Oil & Natural Gas Technology

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Quarterly Research Performance Progress Report
(Period ending: 03/31/2017)

Marcellus Shale Energy and Environment Laboratory (MSEEL)
Project Period: October 1, 2014 – September 30, 2019

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NETL

Office of Fossil Energy

Quarterly Progress Report

January 1 – March 31, 2017

Executive Summary

The objective of the Marcellus Shale Energy and Environment Laboratory (MSEEL) is to provide a long-term field site to develop and validate new knowledge and technology to improve recovery efficiency and minimize environmental implications of unconventional resource development.

This quarter field work focused on undertaking production logging at the MIP-3H well. Logging was delayed from January into early March due unseasonably warm weather during early February and also to issues cleaning out the lateral. The preliminary Flow Scanner Logging data was delivered at the end of March and looks good and is being evaluated. The data will permit a thorough evaluation of different completion strategies, stages and clusters and will be the final input to flow simulation.

Numerous papers were being prepared for a special session at Unconventional Resources Technology Conference (URTeC) and at the Society of Exploration Geophysicists (SEG).

Quarterly Progress Report

January 1 – March 31, 2017

Project Performance

This report summarizes the activities of Cooperative Agreement DE-FE0024297 (Marcellus Shale Energy and Environment Laboratory – MSEEL) with the West Virginia University Research Corporation (WVURC) during the second quarter of FY2017 (January 1 through March 30, 2017).

This report outlines the approach taken, including specific actions by subtopic. If there was no identified activity during the reporting period, the appropriate section is included but without additional information.

A summary of major lessons learned to this point of the project are provided as bullet points and will be added to as research is completed. New lessons are highlighted.

1) Synthetic based drilling mud is ecofriendly as well as helps with friction which resulted in faster drilling and reduced costs while leading to drilling waste from both the vertical and horizontal portions of the wells that passed all toxicity standards.

2) Microseismic monitoring does not completely define propped fractures and the extent of stimulated reservoir volume from hydraulic fracture stimulation. Requires integration of data from core, logs and slow slip seismic monitoring.

3) Production logging documents significant variations in production between completion types, stages and even clusters. Variations in production provide the necessary data for robust reservoir simulation.

4) Complex geology in laterals can lead to intercommunication between stages and reduced fracture stimulation efficiency. This can be mitigated with limited entry (engineered completions) that significantly improves fracture stimulation efficiency. NNE has continued the practice in subsequent wells. Planned production logging will help to define production efficiency.

5) The significant part of air emissions are in truck traffic, not in drilling and fracture operations on the pad. Emissions from both the pad and trucking can be reduced with operational modifications such as reducing dust and truck traffic during fracture stimulation (e.g., Sandbox) from bifuel (natural gas-diesel) engine operations.

6) Dual fuel engines demonstrated lower carbon monoxide (CO) emissions than diesel only operation. Dual fuel operations could reduce onsite diesel fuel consumption by 19 to 63% for drilling and 52% for hydraulic stimulation.

7) Biologic activity cannot be eliminated with biocides, only delayed. The biologic activity results in a unique biota that may affect operations. There may be other methods to control/influence biologic activity.

8) Water production changes rapidly after fracture stimulation in terms of volume (500 bbl/day to less than 1 bbl/day) and total dissolved solids (TDS from freshwater, 100 to 150g/L). Radioactivity is associated with produced water, not drill cuttings.

A MSEEL session and related presentations is scheduled for Unconventional Resources Technology Conference (http:// http://urtec.org/2017/) on 24-26 July. MSEEL has a dedicated session for Monday afternoon (http://urtec.org/2017/Technical-Program/Monday/Monday-Afternoon-Oral-Presentations). Papers include:

Oral Session
Marcellus Shale Energy and Environment Laboratory (MSEEL)

Introductory Remarks – NETL, DOE

Marcellus Shale Energy and Environment Laboratory (MSEEL): Subsurface Reservoir Characterization and Engineered Completion; Presenter: Tim Carr; West Virginia University (2670437)

Depositional environment and impact on pore structure and gas storage potential of middle Devonian organic rich shale, Northeastern West Virginia, Appalachian Basin; Presenter: Liaosha Song, Department of Geology and Geography, West Virginia University, Morgantown, WV, (2667397)

Seismic monitoring of hydraulic fracturing activity at the Marcellus Shale Energy and Environment Laboratory (MSEEL) site, West Virginia; Presenter: Abhash Kumar, DOE, National Energy Technology Laboratory (2670481)

Geomechanics of the microseismic response in Devonian organic shales at the Marcellus Shale Energy and Environment Laboratory (MSEEL) site, West Virginia; Presenter: Erich Zorn, DOE, National Energy Technology Laboratory (2669946)

Application of Fiber-optic Temperature Data Analysis in Hydraulic Fracturing Evaluation- a Case Study in the Marcellus Shale; Presenter: Shohreh Amini, West Virginia University (2686732)

