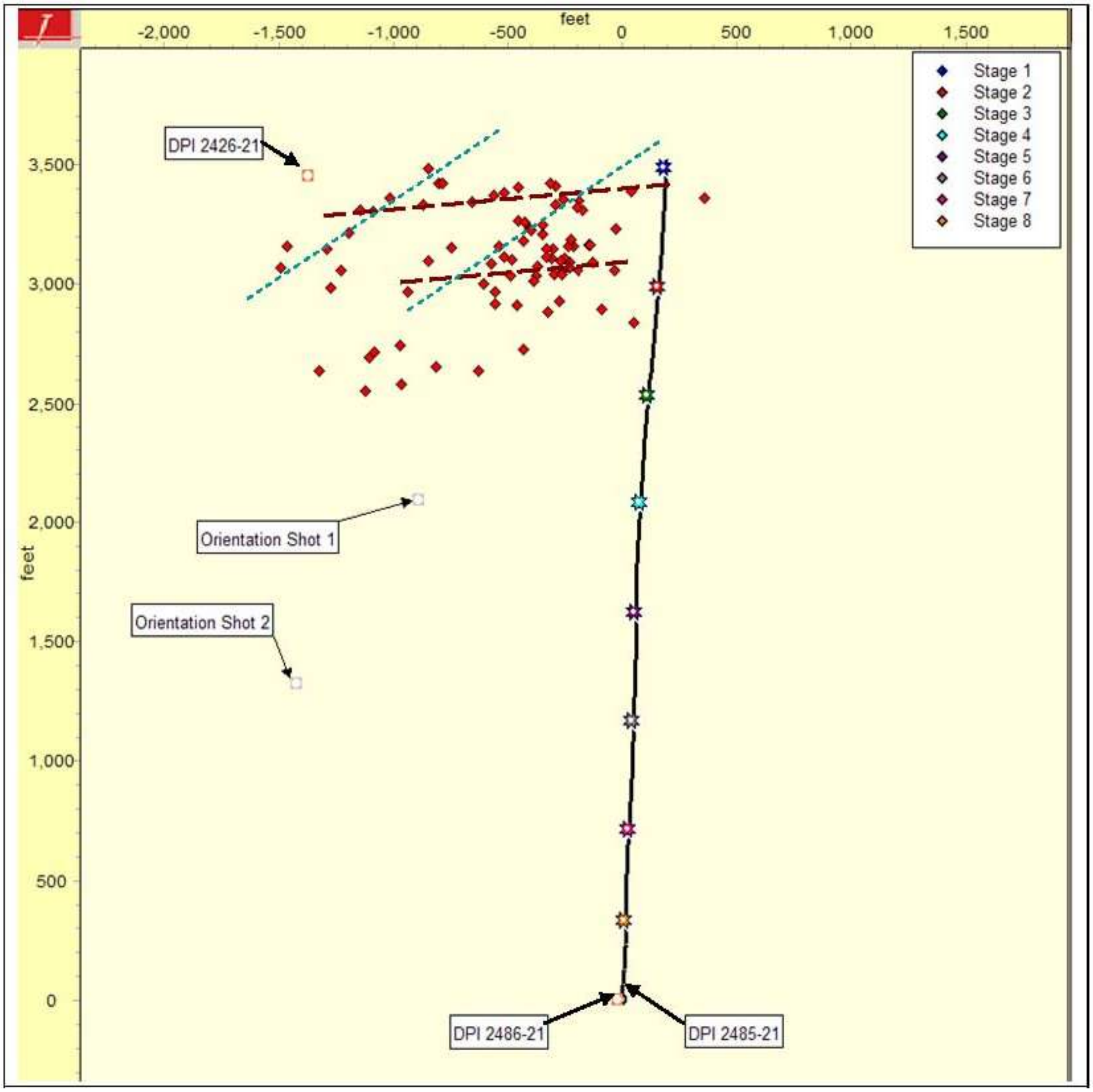

Figure 8. Microseismic map shows network growth and the potential stimulated volume in shale (GTI-NAS-Project).

Chipperfield, S.T., Wong, J.R., Warner, D.S. et al. (2007). Shear dilation diagnostics: A new approach for evaluating tight gas stimulation treatments. SPE Hydraulic Fracturing Technology Conference, College Station, Texas USA. SPE 106.

Cipolla, C.L., Warpinski, N.R., Mayerhofer, M.J. et al. (2008). The relationship between fracture complexity, reservoir properties, and fracture treatment design. SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA. SPE 115.

Cramer, D.D. (2008). Stimulating unconventional reservoirs: lessons learned, successful practices, areas for improvement. SPE Unconventional Reservoirs Conference, Keystone, CO. SPE# 114172.

Ge, J., Ghassemi, A. (2011). Permeability enhancement in shale gas reservoirs after stimulation by hydraulic fracturing. Proc. 45th U.S. Rock Mechanics Symposium, June 26 –29, San Francisco.

Ge, J., Ghassemi, A. (2008). Analysis of failure potential around a hydraulic fracture in jointed rock. Proc. 42nd U.S. Rock Mechanics Symposium, June 29 – July 2, San Francisco.

Koshelev, V. & Ghassemi, A. (2003). Numerical modeling of stress distribution and crack trajectory near a fault or a natural fracture. Soil-Rock America Symp., Boston.

Nelson, E.J., et al. (2007). Using geological information to fracture optimize stimulation practices in the Cooper Basin, Australia. Petroleum Geoscience, (13), 3–16.

Nygren, A. and Ghassemi, A. (2005). Influence of cold water injection on critically stressed fractures in Coso Geothermal Field, CA. 40th U.S. Rock Mech. Symp., Anchorage, Alaska, June 25-29.

Palmer, I. D., Moschovidis, Z. A., and Cameron, J. R. (2005). Coal failure and consequences for coalbed methane wells. SPE 96872, ATCE, Dallas, 9-12 Oct 2005.

Peasron, C. (1981). The relationship between micro-seismicity and high pore pressure during hydraulic stimulation experiments in low permeability rocks. J. Geophy. Res., 86, B9, 7855.

Rawal, C., Ghassemi, A. (2011). Poroelastic rock failure analysis around multiple hydraulic fractures using a BEM/FEM model. Proc. 45th U.S. Rock Mechanics Symposium, June 29 – 29, San Francisco.

Rutledge, J., and Philips, W. (2003). Hydraulic stimulation of natural fractures as revealed by induced microearthquakes, Carthage Cotton Valley gas field, east Texas, Geophysics, 68(2), 441–452.

Warpinski, N.R., Wolhart, S.L., and Wright, C.A. (2001). Analysis and prediction of microseismicity induced by hydraulic fracturing. SPE 71649.

Fracture Growth in Layered and Discontinuous Media

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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.

Fracture behavior in the vicinity of layered and discontinuous rock masses has been the subject of numerous papers. The major factors that have been investigated are stress variations, modulus variations, fracture toughness variations, interface properties, high permeability zones, combined layering and interfacial behavior, and fluid pressure gradient changes. Of these, stress changes are clearly the largest influence on fracture growth across layers and stress bias is clearly the largest factor in the development of complexity in discontinuous media. Nevertheless, many of the other factors play a significant role in cases where the stress contrasts are not large and in the general development of complex fractures.

In Situ Stress

The in situ stress contrasts clearly have the most significant effect on fracture height growth. The importance of stress was recognized early on (e.g., Perkins and Kern 1961) and has been extensively studied in modeling (e.g., Simonson et al. 1978, Voegele et al. 1983, Palmer and Luiskutty 1985), mineback tests (Warpinski et al. 1982), and numerous laboratory experiments. Fracture height growth can be easily restricted if the layers above and below have higher stress than the reservoir rock, and this is a common occurrence in sedimentary basins.

An equilibrium (static) analysis of the Linear Elastic Fracture Mechanics behavior of a fracture surrounded by rocks with higher stress was first given by Simonson et al. (1978) for a symmetric case (stresses above and below are equal). Given the geometry in Figure 9, an equation can be written as

$$\sigma_2 - P = \frac{2}{\pi}[\sigma_2 - \sigma_1]\sin^{-1}\left(\frac{h}{H}\right) - \frac{K_{Ic}}{\sqrt{\pi H/2}}$$

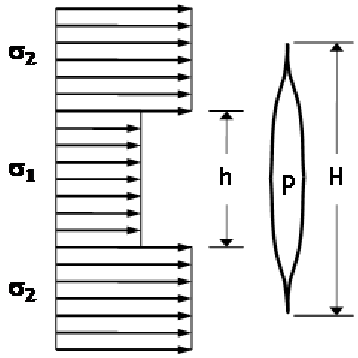

Figure 9. Geometry for stress effects.

where P is the net pressure in the fracture, σ_1 is the stress in the pay zone, σ_2 is the stress in the bounding layers, h is the thickness of the pay zone, H is the total fracture height, and K_{Ic} is the fracture toughness of the bounding layers. In this equation, the first term on the right is due to the stress contrasts, while the second term is due to fracture toughness. For standard laboratory values of fracture toughness, the term on the left is generally small (unless the fracture is very small) and the height of the fracture is mostly dependent on the stress contrasts. In general, this equation is conservative since there are other dynamic factors that affect the amount of height growth that will occur. Similar equations can be developed for non-symmetric stress contrasts, but more complete dynamic analyses are usually performed in fracture models.

Layer Material Property Differences

While Simonson et al. (1978) show that a material property interface in an ideal situation could blunt fracture growth, years of fracturing experience (Nolte and Smith 1979), fracture diagnostic monitoring (Warpinski et al. 1998, Wright et al. 1999), mineback testing (Warpinski et al. 1982), and other research (Smith et al. 1982; Teufel and Clark 1984; Palmer and Sparks 1990) have shown that this is not the case. Figure 10 shows an example of a dyed water fracture that has propagated through an interface from a low modulus material into a high modulus material (Warpinski et al. 1982). A more complete discussion of the role of the interface has been given by Cleary (1978), where the complexities of the interface, the micromechanics of the fracturing process, the potential for blunting and twisting (no longer only mode I fracture growth), and various other factors make the problem difficult to analyze with standard analysis tools. What is clear from these studies is that crossing interfaces requires additional energy and can hinder vertical growth.

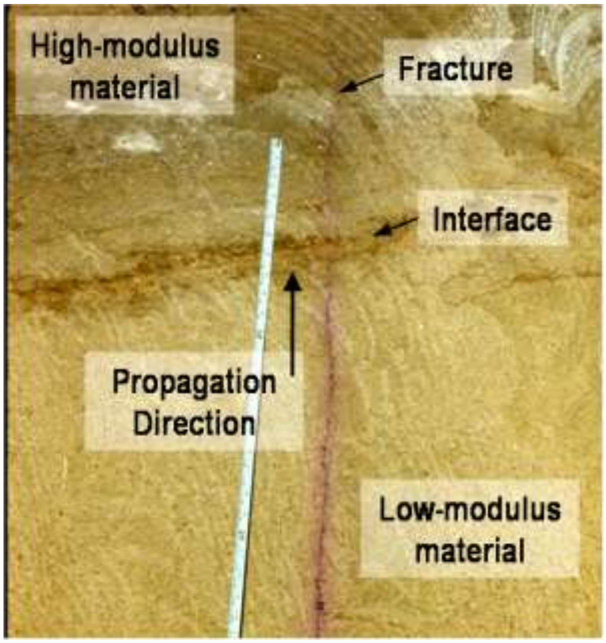

Figure 10. Mineback photo of fracture propagating across interface.

Modulus contrasts clearly have an effect on the width of the fracture and can be expected to enhance or restrict fluid flow appropriately. Cleary (1980) provided a time-constant analysis of the effect of modulus, while Van Eekelen (1980) developed a relationship based on relative height changes in the layers, given by

$$L = \frac{H}{2}\left[1 + \frac{12G_2}{19G_1}\left\{\log\left(\frac{H}{h}\right) + \frac{1}{4}\left(3 + \frac{G_1}{G_2}\right)\left(\frac{H}{h} - 1\right)\right\}\right]^{1/2}.$$

As discussed by Van Eekelen (1980) and Smith et al. (2001), these effects are generally small and cannot be expected to provide significant containment of fractures. Gu and Siebrits (2008) also show that low modulus layers surrounding a higher modulus pay zone can be restrictive due to a lowered stress intensity factor, but this also depends on the relative fracture toughness of the different materials.

Fracture Toughness

Fracture toughness can have a very significant impact on fracture growth, and a large value of K_{Ic} can either induce a high pressure, restrict the height, or both. For a homogeneous formation, the stress intensity factor at the top of the fracture can be computed if the net stress distribution is known by

$$K_I = \frac{1}{\sqrt{\pi H/2}} \int_{-H/2}^{H/2} p(y) \sqrt{\frac{H/2+y}{H/2-y}} dy \ ,$$

where p(y) is the net stress distribution vertically. If the stress intensity factor exceeds the fracture toughness of the material, the fracture will propagate. Obviously, the situation becomes more complex (and not analytic) for layered materials with different elastic properties, but the equation above gives a rough estimate of the fracture stability.

Laboratory experiments have generally shown that fracture toughness varies over only a limited range (e.g., Hsiao and El Rabaa 1987), which suggests that fracture toughness effects will be rather limited. Figure 11 shows a compendium of fracture toughness measurements made at the DOE MWX experiment that shows the relatively small range for both reservoir and non-reservoir rocks. However, the scale dependence of fracture toughness (or potentially other types of tip effects) is not well understood for large scale fractures, so there may be potential for fracture containment due to this mechanism (Shlyapobersky et al 1998).

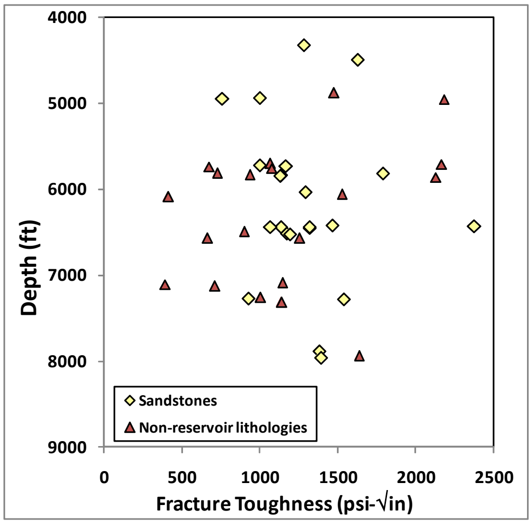

Figure 11. Fracture toughness data from MWX.

Interfaces

It is well known that weak interfaces can blunt fracture growth, and such a mechanism is often cited for the use of KGD (Khristianovich, Geertsma and De Klerk) models (Nierode 1985). Examples of blunting have been noted in mineback experiments (Warpinski et al 1982, Warpinski and Teufel 1987, Jeffrey et al. 1992, Zhang et al. 2007) and laboratory experiments (Anderson 1981, Teufel and Clark 1984). While it is generally expected that weak interfaces will be most important at shallow depths where friction due to the overburden stress is a minimum, other factors such as overpressuring or embedded particulates (equivalent to a fault gouge) can clearly minimize frictional effects even at great depths. Weak interfaces have the potential of totally stopping vertical fracture growth, initiating interface fractures, or causing offsets in the fracture. In addition to restricted growth effects, weak interfaces above and below the reservoir can decouple the fracture walls (Barree and Winterfeld 1998, Gu et al. 2008), resulting in poor coupling of the fracture pressure in the reservoir to the fracture outside of the weak interfaces. This reduced coupling would create narrower fractures in the layers across the interface and much wider fractures within the reservoir rock.