The Marcellus Shale Energy and Environmental Laboratory (MSEEL): water and solid waste findings-year one; Presenter: Paul Ziemkiewicz WRI, West Virginia University (2669914)

Role of organic acids in controlling mineral scale formation during hydraulic fracturing at the Marcellus Shale Energy and Environmental Laboratory (MSEEL) site; Presenter: Alexandra Hakala, National Energy Technology Laboratory, DOE (2670833)

CONTROL ID	TITLE	PRESENTER
2670833	Role of Organic Acids in Controlling Mineral Scale Formation During Hydraulic Fracturing at the Marcellus Shale Energy and Environmental Laboratory (MSEEL) Site	Alexandra Hakala
2670060	Diglyceride Fatty Acid Profiles at the Marcellus Shale Energy and Environment Laboratory as Evidence of Non-Viable Microbial Community and Paleo-Environmental Conditions	Rawlings Akondi
2669965	Biogeochemical Characterization of Core, Fluids, and Gas at MSEEL Site	Shikha Sharma

Additional MSEEL Related Presentation at URTeC

Integrating High-Tier Measurements and Advanced Engineering Workflows to Understand and Improve Production Performance in the Marcellus Shale: A Field Case Study (2671506): Presenter Olatunbosun Anifowoshe in Theme 10: Well Completion Integration, Optimization, and Refracturing III

Also submitted were extended abstracts for the Society of Exploration Geophysicists (SEG) Annual meeting in Houston, TX, 24-29 September, 2017 (http://seg.org/Annual-Meeting-2017). Titles and authors are:

Correlating distributed acoustic sensing (DAS) to natural fracture intensity for the Marcellus Shale, Authors: Payam Kavousi*, Timothy Carr, Thomas Wilson, and Shohreh Amini, West Virginia University; Collin Wilson, Mandy Thomas, Keith MacPhail, Schlumberger; Dustin Crandall, US Department of Energy/National Energy Technology Laboratory; BJ Carney, Ian Costello, and Jay Hewitt, Northeast Natural Energy LLC.

Relationships of $\lambda\rho$, $\mu\rho$, brittleness index, Young's modulus, Poisson's ratio and high TOC for the Marcellus Shale, Morgantown, West Virginia, Authors: Thomas H. Wilson*, Payam Kavousi, Tim Carr, West Virginia University; B. J. Carney, Northeast Natural Energy LLC; Natalie Uschner, Oluwaseun Magbagbeola and Lili Xu, Schlumberger

Project Management Update

Approach

The project management team will work to generate timely and accurate reporting, and to maintain project operations, including contracting, reporting, meeting organization, and general oversight.

Results and Discussion

The project team is tracking eight (8) milestones in this budget period.

3/1/2017 - Completed Production Logging (Scheduled 2/15/2017; Completed 3/15/2017)
4/30/17 - Conduct preliminary analysis of production log data and present to DOE (Underway)
8/15/17 - Coordinate and hold MSEEL session at URTEC 2017
8/30/17 - Complete rock geochemistry and geomechanical data analysis and integration with log & microseismic data to develop preliminary reservoir simulation and fracture model(s)
8/30/17 – Create a comprehensive online library of MSEEL presentations and papers that can be downloaded. Maintain with additional material through end of project.
8/30/17 – Reorganize MSEEL data portal and prepare to transfer to NETL for public dissemination.
12/31/17 – Complete a detailed reservoir simulation incorporating fracture geometry and flow simulation
12/31/17 - Determine changes in kerogen structure and bulk rock interactions and composition on interaction with fracturing fluids under simulated subsurface conditions. (Note: as soon as I get budget addition o.k., I plan to extend BP3 from current 9/30/17 to 12/31/17)