Many mechanism, such as those described above and others, can be bundled together to describe fracturing across a succession of interfaces. The possibility that such layered media could contain hydraulic fractures has been derived from fracture diagnostic information (Warpinski et al. 1998, Wright et al. 1999, Griffin et al. 1999). It is easy to conceive of multiple mechanisms serving to blunt, kink, offset, bifurcate, and restrict growth in various layers, much as a composite material hinders fracture growth across it. Various methods are now being used to model such behavior (Wright et al. 1999, Miskimmins and Barree 2003, Weijers et al. 2005).

Several of the mechanisms can be seen in Figure 12, which is a mineback photo of a fracture propagating upward across several interfaces. The left-hand side is the unaltered photograph, while the right-hand side has the fracture accentuated with a line drawn over it. There is kinking, offsetting, and bending occurring as the fracture makes its way through the layers. In other cases, additional fractures are initiated or some fractures are terminated.

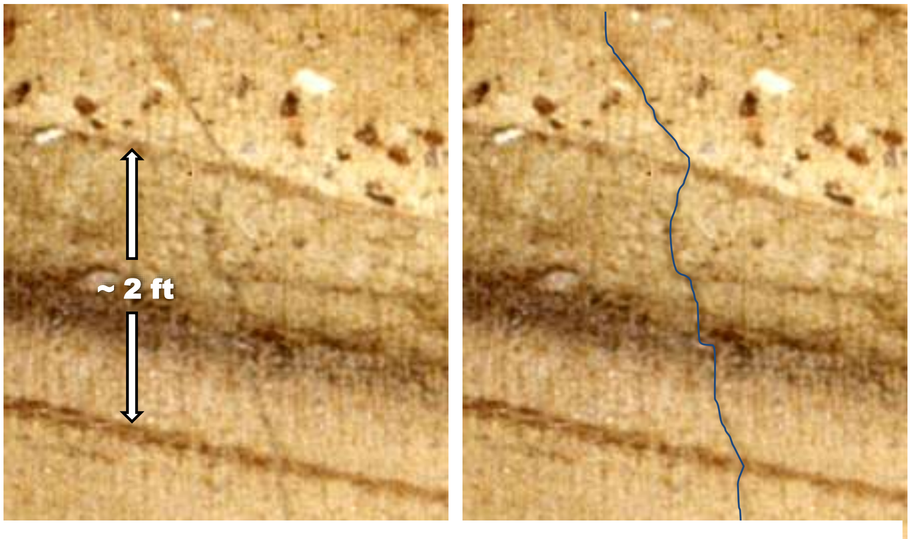

Figure 12. Photograph and line drawing of fracture behavior crossing interfaces.

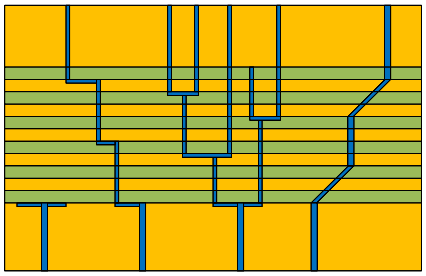

Figure 13. Schematic of types of observed fracture behavior crossing interfaces.

Figure 13 shows a schematic of several types of behavior that have been observed in minebacks or laboratory tests. The result of these behaviors could be any combination of complexity, restriction, or termination of the fracture as it propagates across the layered medium. Restrictions should be common if kinking or offsets occur, as the width in the kink or offset will necessarily be less than in the vertical part of the fracture due to both geometric and stress considerations.

Discontinuities

Any heterogeneities and discontinuities can modify the propagation behavior of fractures in a rock mass. Figure 14 shows an example of a fracture that is crossing unhealed natural fractures (Warpinski et al. 1981), which is also equivalent to the case of a weak interface with some permeability along the interface. This example shows offsets of the fractures at a location that is very close to the wellbore. Cement was used as the fracturing fluid for this test in order to preserve the width of the fracture. Such offsets would clearly restrict fracture growth because of the narrower width of the fracture in the offset and the possibility of sand bridging.

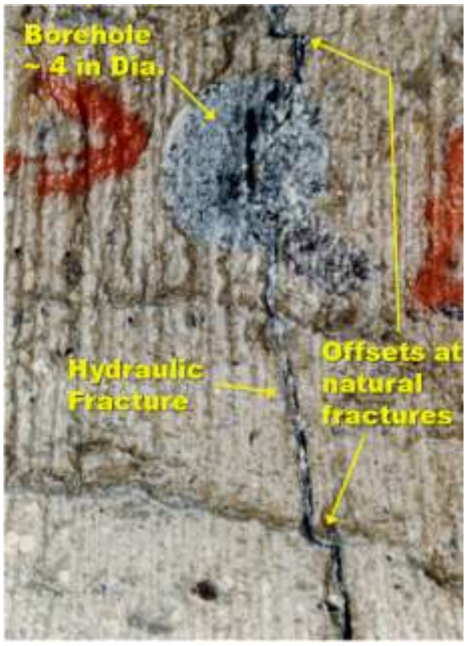

Figure 14. Fracture crossing discontinuities.

There have been many studies of the factors that influence fracture growth across discontinuities (e.g., Teufel 1979). These studies have demonstrated the effects of stress, angle of approach, and various material properties in blunting or offsetting fractures. These types of offsets are likely responsible for much of the complexity observed in hydraulic fractures in cores (Warpinski et al. 1993, Branagan et al 1996) and mineback tests. They prevent fractures from propagating as a single planar feature and instead force it into multiple, variably connected, intersecting components. This complexity makes it difficult for fractures to grow large distances as planar features.

High permeability interval

High permeability zones can also terminate vertical fracture growth by dehydrating the slurry through high leakoff. Coals are excellent examples of zones where fracture growth might be terminated by this mechanism.

Summary

Hydraulic fracture growth is influenced by a multiplicity of factors that are common in any reservoir. Of most importance is the in situ stress distribution, but interfaces, natural fractures, and other heterogeneities may also significantly affect behavior.

References

Anderson, G.D. 1981. Effects of Friction on Hydraulic Fracture Growth near Unbonded Interfaces in Rocks. SPEJ 21:21-29.

Baree, R.D. and Winterfeld, P.H. 1998. Effects of Shear Planes and Interfacial Slippage on Fracture Growth and Treating Pressures. Paper SPE 48926 presented at the SPE Annual Technical Conference and Exhibition. New Orleans, Louisiana, 27-30 September.

Branagan, P, Peterson, R, Warpinski, N, and Wright, T. 1996. Results of Multi-Site Project Experimentation in the B-Sand Interval: Fracture Diagnostics and Hydraulic Fracture Intersection. Gas Research Institute Report GRI-96/0225, Chicago, Illinois.

Cleary, M.P. 1978. Primary Factors Governing Hydraulic Fractures in Hetrogeneous Stratified Porous Formations. Paper 78-Pet-47 presented at the 1978 ASME ETC Conference. Houston, Texas, Nov 5-9.

Cleary, M.P. 1980. Analysis of Mechanisms and Procedures for Producing Favourable Shapes of Hydraulic Fractures. Paper SPE 9260 presented at the 55th SPE Annual Fall Technical Conference and Exhibition. Dallas, Texas. 21-24 September.

Griffin, L.G., Wright, C.A., Davis, E.J., Weijers, L., and Moschovidis, Z.A. 1999. Tiltmeter Mapping to Monitor Drill Cuttings Disposal. Proceedings of the 37th Annual Rock Mechanics Symposium. Vail, Colorado. 2:1033-1040, 6-9 June.

Gu, H. and Siebrits, E. 2008. Effect of Formation Modulus Contrast on Hydraulic Fracture Height Containment. *SPE Production and Operations* 23:2-170-176.

Gu, H., Siebrits, E. and Sabourov, A. 2008. Hydraulic-Fracture Modeling with Bedding Plane Interfacial Slip. Paper 2008 presented at the SPE Eastern Regional/AAPG Eastern Section Joint Meeting. Pittsburgh, Pennsylvania. 11-15 October.

Hsiao, C. and El Rabaa, A.W. 1987. Fracture Toughness Testing of Rock Cores. Presented at the 28th U.S. Symposium on Rock Mechanics. 141-148. Tucson, Arizona, 29 June – 1 July.

Jeffrey, R.G., Byrnes, R.P., Lynch, P.A. and Ling, D.J. 1992. An Analysis of Hydraulic Fracture and Mineback Data for a Treatment in the German Creek Coal Seam. Paper SPE 24362 presented at the SPE Rocky Mountain Regional Meeting. Casper, Wyoming, 18-21 May.

Miskimmins, J.L. and Barree, R.D. 2003. Modeling of Hydraulic Fracture Height Containment in Laminated Sand and Shale Sequences. Paper SPE 80935 presented at the SPE Production Operations Symposium, Oklahoma City, Oklahoma, 22-25 March.

Nierode, D.E. 1985. Comparison of Hydraulic Fracture Design Methods to Observed Field Results. *JPT* 37:1831-1839.

Nolte, K.G. and Smith, M.B. 1981. Interpretation of Fracturing Pressure. *JPT* 33:1767-1775.

Palmer, I.D. and Luiskutty, C.T. 1985. A Model of the Hydraulic Fracturing Process for Elongated Vertical Fractures and Comparisons of Results with Other Models. Paper SPE 13864 presented at the SPE/DOE Low Permeability Gas Reservoirs Symposium. Denver, Colorado, 19-22 May.

Palmer, I.D. and Sparks, D.P. 1991. Measurement of Induced Fractures by Downhole TV Camera in Black Warrior Basin Coalbeds. *JPT* 43:270-275; 326-328.

Perkins, T.K. and Kern, L.R. 1961. Widths of Hydraulic Fractures. *JPT* 13:937-949.

Shlyapobersky, J., Issa M.A., Issa, M.A., Islam, M.S., Dudley, J.W., Shulkin, Y. and Chudnovsky, A. 1998. Scale Effects on Fracture Growth Resistance in Poroelastic Media. Paper SPE

48929 presented at the SPE Annual Technical Conference and Exhibition. New Orleans, Louisiana, 27-30 September.

Simonson, E.R., Abou-Sayed, A.S., and Clifton, J.J. 1978. Containment of Massive Hydraulic Fractures. *SPEJ* 18:27-32.

Smith, M.B., Rosenberg, R.J. and Bowen, J.F. 1982. Fracture Width – Design vs. Measurement. Paper SPE 10965 presented at the SPE Annual Technical Conference and Exhibition. New Orleans, Louisiana, 26-29 September.

Smith, M.B., Bale, A.B., Britt, L.K., Klein, H.H., Siebrits, E., and Dang, X. 2001. Layered Modulus Effects on Fracture Propagation, Proppant Placement, and Fracture Modeling. Paper SPE 71654 presented a the SPE Annual Technical Conference and Exhibition. New Orleans, Louisiana, 30 September – 3 October.

Teufel, L.W. 1979. An Experimental Study of Hydraulic Fracture Propagation in Layered Rock. Phd Dissertation. Texas A&M University. College Station, Texas.

Teufel, L.W. and Clark, J.A. 1984. Hydraulic Fracture Propagation in Layered Rock: Experimental Studies of Fracture Containment. *SPEJ* 24:19-32.

Van Eekelen, H.A. 1982. Hydraulic Fracture Geometry: Fracture Containment in Layered Formations. *SPEJ* 22: 341-349.

Voegele, M.D., Abou-Sayed, A.S. and Jones, A.H. 1983. Optimization of Stimulation Design through the Use of In-Situ Stress Determination. *JPT* 35:1071-1081.

Warpinski, N.R., Northrop, D.A., Schmidt, R.A., Vollendorf, W.C., and Finley, S.J. 1981. The Formation Interface Fracturing Experiment: An In Situ Investigation of Hydraulic Fracture Behavior Near a Material Property Interface. Sandia National Laboratories Report SAND81-0938. June 1981.

Warpinski, N.R., Fnley, S.J., Vollendorf, W.C., O’Brien, M., and Eshom, E. 1982. The Interface Test Series: An In Situ Study of Factors Affecting the Containment of Hydraulic Fractures. Sandia National Laboratories Report SAND81-2408. February 1982.

Warpinski, N.R., Schmidt, R.A., and Northrop, D.A. 1982. In Situ Stresses: The Predominant Influence on Hydraulic Fracture Containment. *JPT*. 34:653 – 664.

Warpinski, N.R. and Teufel, L.W. 1987. Influence of Geologic Discontinuities on Hydraulic Fracture Propagation. *JPT* 39-1: 209.

Warpinski, N.R., Lorenz, J.C., Branagan, P.T., Myal, F.R., and Gall, B.L. 1993. Examination of a Cored Hydraulic Fracture in a Deep Gas Well. *SPE Production & Facilities* 8-3:150.

Warpinski, N.R., Branagan, P.T., Peterson, R.E., and Wolhart, S.L. 1998 An Interpretation of M-Site Hydraulic Fracture Diagnostic Results. Paper SPE 39950 presented at the SPE Rocky Mountain Regional/Low Permeability Reservoirs Symposium, Denver Colorado, 5-8 April.

Weijers, L., Wright, C., Mayerhofer, M. and Cipolla, C. 2005. Developing Calibrated Fracture Growth Models for Various Formations and Regions across the United States. Paper SPE 96080 presented at the SPE Annual Technical Conference and Exhibition. Dallas, Texas, 9-12 October.

Wright, C.A., Weijers, L., Davis, E.J. and Mayerhofer, M. 1999. Understanding Hydraulic Fracture Growth: Tricky but Not Hopeless. Paper SPE 56724 presented at the SPE Annual Technical Conference and Exhibition. Houston, Texas, 3-6 October.

Zhang, X., Jeffrey, R.G., and Thiercelin, M. 2007. Effects of Frictional Geological Discontinuities on Hydraulic Fracture Propagation. Paper SPE 106111 presented at the SPE Hydraulic Fracturing Technology Conference. College Station, Texas. 29-31 January.

Flow of Gas and Water in Hydraulically Fractured Shale Gas Reservoirs

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Underground fluid flow is primarily controlled by two physical factors: hydraulic conduits and pressure gradients. Both are required, or fluids will not move. In their natural state, shale formations are very impermeable, which means that there are virtually no natural hydraulic conduits in the rock. Because of this, shale has often acted as a cap rock and effectively limited and/or prevented fluids from escaping or migrating into other geologic formations over millions of years (i.e., geologic time).

The flow capacity of the rock can be quantified by permeability. The permeability of the shale matrix typically ranges from tens of nanodarcy to hundreds of nanodarcy (1 nanodarcy equals 10^{-6} microdarcy or 10^{-9} darcy). The shale matrix has such ultra-low permeability because of its very small pore size, which typically is on the order of tens of nanometer. Although natural fractures may exist in shale formations, most of them are filled with minerals in their in-situ conditions.

Because shale is so impermeable in its natural state, technologies such as horizontal drilling and hydraulic fracturing are necessary to enable economical production of gas from these formations. The process of hydraulic fracturing involves creating man-made fractures or fracture networks (i.e., hydraulic conduits) by pumping water and proppants (typically sand) at high rates down the wellbore. By placing proppant into the conduits, they can be held open over time so gas can be effectively produced from the formation. By drilling horizontal wells, multiple hydraulic fractures can be created in a single wellbore, which significantly increases the ability of gas and water to flow out of the shale.

The horizontal and vertical extent of hydraulically induced fractures are typically limited, being confined by such factors as in-situ stress differences, formation leak-off and the relative properties of the target shale formation and surrounding geological strata. When in-situ stress contrasts are high, propagation of the hydraulic fracture is prevented because the stress contrasts serve as a barrier to fracture growth. Even in the absence of stress barriers, formation leak-off will always arrest the fracture height growth, meaning the injected fracturing fluid will be absorbed into the strata with enough porosity and permeability, therefore stopping fracture extension. Typically, hydraulic fractures grow on the order of only a few hundred feet vertically and hundreds of feet horizontally. To evaluate fracture geometry, there is a service industry that collects data during fracture treatments. In addition, numerous hydraulic fracture models have been developed to model fracture geometry. Considering that gas shales are often buried several thousand feet (sometimes more than ten thousand feet) below the surface of the earth, even large hydraulic fractures would still be confined many thousands of feet below the earth's surface.

Not all induced fractures will result in conductive pathways between the formation and the wellbore. After a fracturing treatment, the in-situ stress of the formation will close some of the induced fractures, typically those without proppant. Those unpropped fractures may lose their width, and become disconnected with the propped fractures. Therefore, the effective post-treatment propped fracture lengths and heights are always less than the induced lengths and heights achieved during treatment.

During production, the horizontal wellbore serves as a pressure sink (i.e., the pressure is much lower in the wellbore than in the surrounding shale formation), causing the gas to flow from the shale formation (high pressure environment) into the fractures, and through the fractures to the wellbore (low pressure environment). Since the shale matrix has ultra-low permeability, flow of gas in the unstimulated shale zone is minimal. Virtually no conduits allow water to flow through the unstimulated zone. Consequently, the gas/water movement is within the stimulated zone and towards the wellbore since the pressure gradient is in that direction. Migration of gas and water away from the stimulated zone is precluded.

Wells may be shut-in periodically. During the shut-in, pressure will build up within the stimulated shale zone. However, the pressure within the stimulated zone will be always less than the pressure outside the stimulated zone. A minimum amount of gas will keep flowing from the unstimulated shale zone into the stimulated shale zone. Again, migration of gas and water away from the stimulated zone is precluded.

Fracturing treatment in shale gas reservoirs typically uses water as the fracture fluid to propagate the fractures and transport sands. A portion of this frac water will be produced up the wellbore, which is isolated from the surrounding rock by the steel casing strings and cement, back to surface during production. It is often referred to as flowback water. The flow of water mainly exists within the fractures. Both water and gas flows together as multiphase flow within the fractures toward the wellbore. The flow capacities of water and gas depend on the relative permeabilities of each phase, which are functions of the water saturation in the fractures and matrix. Initial water rates are high, but they decline quickly as water saturation is reduced. The water production typically tends to stabilize at low rates after a short period of production. Over many years, about 20-40 % of the injected water will be produced back.

Since frac water is in contact with the shale matrix through fracture surfaces, water-phase imbibition also plays an important role in water flow. The imbibition effect is caused by the capillary pressure between the gas and water phases. The lower the reservoir permeability, the higher the capillary pressure will be. In low-permeability reservoirs such as shales, the capillary pressure can be thousands of psi. Once water is imbibed into the micropores of the shale matrix, it will quickly become immobile and therefore be retained in the matrix permanently.

As discussed before, some induced but unpropped fractures may lose their width and become disconnected from the propped fractures during the initial flowback period and long-term. In this case, the water filling these fractures will become trapped and remain immobile during production operations.

Because integrated reservoir models consider reservoir geology, the physics of fluid flow in porous media, the nature of the fracturing treatment, production conditions, etc., they can be used to effectively quantify the flow of fluids in subsurface formations. These models show that the injected and produced fluids are contained within the shale formation or in the formations immediately adjacent to them. These formations are thousands of feet below the surface.

Role of Induced and Natural Imbibition in Frac Fluid Transport and Fate in Gas Shales

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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

Hydraulic fracture modeling and fracture surface area calculations determined from production data analysis and reservoir numerical flow simulation support estimates of created hydraulic fracture (frac) surface areas of 24-60 MM sq ft for representative hydraulic fracture treatment designs. Approximately 30±10% of the frac fluids are recovered and the remaining 70±10% leaks off into the fracture face resulting in elevated frac fluid saturations within 2 – 6 inches of the fracture face. Although natural imbibitions capillary forces can generally be ignored in conventional reservoirs, in gas shales these forces can range from 200-2,000 psi. Drainage and imbibition capillary pressure analysis indicate that the elevated near frac-face saturations are not in equilibrium and capillary forces act to naturally imbibe the fluid back into the reservoir away from the frac face. This process occurs over weeks to months and can be slowed or halted by gas pressure decrease associated with well production. The frac fluids imbibed into the formation are effectively locked in place with the native brine by capillary forces both during the life of the well production and for geologic periods of time after reservoir depletion.

Introduction

Gas shale reservoirs characteristically exhibit low porosity (ϕ = 3-10%), low *in situ* specific permeability (k_i = 50–2,000 nD), low water saturation (Sw = 10-50%) and thickness of H = 50-400 ft over large regions. To achieve economic gas production rates for these matrix properties, flow to the wellbore is enhanced using multi-stage hydraulic fracture stimulation. Present optimum well designs vary among operators and with reservoir properties but can be broadly characterized as comprising horizontal wells with 4,500±1,000 ft of lateral length and with up to 60±20 fracture clusters along the wellbore. In a “large” hydraulic fracture stimulation (frac) as much as 5±2 million pounds of proppant may be used, transported by 120,000±20,000 bbls of frac fluid, where 30±10% of the frac fluid is typically recovered during production. Understanding the transport and fate of these frac fluids is important for environmental and optimum well stimulation design reasons.

Frac fluid flows into and out of the rock formation through the frac face can be characterized as comprising three flow periods: 1) an induced imbibition period during and immediately following the frac treatment and dominated by pressure-induced leakoff, 2) a natural imbibition period when the well is shut-in following stimulation and capillary forces influence frac fluid redistribution, and 3) flow out of the formation resulting from pressure drawdown in the fracture and when capillary and viscous forces are potentially competing. Numerous studies have explored hydraulic fracture modeling, which implicitly involves transport or flow of frac fluids both in induced and natural fractures and into the formation through the created fracture face. Published studies have extensively explored issues involving leakoff of fluids during fracture creation and after pumping during fluid pressure decay. Foundational work by Nolte (e.g., 1979, 1986, 1993) explored the relationships describing fluid leakoff associated with initial spurt loss and subsequent filter-cake limited pressure-dependent leakoff. Additional work has explored and summarized previous work on such issues as fluid loss in natural fractures (Warpinski, 1990), effective fracture length (Barree et al, 2003; Cipolla et al, 2008), leakoff and permeability (Meyerhofer and Economides, 1997), and fracture modeling (Barree, 1983; Meyer et al , 1990; Cipolla et al, 2011).

Fluid flow is influenced by two forces; 1) viscous force associated with induced pressure differences resulting from pumping or well production, and 2) capillary force associated with interfacial tension among fluids and the rock pore surfaces. Capillary forces can generally be ignored in reservoirs with $k > 0.01$ mD because reservoir methane-brine capillary forces are generally only 1-100 psi and these forces are small compared to viscous forces associated with flowing pressure drops. In contrast, very low permeability reservoir ($0.000001 \text{ mD} < k < 0.001$ mD) threshold entry methane-brine capillary pressures ($P_{te} = Pc_{,Sw=1}$) range from approximately P_{te} = 200-2,000 psi and increase with decreasing water saturation. At these levels the influence of capillary pressure on fluid movement and distribution cannot be ignored and can play a significant role in the transport and fate of frac fluids. The influence of high water saturations near the frac face were investigated by Holditch (1979) and more recently by Cheng (2010). Cheng's analysis illustrated the significant role that natural imbibition can play in fluid distribution but did not fully explore properties at high capillary pressures.

This brief abstract will utilize the above work and laboratory data to broadly analyze the transport and fate of frac fluids in representative hydraulic fractures and illustrate that the low fluid recoveries from frac treatments are consistent with the fracture and rock properties and that once frac fluids are imbibed into the reservoir capillary forces act to imbibe them away from the frac face and hold them in place with capillary pressure forces of hundreds to thousands of pounds per square inch (psi). The initial high water saturations result in near-frac face blockage and reduced gas flow rates but natural imbibition results in a decrease in Sw over time and "cleanup" of the frac face and consequent increase in gas flow rates. The cleanup period is influenced by such variables as the volume of water introduced, the permeability and effective water permeability of the reservoir, whether the well is flowing or shut-in, the near-frac face pressure, and the specific capillary pressure properties of the reservoir rocks and can occur over periods of weeks to months.

Frac Fluid Composition

Many variables are involved in fracture fluid chemistry design. Prior to pumping any fluid systems, fluid-rock core measurements are used to determine the minimum fluid additives necessary in each play to prevent formation damage from drilling or fracture fluids. The majority of the shale plays in North America are treated with a large percentage of "slickwater."

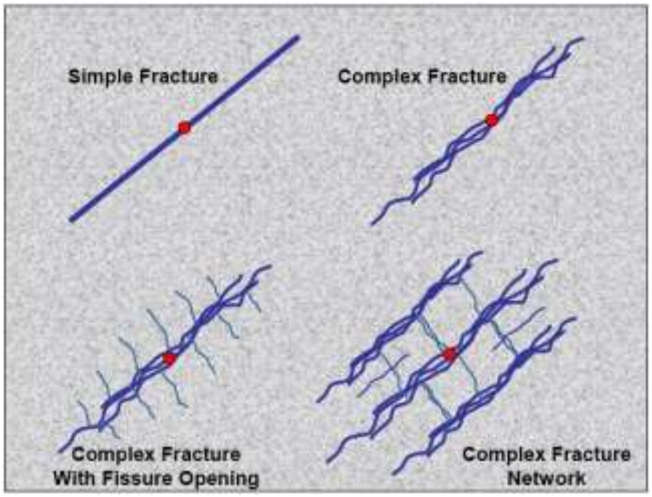
Slickwater is predominantly fresh water with four to eleven chemical additives at a combined concentration of 1,000-6,000 parts per million by volume (ppmv) or 0.1-0.6 percent by volume of the liquid pumped. Light gels are often used at the end of a stage to transport higher sand concentrations. Chesapeake Energy's Green Frac™ program was initiated in 2009 to eliminate additives not critical to successful completion and to replace necessary additives with more environmentally benign chemicals.

Hydraulic Fracture Architecture and Induced Frac Fluid Imbibition

Numerous models exist for hydraulic fracture architectures and can broadly be classified as ranging from simple planar fractures to complex fracture networks (Figure 15). The nature of the fracture architecture that develops at any given location is a function of numerous variables including but not limited to: magnitude of direction of horizontal stress field; vertical stress profile; regional and local principal stress anisotropy; presence and orientation of one or more natural fracture sets; rock elastic properties; fracture toughness; vertical and lateral heterogeneity of rock properties; frac fluid properties; frac pump rates, pressures, and times between injection period; proximity to frac barriers, nearby wells, and adjacent well histories; and reservoir rock properties including porosity, permeability, relative permeabilities, initial water saturations, capillary pressure properties, pore throat size distribution, etc.

Based on the influence and interaction of these variables, fracture architecture will vary among different shale plays, within a shale play, along a given horizontal well, and potentially even within a given frac stage. Microseismic data can be interpreted to support the predominance of a given frac architecture within given areas. For the range of frac architectures that can occur, frac modeling indicates that the proppant is deposited in a region representing only 20-50% of the total fracture system (Figure 16).

Figure 15. Example of range of fracture architectures for a single initiation site. (modified from Fisher et al, 2002).



Total effective surface area can be estimated using frac modeling, pressure transient analysis (PTA), production data analysis (PDA), and numerical flow simulation (NFS). These methods provide non-unique solutions that model observed pressure and flow behavior through time. Production decline analysis provides a solution for A√k (Area * $k^{0.5}$). Knowing *in situ* reservoir effective gas matrix permeability from core analysis, it is possible to define the total effective fracture surface area from the early production and pressure data that is characterized by transient unsteady-state flow (e.g., Miller et al, 2010). These methods indicate that "large" hydraulic fracture stimulation treatments utilizing approximately 120,000 bbls of fluid and 5 million pounds of proppant create effective fractures with surface

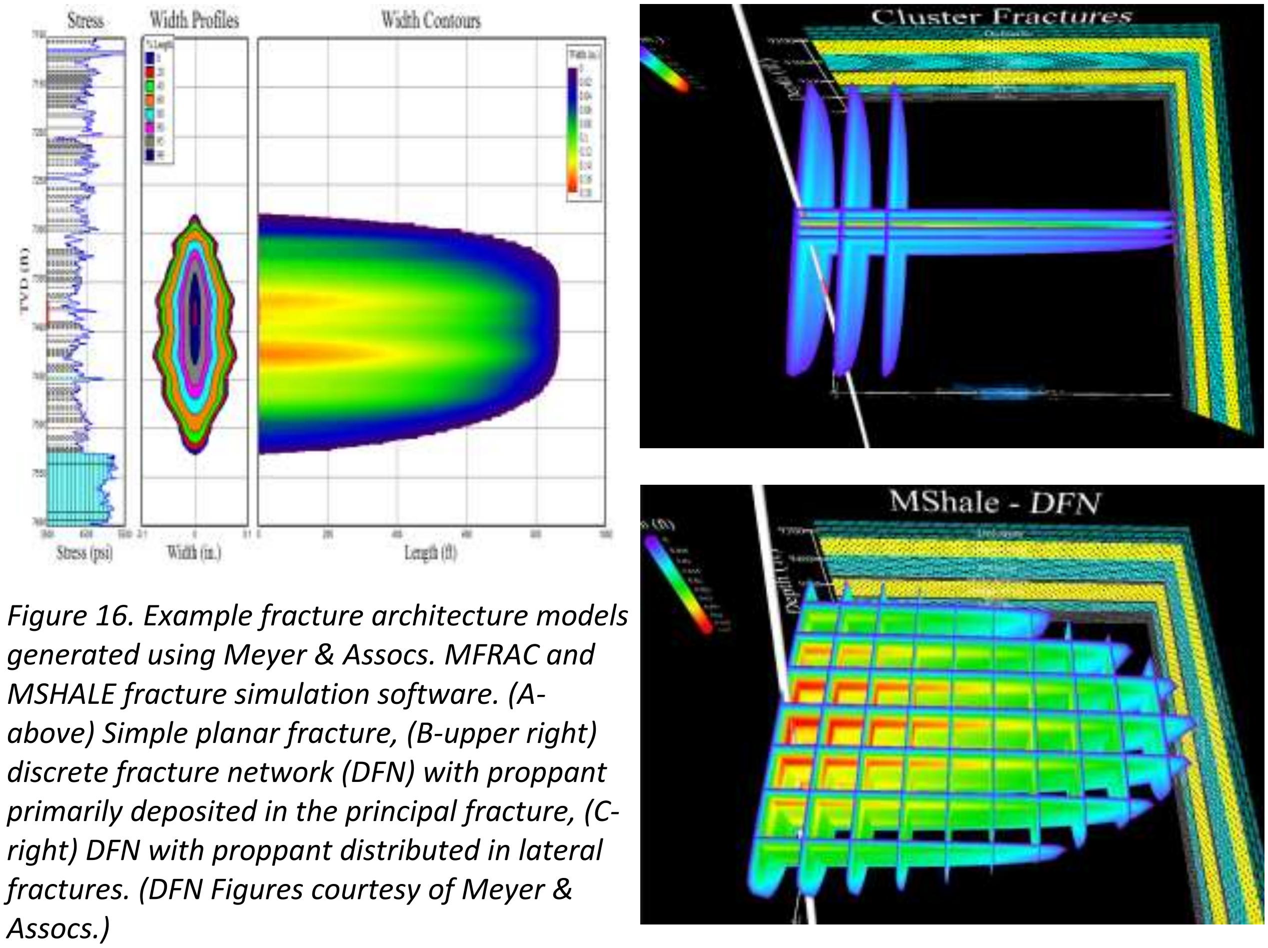


Figure 16. Example fracture architecture models generated using Meyer & Assocs. MFRAC and MSHALE fracture simulation software. (A-above) Simple planar fracture, (B-upper right) discrete fracture network (DFN) with proppant primarily deposited in the principal fracture, (C-right) DFN with proppant distributed in lateral fractures. (DFN Figures courtesy of Meyer & Assocs.)

areas of approximately 12 MM sq ft ($12 * 10^6$ sq ft). Assuming the effective fracture surface area is 20-50% of the total, the total fracture surface area created is approximately 24-60 MM sq ft. This range in values is consistent with the total surface area estimated for either a simple planar fracture, compared to the high proppant concentration area (Figure 16), or for a central principal fracture or fracture set surrounded by unpropped or stranded lateral complex fractures (Figure 16). Generally, limited by material balance constraints and the PDA-defined surface area, a simple planar fracture potentially exhibits greater height or more effective half-length than the DFN architectures.

Although the three fracture models shown in Figure 16 differ in architecture, PDA and numerical flow simulation show that for the same effective fracture surface area, the initial transient unsteady-state flow is identical and that differences in production do not occur until inter-frac interference begins. This issue is highly relevant to optimum gas well production. However, for frac fluid transport, the surface area created by the fracing process, and the surface area into which frac fluids are injected, is approximately or can be exactly the same for all three architectures. Differences in fracture architecture do not necessarily significantly change the total surface area into which frac fluids flow.

Fracture modeling shown in Figure 16 provides the basis for defining the distribution of frac fluid in the near-frac face region for all fractures shown. Volumes of frac fluid induced to imbibe into the formation are defined by various forms of the leakoff equation that describes initial spurt loss (i.e., the initial loss of fluid before a filter cake is formed) followed by filter-cake controlled leakoff. In it simplest 1D form (Carter, 1957), the total fluid leakoff rate can be characterized by:

$$q(t) = 4 \int_0^{A(t)} C/(t-t_o)^{0.5}\, dA \qquad [1]$$

where q(t) is the fluid loss rate at time t, A(t) is the fracture area of one face, C is the total leakoff coefficient (including the initial spurt loss coefficient), t_o is the time of fracture area creation.

Although injected volumes are greater near the fracture initiation location due to longer times of injection, and are greater in higher permeability rocks, the volume of frac fluid injected at any given point on the frac face can be very approximately estimated assuming the total volume injected is uniformly distributed over the frac face surface area. For 120,000 bbls (670,000 ft^3) of frac fluid pumped, assuming this is uniformly injected into 24-60 MM sq ft, then the depth of penetration (D_{ffp}) of a 100% saturated interval, in a rock with $\phi = 0.06$ is $D_{ffp} \simeq$ 2-6 inches.

Typically, following a large fracture stimulation treatment a well will be produced to recover as much frac fluid as possible and then the well will be shut in for different time periods depending on operator practices, surface facilities construction or hookup, or pipeline scheduling. This initial production removes most of the frac fluid in the effective propped fracture and the shut-in period initiates the time of natural imbibition. Whether the well is shut-in or begins production, following induced imbibition the frac fluids in the near-frac region are influenced by natural imbibition resulting from capillary pressure forces.

Natural Imbibition

Elevated frac water saturations in the near frac-face region are not in capillary pressure equilibrium. Air-mercury capillary pressure curves (converted to equivalent reservoir-condition methane brine pressures), generally representing the bounding range of those observed for gas shales with specific *in situ* Klinkenberg permeability ranging between 0.0002 mD > ki > 0.00005 mD, illustrate that threshold entry methane-brine capillary pressures ($P_{te} = Pc,_{Sw=1}$) range from approximately 2,000 psi > P_{te} > 250 psi and increase with decreasing water saturation (Figure 17). These threshold entry pressures are consistent with threshold entry pressure-permeability relationships exhibited by lithic low-permeability sandstones and siltstones (Figure 18). Because the drainage curves in Figure 17 were measured using air-mercury, they represent drainage conditions where all pore surfaces are wetted by the wetting phase. The capillary pressures required to achieve or maintain the brine saturations in the present-day reservoirs (0.2 < Sw < 0.5) do not exist in the reservoirs today. It can be hypothesized that the low reservoir water saturations were created by displacement of connate brine from the rock pore space during oil or gas generation when the formation rock was more porous, permeable and exhibited a lower capillary pressure. Additionally, the development of intra-kerogen porosity during catagenesis, which did not require displacement of brine, increased the total porosity and consequently decreased brine saturation because the brine saturation is referenced to the total pore volume. Water adsorption measurements indicate that kerogen surfaces exhibit mixed wettability and portions are both hydrophobic and hydrophilic. Under these conditions, the capillary pressure curves shown represent an end-member condition and methane-brine capillary pressure curves at reservoir conditions can exhibit lower slopes but still require similar threshold entry pressures because these are determined by the interparticle pore system of the water-wet mineral grains. An alternate model for capillary pressure-saturation conditions is that the reservoirs are presently undersaturated and are not in capillary equilibrium. For this nonequilibium condition, the reservoir would presently be working to naturally imbibe water from surrounding formations but may be limited by availability of water, extremely low water relative permeability, and potential partial influence of a mixed wettability condition.

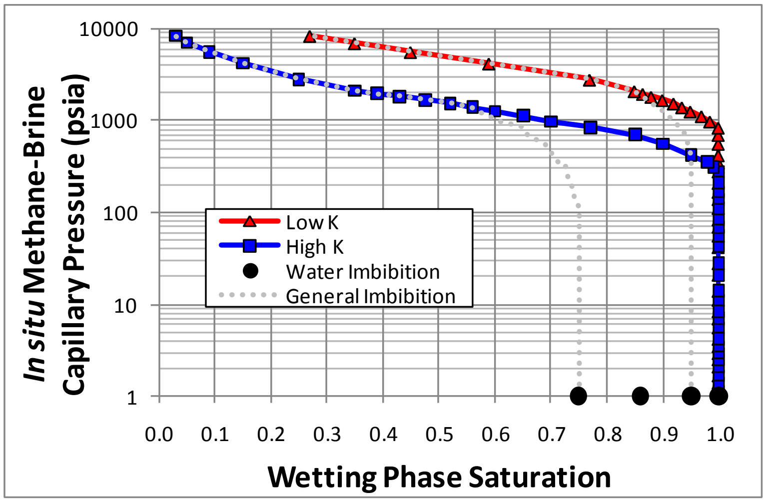


Figure 17. General representative drainage capillary pressure curves for gas shales of low k (0.00005 mD; red triangles) and high k (0.002 mD; blue squares) measured using air-Hg and converted to equivalent reservoir CH4-Brine pressures. Also shown are measured water saturations for natural imbibition of core from as-received saturation (black circles). Grey dashed curves represent generalized imbibition curves modeled from low-k sandstones.

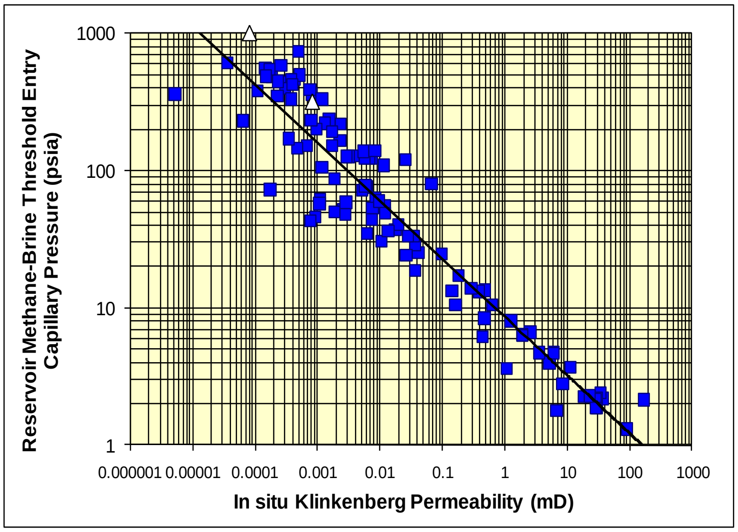


Figure 18. Threshold entry capillary pressures (P_{te}) versus specific in situ Klinkenberg permeability for lithic sandstones (blue squares) and representative gas shales (open triangles). P_{te} were measured using air-Hg and converted to equivalent reservoir CH_4- Brine pressures. Data for shale show continuity with trend for sandstones and siltstones. Relationship can be expressed: $P_{te} = 12.25\ k_i^{-0.424}$.

The wettability and imbibitions properties of gas shales can be tested by performing imbibition capillary pressure measurements on core in as-received condition. Typically wettability is measured using the Amott or USBM methods but these methods are experimentally difficult to perform on gas shales due to their low permeability and high capillary pressures. A simple limiting condition test is to perform a natural imbibition test which represents the condition of brine imbibition at low gas-brine capillary pressure and the resulting equilibrium brine saturations. For this test, if kerogen surfaces are hydrophobic then brine will only be imbibed into the water-wet portions of the mineral-lined pore pace and a trapped residual gas saturation, representing the gas in the kerogen pores, will result. If the kerogen pore surface is sufficiently hydrophilic then water is imbibed into the complete pore space and residual trapped gas saturations are low. The imbibition data shown in Figure 17 for the condition of 1 psi capillary pressure indicate that gas shales are capable of naturally imbibing water leaving very low residual gas saturations.

Research on the exact imbibition capillary pressure curve shape is on-going but curve shapes characteristic of low-permeability sandstones and siltstones (Byrnes and Cluff, 2009) are likely to be representative (Figure 17). These curves indicate that imbibition capillary pressure forces between the elevated water saturations near the frac face and the lower water saturations in the reservoir produce a capillary pressure drive mechanism of hundreds to thousands of psi. This force acts to naturally imbibe the frac water away from the frac face and into the formation where it is held in place by those same forces.

If the well is produced before the high water saturations are reduced near the frac face then the elevated near frac-face water saturations can be stabilized by the lower capillary pressures that can result from gas pressure depletion. When a well is fully pressure depleted it can be projected that the reservoir would naturally imbibe water from surrounding intervals. The time period over which this occurs would be a function of many variables including the formation effective water permeability, surrounding formation effective water permeabilities and capillary pressures in the formation and in the surrounding formations.

Discussion

Hydraulic fracture modeling and fracture surface area calculations determined from pressure decay analysis and reservoir numerical flow simulation support estimates of created hydraulic fracture surface areas of 24-60 MM sq ft. Approximately 30±10% of the frac fluids are recovered and the remaining 70±10% leaks off into the fracture face resulting in elevated frac fluid saturations within 2 – 6 inches of the frac face. Drainage and imbibitions capillary pressure analysis indicate that these saturations are not in equilibrium and capillary forces act to imbibe the fluid back into the reservoir away from the frac face over a period of weeks to months and can be slowed or halted by gas pressure decrease associated with well production. The frac fluids imbibed into the formation are effectively locked in place by capillary pressure forces of hundreds to thousands of pounds per square inch (psi) both during the life of the well production and for geologic periods of time after reservoir depletion. Further research is needed and is ongoing as to the exact shape of the imbibition capillary pressure curves and imbibition water relative permeability curves to fully quantify the imbibitions process and timing.

Selected References

Barree, R.D., Cox, S.A., Gilbert, J.V., and Dobson, M.: "Closing the Gap: Fracture Half Length from Design, Buildup, and Production Analysis," SPE 84491, *Proc.* 2003 SPE Annual Technical Conference and Exhibition, Denver, Colorado, 5-8 October.

Barree, R.D, 1983, “A Practical Numerical Simulator for Three Dimensional Fracture Propagation in Heterogeneous Media,” SPE 12273, presented at the 1983 SPE Symposium on Reservoir Simulation, San Francisco, CA, Nov. 15-18, 12 pgs.

Byrnes, A.P., and R.M. Cluff, 2009, “Analysis of Critical Permeablity, Capillary Pressure and Electrical Properties for Mesaverde Tight Gas Sandstones from Western U.S. Basins”, Final Report, U.S. Department of Energy contract #DE-FC26-05NT42660, 355 pgs.

Cipolla, C., X. Weng, M. Mack, U. Ganguly, H. Gu, O. Kresse, and C. Cohen, 2011, “Integrating Microseismic Mapping and Complex Fracture Modeling to Characterize Fracture Complexity,” SPE 140185-MS, SPE Hydraulic Fracturing Technology Conference, 24-26 January 2011, The Woodlands, Texas, USA, 22 pgs.

Fisher, M.K., Davidson, B.M., Goodwin, A.K., Fielder, E.O., Buckler, W.S., and N.P. Steinberger, 2002, “Integrating Fracture Mapping Technologies to Optimize Stimulations in the Barnett Shale,” SPE 77411-PA_P, presented at the 2002 SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, Sept 29-Oct 2, SPE Production and Facilities, May, p. 85-93, Mayerhofer, M.J., and M.J. Economides, 1997, “fracture-Injection-test Interpretation: Leak-Off vs. Permeability, SPE 28562, SPE Production and Facilities, Nov., p. 231-236.

Meyer, B.R., Cooper, G.D., and S.G. Nelson, 1990, “Real-Time 3-D Hydraulic Fracturing Simulation: Theory and Field Case Studies,” SPE 20658-MS, Proc. SPE Annual Technical Conference and Exhibition, 23-26 September 1990, New Orleans, Louisiana, p. 417-432.

Miller, M.A., Jenkins, C., and R. Rai, 2010, “Applying Innovative production Modeling techniques to Quantifying fracture Characteristics, Reservoir properties, and Well Performance in Shale Gas Reservoirs,” SPE 139097, presented at 2010 SPE Eastern Regional Meeting, Morgantown, West Virginia, USA, Oct 12-14, 12 pgs.

Nolte, K.G., 1986, “A General Analysis of Fracturing Pressure Decline With Application to Three Models,” SPE Formation Evaluation, Dec., p. 571-583.

Nolte, K.G., Mack, M.G., and Lie, W.L.: “A Systematic Method of Applying Fracturing Pressure Decline : Part I,” SPE 25845, Proc., SPE Rocky Mountain Regional/Low Permeability Reservoirs Symposium, Denver (1993), p. 31-50.

Warpinski, N., 1988, “Dual Leak-off Behavior in Hydraulic Fracturing of Tight, Lenticular Sands,” SPE 18259, SPE Production Engineering, p. 243-252.

Summary and Abstracts from Theme 3: Models to Predict Transport

Summary of Presentations on Theme 3: Models to Predict Transport

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.

Technical Presentations

This set of technical presentations addressed demonstration of models and determinations of model accuracy.

Andrew Havics, pH2 LLC, discussed modeling philosophies and applications. He described key aspects of modeling for risk assessment, fate and transport, and exposure, including assumptions, model selection, selection of input parameters, sensitivity, and validation. Mr. Havics also emphasized the importance of understanding the limitations of models, referring to the quote, “All models are wrong and some are useful.” He pointed out that models are most often tied to a region or area for which specific site data is required. He also noted that once a model is chosen it would create a framework from which parameter selection would then drive the model output.

Denise Tuck, Halliburton, provided information on modeling HF fluid fate and transport. She gave an overview of potential migration pathways, discussed key input parameters, and reviewed sources of data for these parameters, including HF fluid additive information from industry, information collected as part of spill response measures, and information collected during well installation and stimulation. Ms. Tuck recommended that EPA identify key marker compounds for fate and transport evaluation. She also recommended that EPA utilize all available data, particularly historic data on spills/releases, and assess human health risks associated with drinking water contamination. She emphasized that data collection at the time of installation is important. She also indicated possible confounding factors to consider, such as naturally migrating gases and abandoned wells.

Manu Sharma, Gradient, described an approach for modeling drinking water-related human health risks from HF fluid additives. He described toxicity and exposure implications for two surface release scenarios (acute and diffuse) and various migration pathways, using available information on HF fluid composition, flowback characteristics, and chemical toxicity. Mr. Sharma concluded that, based on the resulting dilution attenuation factors (DAFs), which are conservatively high, human health risks associated with HF additives and flowback are very small.

Summary of Discussions Following Theme 3: Models to Predict Transport Presentations

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Clarifying items from the technical presentations. A participant asked about the log-normal hydraulic conductivity plot in Mr. Havics' presentation (and included in the abstract) *Modeling Philosophies and Application*. This plot includes data from 28 sites in the Denver-Julesburg (DJ) and Piceance Basins. The results reflect fluid flow in the shallow subsurface. Mr. Havics added that the model was deterministic and that the results show concentrations at the leading edge of the plume. Another participant asked why Mr. Sharma's analysis did not include an impoundment scenario. The presenter indicated that while an impoundment scenario was not considered relevant to this particular investigation, impoundment results are available and have been filed with the New York Department of Environmental Conservation (NYDEC). A participant asked which metals were included in Mr. Sharma's analysis (described in the abstract *Modeling Drinking Water Related Human Health Risks from Hydraulic Fracturing Additives*). The list of metals is included on Slide 17 of Mr. Sharma's presentation; radium was not included because, in this initial data set from the Marcellus Shale, the radium detection frequency was very low. Participants noted that this low detection frequency may be related to limitations of the analytical methods used.

Stray gas migration. A participant asked about the industry's position on stray gas migration. The presenters indicated that, in their experience, most (though not all) gas migration incidents are related to natural stray gas migration and that they have not seen evidence that gas migration incidents are related to HF at depth. Another participant suggested that pumping ground water for refracturing water needs could lead to depressurization of the shallow aquifer, possibly resulting in methane outgassing or desorbing—in other words, an indirect source of gas migration. Other participants indicated that this could be possible, especially for pads with large numbers of wells.

Probabilistic modeling. A participant asked about the possibility of using simple deterministic models in a Monte Carlo approach to characterize uncertainty. The presenters responded that probabilistic approaches can be very useful. However, according to the presenters, challenges include identifying available data and selecting relevant underlying distributions.

Risk and DAFs. A participant asked about the basis for the vadose zone DAFs in Mr. Sharma's presentation. The presenter explained that the DAFs are the result of simple analytical solutions that consider various processes separately. The presenter indicated that a more complex numerical model would allow the user to vary the organic fraction and other parameters. The presenters noted that the DAFs are quite conservative and are comparable to previous EPA results. Another participant asked if surface water impacts were quantified. The lowest annual average mean daily discharge was calculated based on data from USGS gauging stations and records. This DAF was on the order of 60,000 on an annual average basis. A participant asked for a comparison of DAFs relative to underground storage tank (UST) petroleum releases. These two scenarios are quite different; the UST release is a non-aqueous phase liquid release, which is modeled as an infinite source. The DAFs are much smaller because the plume is constantly fed by concentrations that are at or near the solubility limit for the compound. The HF scenario, on the other hand, is a discrete spill in the dissolved phase. One presenter recommended a paper that provides information on maximum plume sizes for UST releases.

Sources of information. A participant noted that spill information and other types of state data are generally available online in well-by-well format and not compiled into databases. Other participants also indicated that data are often presented in well-by-well format, though Colorado does maintain a database and the state allows outside groups to perform some data mining. Participants noted that some states are more willing to provide data than others; in addition, states all collect different types of information. Another participant explained that data mining efforts can be extensive; even matching well names and numbers can be a challenge.

Mixing in bedrock. A participant asked about the DAF for mixing in bedrock (DAFBR), specifically whether the migration would be more similar to slug movement or diffusion and mixing. The presenter explained that this scenario is similar to slug movement, though it only involves gradual migration through pore spaces (not fractures), and that this type of migration would occur on the scale of thousands of years. According to the presenter, the DAF is based on mass loss over a distance in addition to dilution factors, and above a certain zone, migration is more convection based than diffusivity based. Also, the presenter noted that all of the fluids moving through this system are essentially exposed to activated carbon over large surface areas.

Octanol-water portioning coefficient (K_{ow}) analyses. A participant asked about the limitations of log K_{ow} analyses. A presenter noted that different lab tests can be run with different soil materials, but that K_{oc} analyses might be better, especially when clays are present. Another participant asked whether ionic and non-ionic surfactants should be considered separately when determining K_{ow}. While it would be possible to compile the data and separate the types of surfactants, a presenter noted that it is generally easier and more cost-effective to consider them together and select conservative values. A participant indicated that there is a lot of existing information on this topic, though it is generally available only through older or foreign journals.

Abstracts for Theme 3: Models to Predict Transport

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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Modeling Philosophies & Application

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Models are mere surrogate test fields for answering a question(s) or solving a problem expediently. They can be physical analogs or computer-based (Bear, 1972). Regardless, they all begin with a framework and a set of assumptions and limitations that go along with that framework. As a result, all models are wrong, but some are useful. Assumptions and limitations begin before selecting models but also arise from the selection or specialized application of a model. In terms of fracing and Risk Assessment (RA), there are several places where models and parameters must be chosen to complete hazard identification including chemical selection, fate & transport, exposure assessment, and risk determination aspects. Furthermore, to evaluate the model(s) chosen, and at a minimum qualitative assess or rank their values of data (response/output), an analysis of sensitivity and validity of the models should be completed. The level of complexity in the model, its use, and evaluation will be based on a number of factors derived for the purposes, objectives and goals of the model's use, many of which may be directed by policy.

Assumptions, leading to Limitations

Beginning with the assumptions, there are *de facto* policy aspects. The first is whether the parameters for the models will be either (a) discrete - single point values, or (b) stochastic - continuous function of the probability of a value. By choosing a discrete model, one must then decide what are the appropriate parameters, constraints, or additional assumptions. For instance, should one use a Maximum Likelihood Estimator (MLE), Mean, Median, Maximum, or some stochastic upper limit as the single point value input. Compiled or repeated use of maximums or extreme values in equations, such as hydrogeologic data or human exposure estimates, increase the likelihood of overestimating risk and in some cases the cost of subsequent actions; but this must be weighed against benefits of communicating the level of conservatism and the simplicity of using it as a screening tool. At some point, the weight of evidence surrounding the parameter such as distance to point of exposure (POE) must be assessed and a professional judgment made. In certain cases, regulatory restrictions will determine initial estimates. In the case of fracing, the source material composition by basin will influence the selection of a parameter, e.g., the chemicals of interest and their anticipated concentrations. Again, regulatory stipulations, such as pre-treatment can and will affect the selection of an *appropriate* input value. Furthermore the geology & hydrogeology of a region or local area can also influence chemical selection and fate and transport parameters, whether the selection of PAHs from coalbed deposits or hydraulic conductivity of a formation. Based on these variations, it is clear from the science that a single model of predicting fate, transport, or risk (or even one method of regulatory control) should not be applied to all locations.

Limitations

There are limitations in model selection, either constrained from the geology/hydrogeology, or constrained from the chemical side (metal versus organic), from the media of concern selected or from the pathways of anticipation. The limitation of sufficient, good quality or robust data will certainly restrict the use of stochastic estimates, but will also require a good analysis of sensitivity. The models themselves can (and usually are) created to permit a bias in the way of either over- or under-prediction of transport or exposure depending on how values are selected. Thus, a listing of all input values as well as the model structure should be available in any prediction using a model. There are limitations that are derived from precision of the model, and those that come from precision of the parameters. Calibrating the model to known field scenarios or lab-based experiments can provide an estimate of that precision. An analysis of sensitivity should follow to gage the relative importance of model variability versus model sensitivity.

Model Selection

By default, model selection restricts options. The more complex the model, generally the more costly, the more difficult to assess precision, the more difficult to understand the results and communicate them. One should consider the value of model refinement and model complexity relative to any gain in understanding the ultimate endpoint - risk. Regardless, in selecting a model, boundary conditions must be chosen and applied. In some models, these will drive fate and transport more than others. Because boundary conditions are likely to differ between geologic formation, application of one model from one formation to another should proceed cautiously.

Toxicology in the RA Model

In terms of RA, orders of magnitude are the norm. For toxicologists 3 times 3 is 10, and this level of rounding or semi- to multi-order-of-magnitude math pervades. First, one must recognize that parameters for doses that represent safe levels from toxic endpoints are selected with certain safety and uncertainty factors built in. For non-cancer agents these are typically 10- to 100-fold lower than No Observed Adverse Effect Levels (NOAELs) which are usually 10-50 times lower than Lowest Observed Adverse Effect Levels (LOAELs) [Dourson, 1996; Haber, 2002]. These are based on many studies indicating ratios of low or no response to a response between species and over differing times (days-months-years) and generally represent a conservative estimate times another conservative estimate. If less data is available or equivocal, a Benchmark Dose Level (BMDL) approach can be applied first; it brings a more stochastic approach to another deterministic aspect [EPA, 2000]. Examples are Barium (300-fold factor) [EPA, 2005] and Benzene (<10 factor) [ATSDR, 2007]. For cancer agents, risk is usually presumed to follow a straight from a projected 95% confidence limit to zero, thus is intentionally conservative in its application. The ultimate acceptable risk level is a policy decision but usually ranges in the 1 in 100,000 to 1 in 1,000,000 for residential settings and 1 in

10,000 to 1 in 100,000 for commercial or industrial settings [Kocher, 1991]. For comparison sake, one can consider two scenarios - a) struck by lightning and b) killed in a vehicle accident, both over a lifetime. The first, the lightning strike, is on the order of 6 in 1,000,000, the second (vehicular death) is about 1-2 in 100 people. Basic risk aside, there are assumptions or defaults that must be made with regard to multiple pathways from fate and transport, multiple routes of exposure, multiple toxic endpoints, and multiple mixtures. The most sensitive toxic endpoint, say liver damage, would generally be used. Generally, all doses are added for multiple routes of exposure or multiple pathways. As for mixtures of chemicals, this is a policy aspect and can range from no summing of risk, to summing only like toxic endpoints, to summing all aspects. Even after consideration of risk is made, there are potential limitations such as background amounts of an agents (e.g., arsenic in soils), and lack of tox data for additives or proprietary mixtures. The lack of data might be able to be handled using a control banding technique (Nelson, et al., 2011). Ultimately, the chemical selection and fate and transport aspects cannot be divorced from the models or the remainder of the RA, and science and policy must find consensus.

Fate & Transport

The selection or input of physical-chemical properties such as solubility, retardation, and Log Octanol Water partition coefficient (Log K_{ow}), can drive an equation in terms of fate and transport. There are, however, certain generalities as well as pitfalls in their selection and use. K_{ow} within a group of chemicals can be estimated within reason, but the value can easily affect transport estimates but will also affect dermal exposure. Barium Sulfate ($BaSO_4$) is generally considered to be relatively insoluble, but it can become more soluble, thus available for transport and human uptake, in the presence of high chlorides (Templeton, 1960). High chlorides were found present in our study and the dissolved Barium also tended to rise with increasing chlorides. Despite these effects, the effect of the hydrogeology in the Colorado pathway scenarios was not affected by this in terms of showing a significant risk.

Hydrogeologic parameters can vary widely from region to region and formation to formation. Thus, either a conservative selection or field data should be used. Because hydraulic conductivity (K_{ha}) can significantly influence transport models, a review of 28 sites in the DJ and Piceance were selected for detailed assessment of hydrogeological parameters including hydraulic conductivity. Each location was reviewed to establish local a geologic and hydrogeologic setting, and data from the vicinity on these aspects was then gathered. K_{ha} ranged from 0.01-0.0000001 cm/sec, with most values in the 0.001-0.0001 range, and the hydraulic conductivity appeared log normally distributed, which was expected. Using this data (and other representative data from the region) for Benzene with a retardation value of 1.5, the velocity of the benzene might be expected to be 27.5 ft/year at a K_{ha} of 1E-3 versus 0.028 ft/yr at a K_{ha} of 1E-6. One can see the necessity for gathering and entering relevant data into a model. For the modeling in the Colorado study, a K_{ha} of 3.63E-3 was ultimately used, driven by regulatory concerns [CDPHE, 2007].

Similarly for leaching from pits, the depth to groundwater (GW), can strongly affect transport. For the Colorado study, water well logs from <= 1.5 miles from each well pad in the DJ and

Piceance were pulled from state records and depth to GW evaluated. A total of 42 water wells provided sufficient data for analysis. The distribution appeared lognormal. Values ranged from 3 to 315 feet with the 5% quantile at 7.8 feet. Ultimately, 3.3, 9.8, and 20 feet (1, 3, 6.1 m) estimates were used in the modeling. The wells logs also were used to estimate point of exposure (POE) assuming the distance from the oil well directly to the water well. The results ranged from 72 to 2,420 meters (236-7,939 feet) with a 5% quantile at 135 m (442 feet). For the study, the minimum distance of 72 meters was selected by the risk assessor as a POE for the subsequent modeling; however, a 5% quantile value would likely be a reasonable maximum likelihood estimator (MLE). One should note that the 72 m is not likely as regulation restrictions have mandated setbacks to wells of 91-183 m (300-600 feet) with more stringent distances proposed [COGCC, 2008], again, a limitation imposed from outside the science. As a surrogate reference, one could consider plume data from 604 actual sites from other states for known significant pure product releases (only diluted fluids and solids are expected present in the O&G sites) reveal 75% are under 200 ft and most are shrinking [Newell, 1998].

Exposure

Several assumptions go into the exposure assessment process and a number of limitations also arise from this. The first is the selection of what is the exposed resource/population at risk, and it may be a natural resource such as water quality, a defined ecosystem to include fish or ducks, or human health. The toxicity of copper exposure to humans is less significant than to fish; the use of a typical surface water in Colorado isn't quite the recreation use that it might be for typical default scenario the EPA RAGS [EPA, 1989a, 1989b, 1991a, 1991b] or the ASTM RBCA [2002] and thus parameters of exposure might be overestimated. On the other hand, dust generation may be more than that usually considered by EPA or ASTM, as might be irrigation for grass. Furthermore, the determination of the need for a specific fate and transport model to assess these pathways will be controlled by their selection in the first place. Because the selection of completed pathways can be significant in any RA, there is a strong need for accurate transport models. The discrete selection of what is and what isn't complete must be considered in light of typical patterns of use, along with distances and relevant geophysical parameters. It is often driven by the media selected as "contaminated" or of concern. In the study in Colorado a number of media were selected and each relevant pathway was assessed with some form of fate and transport model. Media were:

Solids placed in Pits
Liquids in Subsurface Pits
Fracing Fluid placed in pits
Fracing Fluid placed in containers
Produced Water placed in containers
Produced Water placed in pits
Drilling fluids in drilling
Drilling fluids in pits

Thus, leaching from pits and migration to groundwater followed by transport to a residential well was modeled. On the other hand, because houses are not built on waste pits and distance to houses are so great, direct vapor intrusion was not considered a complete pathway. Because each completed pathway leads to exposure, the dose from each was assessed as additive. Thus the removal of a pathway also removes a potential dose. However, because multiple pathways and thus exposures and doses are modeled on the same population (e.g., person), an overestimate of real exposure is likely to arise. This is where stochastic modeling is very useful. The RA was completed using a variety of assumptions, details of the RA are provided in the QEPA report [QEPA, 2008].

Sensitivity

A sensitivity assessment should be performed on any model, even if crudely done, unless the RA itself evaluates multiple scenarios such that sensitivity to basic parameters is obvious. That said, the purpose of a sensitivity analysis is: (a) to quantify the uncertainty in the calibrated model caused by uncertainty in the estimates of parameters, stresses, and boundary conditions, and (b) to identify the model inputs that have the most influence on model calibration and predictions. ASTM has provided guidelines for assessing GW models in this fashion (ASTM, 2002). A direct sensitivity analysis involves checking the response after varying a particular parameter through a range of values, or alternatively, taking the derivative of the response function and plotting that. Because not all parameters are based on the same scale, a normalized sensitivity measure can be used to more equally evaluate different parameters (Norton, 2008). Even so, this author has found normalizing to the data range (R) or 5%-95% quantile range provides a better representative of response relative to the expected range of values for a parameter.

Validation

It is useful at some point to validate the prediction of a model. This can be accomplished by pre-planned injections, correlating actual (unintentional) releases, running parallel models, or evaluating health outcomes or using biomarkers in the case of RA. The first option has been accomplished for petroleum releases by intentionally injection product into outdoor locations and indoors in laboratory setting, but not at great depths. Correlations to actual field data have been limited or proprietary in nature. Parallel models are run in select situations but don't offer real world calibration. in the case of the Domenico model used in the Colorado study, it has been evaluated for some aspects and found to have errors where the longitudinal dispersivity parameters are high or where the Peclet number (Pe) is low (Guyonnet, 2004; West, 2007) or the study, the Pe was in the range of 80-180. As a follow up in the 2008 study, a review of a 2006 groundwater data study (URS, 2006) from wells in one basin for the O&G drilling locations was conducted, and additional data reviewed (as available) for the site locations in the 2008 RA. For the 2006 study, no Benzene (the most likely contaminant given the local conditions) was detected. For the 2008 review some BTEX compounds were identified, but none of the chemicals was over their respective drinking water limits; also, confounding sources could not be ruled out where detections were observed.

Acknowledgments

The study upon which a portion of this presentation is based was funded by the Colorado Oil and Gas Association (COGA). I would also like to acknowledge Mark Leverson, PG, Principal

Hydrogeologist with URS for his work and assistance on the hydrogeology aspects.

References

ASTM: *E1739-95(2002), Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites.* ASTM, Conshohocken, PA. 2002.

ASTM: *D5611-94, Standard Guide for Conducting a Sensitivity Analysis for a Ground Water Flow.* ASTM, Conshohocken, PA. 2002

ATSDR: *Toxicological Profile for Benzene, Draft*. ATSDR, August, 2007.

Colorado Department of Public Health and Environment, Hazardous Materials and Waste Management Division, Table 1 Colorado Soil Evaluation Values (CSEV) – December 2007

Colorado Oil and Gas Conservation Commission, Draft Rules for Oil and Gas Development in Colorado, (HB 1298 & HB 1341), March 31, 2008.

Bear, Jacob: *Dynamics of Fluids in Porous Media*. Dover, NY. 1972.

Dourson, M., S Felter, and D. Robinson: Evolution of Science-Based Uncertainty Factors in Noncancer Risk Assessment. *Reg Tox Pharmacol*. 24:108-120. 1996.

EPA: *Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part A, Interim Final*. EPA 540/1-89/002. USEPA: Washington, DC. 1989a.

EPA: *Risk Assessment Guidance for Superfund, Volume II, Environmental Evaluation Manual, Interim Final*. EPA 540-1-89-001. USEPA: Washington, DC. March, 1989b.

EPA: *Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part B: Development of Risk-Based Preliminary Remediation Goals, Interim*. EPA 540/R-92/003. USEPA: Washington, DC. December, 1991a.

EPA: *Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Part C: Risk Evaluation of Remediation Alternatives*. USEPA: Washington, DC. December, 1991b.

EPA: *Final Guidelines for Exposure Assessment.* US EPA, Washington, DC. Vol 57, Federal Register No. 104. May 29, 1992.

EPA: Review of risk levels for 32 states. 1996.

EPA: *Benchmark Dose Technical Guidance Document, DRAFT, External Review Draft*, EPA630R-00001. 2000.

EPA: *Toxicological Review of Barium and Compounds (CASRN 7440-39-3)*, EPA-635-R-05-001, June, 2005.

Guyonnet, D. and C. Neville: Dimensionless Analysis of Two Analytical Solutions for 3D Solute Transport in Ground Water. *J Contaminant Hydrology* 75:141–153. 2004.

Haber, L., and A. Maier: Scientific Criteria Used for the Development of Occupational Exposure Limits for Metals and Other Mining-Related Chemicals. *Reg Toxicol Pharmacol*. 36:262-279. 2002.

Kocher, David, and F. Owen Hoffman: Regulating Environmental Carcinogens: Where do we draw the line? *ES&T*. 25(2):1986-1989. 1991.

Nelson, Deborah Imel, Stephen Chiusano, Anne Bracker, Lance Erickson, Charles Geraci, Martin Harper, Carolyn Harvey, Andrew Havics, Mark Hoover, Thomas Lentz, Richard Niemeier, Susan Ripple, Erica Stewart, Ernest Sullivan, and David Zalk: *Guidance for Conducting Control Banding Analyses*. AIHA, Fairfax, VA. 2007

Newell, CJ, and JA Connor: Characteristics of Dissolved Hydrocarbon Plumes, Results from Four

Studies. *API Newsletter* December, 1998.

Norton, JP: Algebraic sensitivity analysis of environmental models. *Environ Model & Soft* 23:963-972. 2008.

QEPA: *Pathway Analysis and Risk assessment (PARA) For Solids and Fluids Used In Oil and Gas Exploration and Production in Colorado*, pp. 1-930, June 2008.

Templeton, C.: Solubility of Barium Sulfate in Sodium Chloride Solutions from 25° to 95° C. *J Chem Eng Data* 4:514-516. 1960.

URS: Phase 1, Hydrogeologic Characterization of the Mamm Creek Area In Garfield County, March 23, 2006 – for Board of County Commissioners Garfield County, Colorado.

West, M.R., B.H. Kueper, and M.J. Ungs: On the Use and Error of Approximation in the Domenico (1987) Solution. *Ground Water* 45(2)126–135. 2007.

Modeling Drinking Water Related Human Health Risks from Hydraulic Fracturing Additives

Manu Sharma, M.S., P.E.; David E. Merrill, M.S.; Ari S. Lewis, M.S.; Sam A. Flewelling, Ph.D.
Gradient

Potential impact of hydraulic fracturing (HF) activities on drinking water aquifers is being studied by the United States Environmental Protection Agency (US EPA) at the request of Congress. Although HF has been widely used for natural gas development for many years, this topic is receiving greater attention in the media and the scientific community as large new natural gas reserves are being proposed for development. A number of regulatory agencies, including the US EPA (2004),[2] have previously assessed potential impacts to drinking water aquifers, and concluded that HF activities are not expected to affect drinking water aquifers. Among them, is a comprehensive evaluation undertaken by the New York State Department of Environmental Conservation (NYSDEC), which published a Draft Supplemental Generic Environmental Impact Statement (SGEIS) addressing permitting requirements for the development of natural gas production wells in the Marcellus Shale formation (NYSDEC, 2009).[3] Our presentation relies on the HF-related information presented in the NYSDEC SGEIS, and evaluates potential human health risks associated with HF-related releases that could affect groundwater or surface water.

Using the HF fluid composition of the "model HF fluid" used by NYSDEC, as well as HF flowback fluid composition from the Marcellus Shale reported in the SGEIS for samples from Pennsylvania/West Virginia, and published information on chemical toxicity, we examined potential HF fluid release scenarios and their associated potential impacts on human health. We focused on possible contamination of drinking water resources – in particular either groundwater aquifers or surface water bodies.

Exposure Analysis

We examined potential contamination of drinking water resources and quantified risk to human health for the following scenarios:

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[2] US EPA. 2004. "Evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs (Final)." Office of Water, June.

[3] New York State Department of Environmental Conservation (NYSDEC). 2009. "Draft Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program—Well Permit Issuance for Horizontal Drilling and High-Volume Hydraulic Fracturing to Develop the Marcellus Shale and Other Low-Permeability Gas Reservoirs." Division of Mineral Resources, September.

Groundwater

- Migration of HF fluid additives that remain in the Marcellus Shale after fracturing, up through the overlying shale and multiple bedrock layers to an overlying drinking water aquifer.

- Spills/releases of HF fluid to the surface during HF operations or from flowback management (*i.e.*, pumping, handling), and subsequent migration to a nearby drinking water well.

Surface Water

- Spills/releases of HF fluid to the surface during HF operations or from flowback management at a surface impoundment, and migration to a nearby stream/river.

For each scenario, we adopted conservative (health-protective) assumptions that tend to overstate, rather than understate, the potential for human exposure *via* drinking water. For example:

- We examined shallow drinking water aquifers with water tables (WTs) from ~15 to 30 feet (ft) below the surface (5 to 10 meters).

- We examined scenarios for shallow drinking water wells, ranging from 65 to 165 ft deep (20 to 50 meters).

- We assigned a hydraulic conductivity to the drinking water aquifer that is lower (less mixing and dilution) than typical values for productive aquifers of the Southern Tier of New York State (NYS).

- We assumed no "setback" for the surface releases in our analysis of impacts to shallow drinking water wells or surface waters, whereas setback requirements are typically used for well siting purposes.

Overall, these assumptions are conservative (health-protective) and expected to yield an upper-bound estimate of human health risks.

Toxicity Evaluation

We adopted established risk analysis methods to evaluate chemical toxicity and potential human exposures. Agency-established toxicity criteria (e.g., drinking water standards, or risk-based benchmarks) were available for most of the model HF fluid and flowback constituents. For HF additives lacking these "agency-established" health drinking water benchmarks or toxicity factors, we developed risk-based concentrations (RBCs) for drinking water based on published toxicity data in order to evaluate the health risks of the HF additives.

Risk Analysis Results

None of the conservatively-modeled HF/flowback constituent concentrations in shallow groundwater and surface water exceeded a risk-based concentration for drinking water. Furthermore, our analysis confirms that migration of HF fluid additives from the Marcellus Shale up through overlying bedrock to a surface aquifer is an implausible contamination pathway. Even if such a pathway were plausible, the rate of migration would be such that the dilution/attenuation of groundwater would be significant, thereby reducing the model HF fluid additive concentrations in drinking water (from the overlying aquifer), to concentrations well below health-based standards/benchmarks and not pose a threat to human health.

Conclusions

To summarize, our analysis indicates that even using conservative (health-protective) exposure assumptions and a combination of agency-developed/Gradient-derived toxicity factors, the potential human health risks associated with model HF fluid additives and measured flowback constituents *via* drinking and household use of water are expected to be insignificant, as defined by agency-based guidelines:

- The migration of HF additives from the Marcellus Shale formation to overlying potable aquifers is implausible, given the thickness of the overlying confining rock layers and the effective hydraulic isolation that these overlying layers have provided for millions of years (resulting in trapping of the natural gas). Even using extreme case assumptions, the migration of HF additives from the Marcellus Shale to potable aquifers would not be sufficient to exceed health-based drinking water concentrations.

- Human health risks associated with surface releases of the model HF fluid additives are also expected to be insignificant due to attenuation mechanisms which are expected to reduce concentrations in potable aquifers and surface waters to levels well below health-based drinking water concentrations. In addition, typically used setback requirements and mitigation measures are expected to further protect these water resources and human health.

Revisiting the Major Discussion Points of the Technical Presentation Sessions

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JP Nicot of the University of Texas at Austin, the workshop lead, described the key points covered by the technical presentations and discussion in the context of a risk assessment. The first step of the assessment is to identify the potential sources of contamination: fracturing fluid itself, flowback water, or produced water. The next step is to identify the situations under which contamination could occur: a surface spill, a defect in the well bore, poor well construction, or leakage through natural pathways. The third step is determining the composition of the fluids of concern, which could correspond to component(s) of the injected fluid, compounds mobilized from the formation, or degradation products from reactions in the subsurface. The next steps are identifying pathways, such as the fracture system itself and abandoned wells, and determining the fate of chemicals. Dr. Nicot identified monitoring as a topic that was not covered in this session. He also emphasized the importance of developing a conceptual model before moving forward with any type of mathematical modeling or laboratory experiment. He added that modeling and analysis tends to focus on the shallow subsurface, bypassing the larger unknowns of fluid flow in deep aquifers and injection zones.

Angus McGrath of Stantec, the Contaminant Identification, Transformation, and Transport theme lead, summarized highlights of the Theme 1 presentations. He mentioned the four-quadrant mobility vs. toxicity risk matrix and suggested it be expanded to cover more aspects of fate and transport such as persistence and degradation. Dr. McGrath also described the data included in the presentations and the importance of determining the source of drinking water or surface water contamination. He described the methods and forensic tools discussed by the presenters, as well as the idea of a conceptual model. He cautioned that conceptual models should be flexible enough to allow for future developments. He emphasized the importance of collecting background data and having a tiered approach to monitoring. Dr. McGrath also described key fate and transport issues for future work, including: developing conceptual models of pathways of fracture fluid release; evaluating chemicals for relative risk of release and potential harm; evaluating geochemical processes and assessing relative risk; quantifying chemicals in potential sources; and designing monitoring approaches. He also provided suggestions for the format of future workshops, recommending that summaries of previous workshops be made available and that direction be provided on the material discussed and the priorities for each theme.

A participant added to Dr. McGrath's list of key issues, noting that it is critical to distinguish between shallow HF and HF at depth. CBM techniques use similar fracture fluids, and there is more potential for contamination due to proximity to drinking water aquifers.

Ahmad Ghassemi of Texas A&M University, the Impacts of Hydraulic Fracturing on Natural Transport Systems theme lead, summarized the key points from Theme 2. First, he stated that HF creates a large stimulated volume, which enhances the rock's permeability and enables production. The resulting fracture system is often complex, involving the interaction of injection pressures, in-situ stresses, and rock properties. Dr. Ghassemi noted that, despite this complexity, diagnostic tools allow us to characterize the fracture geometry and identify out-of-zone fractures. Large height growth is possible, but existing stress gradients tend to limit it and maintain the stimulated volume within the zone of interest. Dr. Ghassemi described how the pressure regime of the stimulated reservoir volume favors the flow of gas into the well and is not conducive to gas migration out of the stimulated zone. In addition, the petrophysical characteristics of shales favor retention of the injected water. He concluded that there is still a need for analysis of the processes of fracture creation to improve the confidence of fracture design.

Andrew Havics of pH2, LLC, the Models to Predict Transport theme lead, listed the key points raised during the Theme 3 presentations. First, he noted that models have limitations, and validation is important both for screening and sensitivity purposes. He stated that model selection should be based on parameter selection, as well as applicability to the region or site and whether discrete or stochastic results are desirable. Data collection at the time of well installation is critical, and data from actual spills and releases are very valuable to modeling. Confounding factors, such as those related to stray gas migration, should also be considered. Mr. Havics noted that case studies tend to focus on extreme events and should be considered within the framework of the underlying distribution. He also repeated the conclusions of Mr. Sharma's presentation: for these conditions, the calculated results show very low health risks associated with the modeled scenarios. Mr. Havics noted that the DAFs presented by Mr. Sharma are consistent with previous EPA modeling. He also emphasized that poor well construction and abandonment present significant potential for problems.

Bob Puls of US EPA, the technical lead for the Hydraulic Fracturing Study, thanked the leads, presenters, and participants and assured all of the attendees that the information from the workshop will be incorporated into EPA's study. Dr. Puls summarized key items from the workshop. First, he noted the importance of identifying which chemicals are most toxic, are used most frequently and at the highest concentrations, and are the most mobile; the presenters emphasized that these characteristics are most likely to have an impact on human health. Dr. Puls also noted that some presentations indicated that potential chemicals of concern occur both in HF additives and in flowback/produced water according to presenters. He also observed some presenters believe contaminants like methane, naturally occurring radioactive material (NORM), and high TDS waters may pose more of a risk than the fracture fluids themselves. Dr. Puls noted it is essential to monitor and understand how these fluids are managed at the surface and ultimately disposed. He also observed that several presenters thought flowback characterization is useful, but it is important to determine the sources of the monitored fluid components. Dr. Puls noted the importance of investigating existing data to provide a realistic context for the case studies and the EPA study as a whole. Dr. Puls also noted that several presenters suggested that the likelihood of fluid transport up from the injection zone into shallow aquifers seems low and that other pathways, such as abandoned wells, may be linked to more significant risks. Dr. Puls thanked all of the participants and organizers again and concluded the workshop.

Poster Abstracts

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

Figures and Tables referred to by the authors in the poster abstracts are found in the respective posters. Poster figures and tables are not listed in the List of Figures (page ii) and List of Tables (page iii).

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Review of Groundwater Quality Data Surrounding Fracing Operations

Dollis M. Wright[1] and Andrew A Havics[2], CHMM, CIH, PE
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Introduction

With the increase in activity of the Oil and Gas Industry on the Western Slopes, comes a heightened awareness of real and perceived health concerns attributed to this activity. A common misperception is that the presence of a chemical equates to the chemical causing a health impact. A review of existing data on domestic wells located within targeted Colorado communities where fracing operations occur was performed by Quality Environmental Professional Associates (QEPA). This activity was conducted as part of a larger study to address data gaps regarding chemicals used in oil and gas activities and their risk to human health.[1]

Objective

A fate and transport evaluation of the constituents was performed for water as well other primary media (soil, air). The water pathways were reviewed and analyzed using qualitative and quantitative methods to determine if a completed pathway is possible or likely under customary operating conditions. As part of the evaluation of these pathways, available sampling from private/domestic wells and documented complaints in the targeted area were reviewed.

Data Reviewed

In an effort to evaluate groundwater as a potential pathway of exposure, QEPA reviewed data from the following sources:

1. Citizen Complaint data from the Garfield County Oil & Gas Office
2. Baseline and post drilling water well data within ½ mile radius of the drilling pad as provided by Operators in the targeted operations area from 2007-2008. (See figure 1)
3. Data from 495 permitted water wells (1963 - 2005) in a 2006 study. [2]

Results

There were a total of 271 complaints registered in the Garfield County Oil and Gas office by citizens. The majority of the complaints focused on odor and water well issues (90%). There were 64 complaints concerning water quality and impact to water wells. It is important to note that none of the concerns were confirmed to be Oil & Gas Operations related. (again, see figure 1)

Part of the 2006 URS study objective was to address the vulnerability of surface water and groundwater resources in the area to impacts from gas well development. A review of this data showed that Benzene (a primary contaminant of concern in the QEPA 2008 (Pathway Analysis and Risk Assessment Report[1]) was not detected in any of the sample results. Some additional findings are that given natural attenuation, the fate of chemicals spilled or released in oil and gas operations do not readily move very far from their point of origin. This is supported by four separate studies covering 604 sites (FL, TX, CA, and a general US database) where plume distances for known significant pure product releases (only diluted fluids and solids are present in the Oil and Gas reviewed) revealed that 75% are under 200 ft and most are shrinking plumes.[3]

It is important to note that these wells are located in 110 square mile area where 978 gas wells were drilled. The number of wells completed in each aquifer is shown below:

- Alluvial (Al)aquifer: 48 wells
- Wasatch (Wt) aquifer: 388 wells
- Both aquifers (Al and Wt): 5 wells
- Unidentified or incomplete logs: 9 wells

Operators in the targeted study area provided maps and sampling results of private well water within a ½ mile area of the Pad where samples were taken for the QEPA 2008 PARA (Pathway Analysis and Risk Assessment). None of the private well samples exceeded drinking water standards. (See figures 2 & 3)

Conclusions

Based on a review of the sampling data and record of complaints:

- Groundwater is not a past or present completed pathway of exposure to chemicals associated with oil and gas operations for citizens living within the targeted study area.
- In an area where there is considerable oil and gas drilling activity, Benzene was not detected in any private well water samples.
- Citizen concerns surrounding drinking water quality and oil and gas activities were not confirmed.

References

QEPA, Pathway Analysis and Risk Assessment for Pit Solids, Fluids and Air in Colorado Energy Basins, June 2008.

URS Phase 1 Hydrogeologic Characterization of the Mamm Creek Field Area in Garfield County, March 23, 2006.

Newell, Characteristics of Dissolved Hydrocarbon Plumes, Results from Four Studies, API Newsletter, December, 1998.

Review of Groundwater Quality Data Surrounding Fracing Operations

*Dollis M. Wright, Andrew A. Havics **

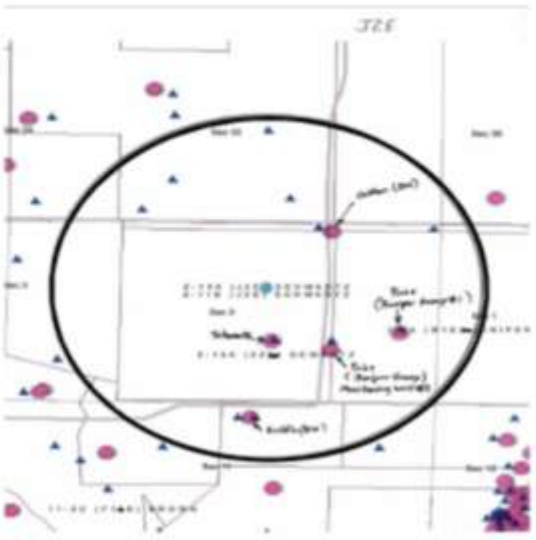
QEPA

Introduction

A review of existing data on domestic wells located within targeted Colorado communities where fracing operations occur was performed.

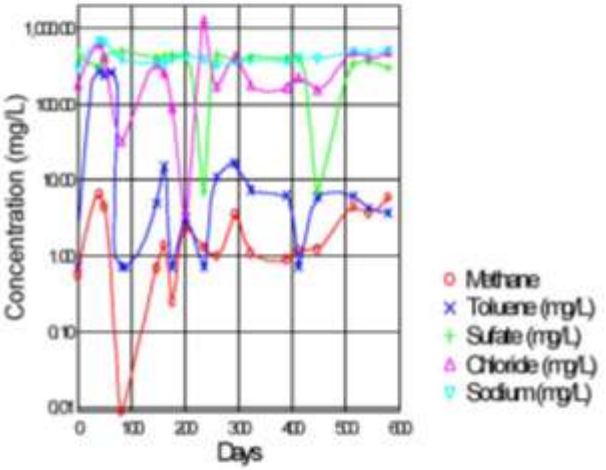
Objective

Assess available data from targeted area on the impact of oil and gas operations on private well water quality. *(Below is a diagram showing an example of a well pad (blue circle) and the location of sampled domestic wells (pink circles) within a ½ mile radius of the pad).*

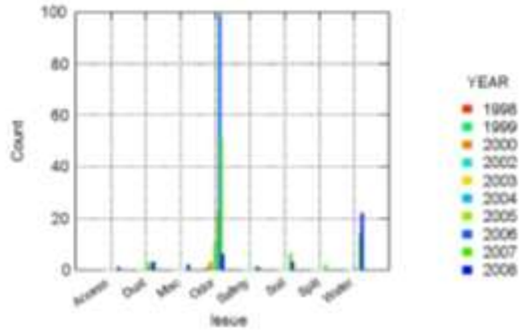


Data Reviewed

- Baseline and post drilling water well data were retrieved from Operators in the targeted operations area from 2007-2008.
- Complaint logs of the targeted area County Health Department were reviewed (*1998 – 2008 see graph to the right for number and type of complaints by year).*
- Data from 495 permitted water wells (1963-2005).[1] These wells are located in 110 square mile area where 978 gas wells were drilled.



The above graph is characterized data for one well over a 1 1/2 year period



Conclusions

- Groundwater quality was second only to odor complaints in communities where there were fracing operations.
- Benzene was not detected in the 495 characterized domestic water wells.
- None of the water samples taken from private wells located within ½ mile radius of the fracing operations exceeded drinking water standards.

References

1. URS Phase 1 Hydrogeologic Characterization of the Mamm Creek Field Area in Garfield County, March 23, 2006.

Acknowledgments

This data is part of the COGA Pathways Analysis and Risk Assessment for Solids and Fluids Used in Oil and Gas Exploration and Production in Colorado, QEPA 2008.

Control Banding as a Means of Hazard Identification & Characterization for Chemicals

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Control Banding (CB) or Performance-Based Occupational Exposure Limits (PB-OELs) have been used intensively in the pharmaceutical and biological industries and are becoming more broadly applied [Naumann, 1996, Nelson, 2007] Control banding can be thought of as a grouping or banding strategy paralleling classical risk assessment components (see Figure 1 above). These components include: Hazard Identification, Dose-Response Relationship, Exposure Assessment, Risk Assessment, and Risk Management. The Hazard Identification and Dose-Response aspects go hand in hand and form a beginning basis for determining inherent risk of a material by reviewing and assessing toxicological parameters and then calculating an acceptable reference value for dose or dose rate. For classical risk assessment, this value is a reference dose (RfD) for non-carcinogens or a slope factor (SF) for carcinogens. For Control Banding, these two components are merged into one step with compounds or materials classified by group, using similar parameters but in a semi-quantitative manner.

One of these methods is the Control of Substances Hazardous to Health (COSHH) process [Brooke, 1998]. For this method, Risk Phrases called R-phrases are used to establish a chemical's band; these can be found on Material Safety Data Sheets (MSDS). Example R-Phrases and a subsequent grouping scheme by R-phrases is presented in Figure 2 [Brooke, 1998]. A modification of this scheme is provided in Table 1 below [Havics, 2008]. This modified scheme was created by and partially validated using over 100 occupational limits and a companion toxicological database [Havics, 2008]. If has been further modified here to include two aspects: a) the addition of another 10 fold safety factor to adjust from occupational limits to those for the general population (this adjustment is consistent with findings of others [Haber, 2007]), and b) conversion to oral dose rates (RfDs) from inhalation concentrations. This second aspect results in an intermediate equivalent RfD conversion parameter, referred to here as RfD*. The molecular weight (MW) of the agent must be multiplied by the intermediate RfD* to provide a final RfD to account for the conversion from parts per million (ppm) to milligrams per cubic meter (mg/m^3) in the original scheme to the present application. Table 2 provides the ranges of RfDs and RFD*s for categorization using the modified process.

Although the scheme is based on ranges or bands, an estimated point value for calculation purposes is also provided for each grouping. Because the groups are numerically arranged in orders of magnitude (factors of 10), the point estimate represents a average $\log_{10}$ value of the range for that category. Examples of standard constituents and products from Colorado fracing operations reviewed in 2008 [URS, 2008; QEPA, 2008] are shown in Table 3. The examples of fracing products are then categorized as shown in Table 4 using this scheme. Not every R-phrase will fit in the same category. As a result, the weighting of the two most conservative categories are assessed before selecting the most appropriate one. In the case of cancer agents, the most conservative is used. For other aspects, the corresponding health effects for the R-phrases are reviewed along with the general amount of data available on the chemical and the number of risk phrases in a category. If it is well-categorized, then a lesser category may be selected, otherwise the more conservative category is chosen. Where a product has more than one category for a component, the most conservative category is selected for that product. Following this, intermediate RfD*s are then estimated followed by the RfD equivalents. These are provided for the same examples as before in Table 5. Also, actual RfDs or Slope Factors converted into equivalent RfDs are provided for comparison. The results suggest that the process tends to be more conservative for known chemicals. Also, by default, poorly characterized chemicals or products will have a tendency to be shifted to more conservative values using this process.

References

1. Brooke, A UK Scheme to Help Small Firms Control Health Risks from Chemicals, Toxicological Considerations, Ann Occ Hyg, 42, 6, 377-390, 1998.
2. Haber, L., and A. Maier: Scientific Criteria Used for the Development of Occupational Exposure Limits for Metals and Other Mining-Related Chemicals. *Reg Toxicol Pharmacol. 36:262-279. 2002.*
3. Havics, A., Susan Ripple, MS, CIH (DOW Chemical), Bob Sussman, PhD, DABT (Safebridge), Tracy Kimmel, PhD, DABT (Safebridge), Bruce Naumann, PhD, DABT (Merck): A Comparison of the Hazard and Dose-Response Characterization of AIHA WEEL Chemicals Using 2 Different Control Banding Approaches"; RT254 Control Banding: Fundamentals, Underlying Issues, Applications and Strategies for Implementation, at the American Industrial Hygiene Conference & Exposition (AIHCE), 2008, May 31-June 5, 2008, Minneapolis, MN.
4. Naumann, Bruce, Edward Sargent, Barry S. Starkman, William J. Fraser, Gail T. Becker, and G. David Kirk: Performance-Based Exposure Control Limits for Pharmaceutical Active Ingredients. *AIHA J* 57(1):33-42. 1996.
5. Nelson, Deborah Imel, Stephen Chiusano, Anne Bracker, Lance Erickson, Charles Geraci, Martin Harper, Carolyn Harvey, Andrew Havics, Mark Hoover, Thomas Lentz, Richard Niemeier, Susan Ripple, Erica Stewart, Ernest Sullivan, and David Zalk: *Guidance for Conducting Control Banding Analyses.* AIHA, Fairfax, VA. 2007.
6. National Research Council (NRC): *Risk Assessment in the Federal Government: Managing the Process.* NAP, Washington, DC. 189 pp. 1983.

7. National Research Council (NRC)*: Science and Judgment in Risk Assessment.* NAP, Washington, DC. 651 pp. 1994.
8. QEPA: *Pathway Analysis and Risk assessment (PARA) For Solids and Fluids Used In Oil and Gas Exploration and Production in Colorado,* pp. 1-930, June 2008.
9. URS: *Phase 1, Hydrogeologic Characterization of the Mamm Creek Area In Garfield County, March 23, 2006 – for Board of County Commissioners Garfield County, Colorado*, 2006.

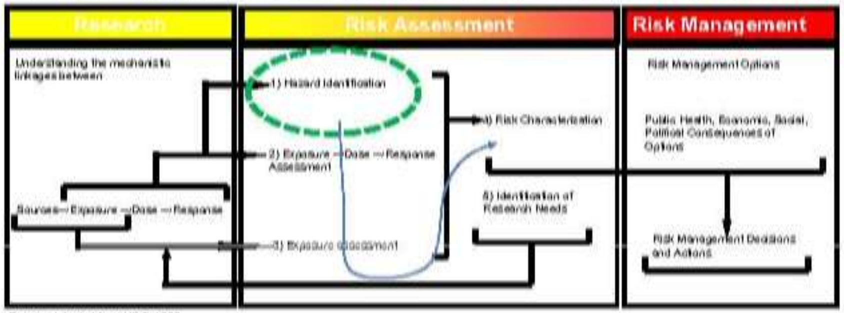
pH$_2$, LLC

Control Banding as a Means of Hazard Identification & Characterization for Chemicals

Andrew Anthony "Tony" Havics, CHMM, CIH, PE

Control Banding (CB) or Performance-Based Occupational Exposure Limits (PB-OELs) have been used intensively in the pharmaceutical and biological industries and are becoming more broadly applied [Naumann, 1996, Nelson, 2007] Control banding can be thought of as a grouping or banding strategy paralleling classical risk assessment components (see Figure 1 above). These components include: Hazard Identification, Dose-Response Relationship, Exposure Assessment, Risk Assessment, and Risk Management. The Hazard Identification and Dose-Response aspects go hand in hand and form a beginning basis for determining inherent risk of a material by reviewing and assessing toxicological parameters and then calculating an acceptable reference value for dose or dose rate. For classical risk assessment, this value is a reference dose (RfD) for non-carcinogens or a slope factor (SF) for carcinogens. For Control Banding, these two components are merged into one step with compounds or materials classified by group, using similar parameters but in a semi-quantitative manner. One of these methods is the Control of Substances Hazardous to Health (COSHH) process [Brooke, 1998]. For this method, Risk Phrases called R-phrases are used to establish a chemical's band; these can be found on Material Safety Data Sheets (MSDS). Example R-Phrases and a subsequent grouping scheme by R-phrases is presented in Figure 2 [Brooke, 1998]. A modification of this scheme is provided in Table 1 below [Havics, 2008]. This modified scheme was created by and partially validated using over 100 occupational limits and a companion toxicological base data [Havics, 2008]. If has been further modified here to include two aspects: a) the addition of another 10 fold safety factor to adjust from occupational limits to those for the general population (this adjustment is consistent with findings of others [Haber, 2007]), and b) conversion to oral dose rates (RfDs) from inhalation concentrations. This second aspect results in an intermediate equivalent RfD conversion parameter, referred to here as RfD*. The molecular weight (MW) of the agent must be multiplied by the intermediate RfD* to provide a final RfD to account for the conversion from parts per million (ppm) to milligrams per cubic meter (mg/m^3) in the original scheme to the present application. Table 2 provides the ranges of RfDs and RFD*s for categorization using the modified process. Although the scheme is based on ranges or bands, an estimated point value for calculation purposes is also provided for each grouping. Because the groups are numerically arranged in orders of magnitude (factors of 10), the point estimate represents a average $\log_{10}$ value of the range for that category. Examples of standard constituents and products from Colorado fracing operations reviewed in 2008 [URS, 2008; QEPA, 2008] are shown in Table 3. The examples of fracing products are then categorized as shown in Table 4 using this scheme. Not every R-phrase will fit in the same category. As a result, the weighting of the two most conservative categories are assessment before selecting the most appropriate one. In the case of cancer agents, the most conservative is used. For other aspects, the corresponding health effects for the R-phrases are reviewed along with the general amount of data available on the chemical and the number of risk phrases in a category. If it is well-categorized, then a lesser category may be selected, otherwise the more conservative category is chosen. Where a product has more than one category for a component, the most conservative category is selected for that product. Following this, intermediate RfD*s are then estimated followed by the RfD equivalents. These are provided for the same examples as before in Table 5. Also, actual RfDs or Slope Factors converted into equivalent RfDs are provided for comparison. The results suggest that the process tends to be more conservative for known chemicals. Also, by default, poorly characterized chemicals or products will have a tendency to be shifted to more conservative values using this process.

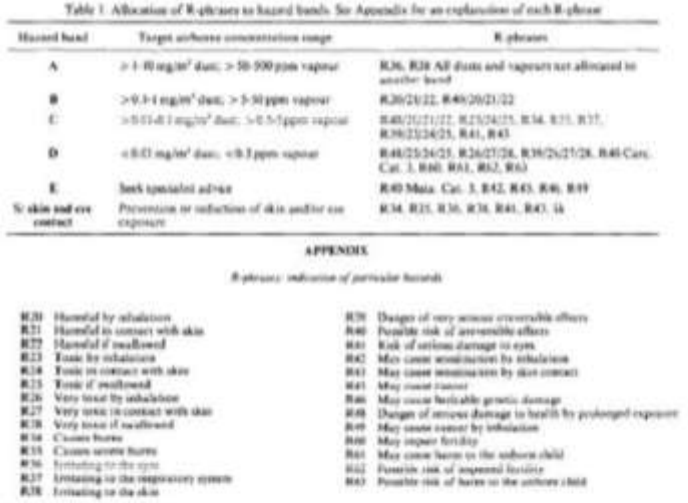
Figure 1. NAS/NRC Risk Assessment/Management Paradigm



Source: Adapted from NRC, 1983.

Figure 2. COSHH Process in Brief

Use R-phrases from MSDS or similar to categorize products or chemicals into a hazard band. For potential exposure and risk, these hazard bands are used as a group along with exposure data and likelihoods to assess risk.



Source: Brooke, 1998.

Table 1. Modified COSHH Categories

A	B	C	D	E
Skin Eye Irritants Unclassified	Harmful on Single Exposure	Toxic, Corrosive, etc.	Very Toxic, Toxic to reproduction	Asthma Sensitizer Genetic Damage
R38 R48 No R All other R	R20 R21 R22	R23, 24, 25 R34, 35 R37 R41, 43 R48/20/21/22	R26, 27, 28 R40 Carc. R48/23/24/25 R60, 61, 62, 63	R42 R45, 49 R46, R68
>1 to 10+ Solids	>0.1 to 1	>0.01 to 0.1	<0.01 mg/m^3 *>0.001-0.01*	*<=0.001*
>50 to 500+ Vapors	>5 to 50	>0.5 to 5	<0.5 ppm *>0.05-0.5*	*<=0.05*

Alternative Use = Respiratory Sensitizers

Not Specified but Implied by A-D Categories

Source: Havics, A., et al, 2008.

Table 2. RfD and RfD* Categories

BAND ➡	**A**	**B**	**C**	**D**	**E**
Est. Equivalent General Population Value for **Solids** **RfD**	>0.14-1.4 mg/kg	>0.014-0.140 mg/kg	>0.0014-0.014 mg/kg	>0.00014-0.0014 mg/kg	<=0.00014 mg/kg
Useful General Population **RfD Point Value**	0.046	0.0046	0.00046	0.000046	0.0000046
Est. Equivalent General Population Value for **Liquids/Vapors** **RfD*** Where RfD = (RfD*) X (MW)	>0.03-0.3+ mg/kg	>0.003-03 mg/kg	>0.0003-0.003 mg/kg	>0.00003-0.0003 mg/kg	<=0.00003 mg/kg
Useful General Population **RfD* Point Value**	0.094	0.0094	0.0009	0.00009	0.000009

Table 3. Example Fracing Materials from Colorado

Product Name	**Product Use**	**Major Constituent**	**CAS No.**
CL-37 Crosslinker	Drilling, Fracturing	Glycerine Propanol Triethanolamine zirconate	56-81-5 71-23-8 101033-44-7
LGC-8	Drilling, Completion, Fracturing	Guar Gum	9000-30-0
Flowback fluids	Fracturing	Benzene Toluene Ethylbenzene Xylenes	71-43-2 108-88-3 100-41-4 1330-20-7

Table 4. Example Fracing Material Categorization

Agent	**A**	**B**	**C**	**D**	**E**
Criteria	R36 R48 No R All other R	R20 R21 R22	R23, 24, 25 R34, 35 R37 R41, 43 R48/20/21/22	R26, 27, 28 R40 Carc. Cat 3 R48/23/24/25 R60, 61, 62, 63	R42 R45, 49 R46, R68
Benzene	R11 R38 R65		R36	R48/23/24/25 (✓)	R45 ✓
Toluene	R11 R65 R67		R48/20 (✓)	*R63* ✓	
Ethylbenzene	R11 R36 R38	R20 (✓)	R37 ✓		
Xylenes	R10 R36 R38	R20 R22 ✓	R37 (✓)		
LC 8 Guar Gum	No R Phrases ✓				
CL-37 Overall			✓		
Glycerine	No R Phrases ✓				
Propanol	R11 R67	✓	R41 (✓)		
Triethanolamine Zirconate	R36 R38	(✓)	R37 ✓		

Table 5. Example RfD Equivalents

Agent	**Hazard Ranking**	**Est. RfD***	**Est. RfD Equivalent**	**Actual RfD**
Benzene	E	0.0000009	0.0007	0.0007 Modified from Slope factor
Toluene	D	0.00009	0.008	0.2
Ethylbenzene	C	0.0009	0.1	*0.1*
Xylenes	C	0.0009	0.1	2
LC-8 Guar Gum	A		0.046	*NA*
CL-37 Overall	C		0.56	*NA*
Glycerine	*A*	*0.094*	*8.7*	*NA*
Propanol	*B*	*0.0094*	*0.56*	*NA*
Triethanolamine Zirconate	*C*	*0.00094*	*0.65*	*NA*

References

1. Brooke, A UK Scheme to Help Small Firms Control Health Risks from Chemicals, Toxicological Considerations, Ann Occ Hyg. 42, 6, 377 390, 1998
2. Haber, L., and A. Maier: Scientific Criteria Used for the Development of Occupational Exposure Limits for Metals and Other Mining Related Chemicals. *Reg Toxicol Pharmacol. 36:262 279. 2002*
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4. Naumann, Bruce, Edward Sargent, Barry S. Starkman, William J. Fraser, Gail T. Becker, and G. David Kirk: Performance Based Exposure Control Limits for Pharmaceutical Active Ingredients. *AIHA J. 57(1)*:33 42. 1996.
5. Nelson, Deborah Imel, Stephen Chiusano, Anne Bracker, Lance Erickson, Charles Geraci, Martin Harper, Carolyn Harvey, Andrew Havics, Mark Hoover, Thomas Lentz, Richard Niemeier, Susan Ripple, Erica Stewart, Ernest Sullivan, and David Zalk: *Guidance for Conducting Control Banding Analyses. AIHA, Fairfax, VA. 2007.*
6. National Research Council (NRC): *Risk Assessment in the Federal Government: Managing the Process. NAP, Washington, DC 189 pp. 1983;.*
7. *National Research Council (NRC): Science and Judgment in Risk Assessment.* NAP, Washington, DC. 651 pp. 1994
8. QEPA: *Pathway Analysis and Risk assessment (PARA) For Solids and Fluids Used in Oil and Gas Exploration and Production in Colorado, pp. 1 930, June 2008.*
9. URS: Phase 1, Hydrogeologic Characterization of the Mamm Creek Area in Garfield County, March 23, 2006 – for Board of County Commissioners Garfield County, Colorado.

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

2-BE 2-butoxyethanol
ASTM American Society for Testing and Materials
ATSDR Agency for Toxic Substances and Disease Registry
BMDL benchmark dose level
BTEX benzene, toluene, ethylbenzene, and xylene
CAE chemicals for analytical evaluation
CAS Chemical Abstract Service
CB control banding
CBM coalbed methane
CCC criteria continuous concentration
CHEC Center for Health Environments and Communities
CMC criteria maximum concentration
COGA Colorado Oil and Gas Association
COGCC Colorado Oil and Gas Commerce Commission
COI compound of interest
COSHH Control of Substances Hazardous to Health
CSM conceptual site model
DBNPA 2,2-dibromo-3-nitrilopropionamide
DRO diesel range organics
EG ethylene glycol
EM electromagnetic
FRV failed rock volume
GW groundwater
HF hydraulic fracturing
K_{ha} hydraulic conductivity
Kow octanol-water partitioning coefficient
LOAEL lowest observed adverse effect level
LOD limit of detection
LOQ limit of quantification
MCL maximum contaminant level
MLE maximum likelihood estimator
MMCF million standard feet of gas
MRL minimum risk level
MRO motor oil range organics
MSDS Material Safety Data Sheets
MW molecular weight
ND not detected
NELAC National Environmental Laboratory Accreditation Conference

NFS numerical flow simulation
NOAEL no observed adverse effect level
NORM naturally occurring radioactive material
NPDES National Pollutant Discharge Elimination System
NYDEC New York Department of Environmental Conservation
NYS New York State
OSHA Occupational Safety and Health Administration
PA DEP Pennsylvania Department of Environmental Protection
PAH polycyclic aromatic hydrocarbon
PARCC Precision, Accuracy, Representativeness, Completeness, and Comparability
PB-OEL performance-based occupational exposure limit
PBT Pennsylvania Brine Treatment
PCOC priority contaminants of concern
PDA production data analysis
POE point of exposure
POTW publicly owned treatment works
PTA pressure transient analysis
QEPA Quality Environmental Professional Associates
RA risk assessment
RAGS Risk Assessment Guide for Superfund
RBC risk-based concentrations
RBCA risk-based corrective action
RCI reactivity, corrosivity, and ignitability
RCRA Resource Conservation and Recovery Act
RfC reference concentration
RfD reference dose
SF slope factor
SGEIS supplemental generic environmental impact statement
SMCL secondary maximum contaminant level
SVOC semivolatile organic compounds
TAL target analyte list
TCLP toxic characteristic leaching procedure
TDS total dissolved solids
TEPH total extractable petroleum hydrocarbons
TIC tentatively identified compounds
TMB trimethyl benzene
USBM United States Bureau of Mines
USGS US Geological Survey
UST underground storage tank
VOC volatile organic compounds
WHO World Health Organization
WT water table

GLOSSARY

Amott imbibition test a comparison of the imbibition potential of water and oil into a rock. It is possible for the same rock to imbibe both water and oil, with water imbibing at low in situ water saturation, displacing excess oil from the surface of the rock grains, and oil imbibing at low in-situ oil saturation, displacing excess water. (Schlumberger)

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

fall-off test The measurement and analysis of pressure data taken after an injection well is shut in. These data are often the easiest transient well-test data to obtain. Wellhead pressure rises during injection, and if the well remains full of liquid after shut-in of an injector, the pressure can be measured at the surface, and bottomhole pressures can be calculated by adding the pressure from the hydrostatic column to the wellhead pressure. Since most water-injection wells are fractured during injection, and injection wells often go on vacuum, the fluid level can fall below the surface. Dealing with this complication requires reverting to bottomhole pressure gauges or sonic devices. (Schlumberger)

filter-cake 1. the layer of solids stranded on the face of permeable formations by liquids driven into the rock by pressure differential towards the formation. When sized correctly the filter cake may completely stop losses. (SPE)

2. The residue deposited on a permeable medium when a slurry, such as a drilling fluid, is forced against the medium under a pressure. Filtrate is the liquid that passes through the medium, leaving the cake on the medium. Drilling muds are tested to determine filtration rate and filter-cake properties. Cake properties such as cake thickness, toughness, slickness and permeability are important because the cake that forms on permeable zones in the wellbore can cause stuck pipe and other drilling problems. Reduced oil and gas production can result from reservoir damage when a poor filter cake allows deep filtrate invasion. A certain degree of cake buildup is desirable to isolate formations from drilling fluids. In openhole completions in high-angle or horizontal holes, the formation of an external filter cake is preferable to a cake that forms partly inside the formation. The latter has a higher potential for formation damage. (Schlumberger)

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)

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

leakoff 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)

modulus of elasticity Modulus refers to stress at a predetermined level of elongation, usually at 100% elongation. The higher the modulus of a compound, the more apt it is to recover from loading or localized force and the better is its resistance to extrusion. (SPE)

pressure transient analysis The analysis of pressure changes over time, especially those associated with small variations in the volume of fluid. In most well tests, a limited amount of fluid is allowed to flow from the formation being tested and the pressure at the formation monitored over time. Then, the well is closed and the pressure monitored while the fluid within the formation equilibrates. The analysis of these pressure changes can provide information on the size and shape of the formation as well as its ability to produce fluids. (Schlumberger)

shut-in stop a well from flowing and close the valves. (SPE)

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

spurt loss the initial loss of fluids from a mud or frac fluid, before the walk cake can be formed. (SPE)

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content and processed chlorine free.

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