Production data for gas and water from the MSEEL 3H and 5H wells are presented through the end of the quarter (Figures 0.1 and 0.2). The erratic data in February and March is due to work-overs on the MIP-3H and curtailment of the other MIP 5H associated with production logging of the MIP-3H.
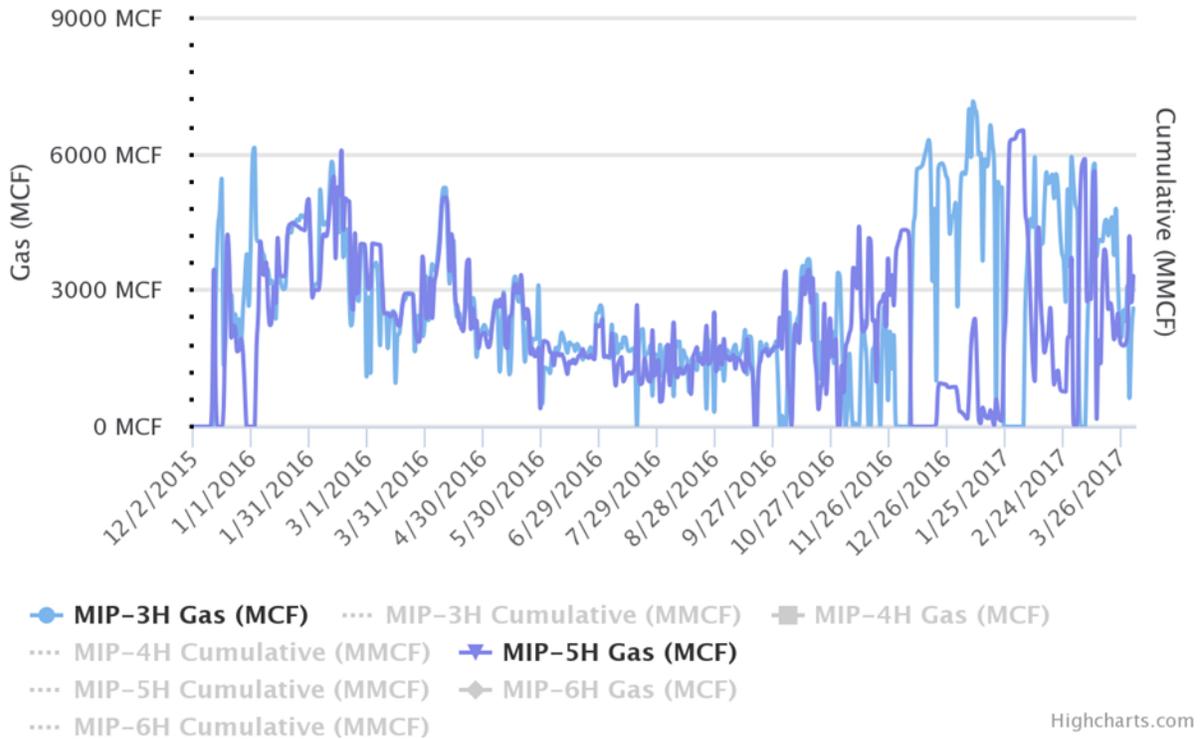
Figure 0.1, Daily gas production from the MIP-3H and MIP-5H wells at the MSEEL site.
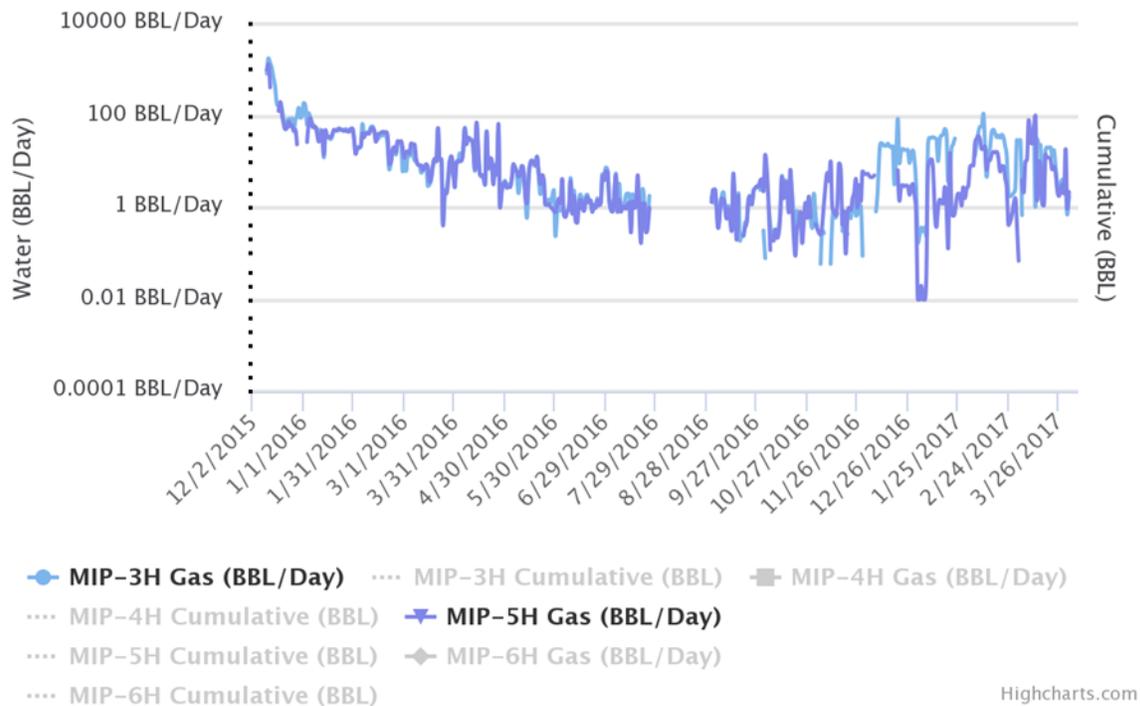

Figure 0.2, Daily water production from the MIP-3H and MIP-5H wells at the MSEEL site. Log scale.

Topic 1 – Geologic Engineering

Approach

The geologic engineering team will work to improve the effectiveness of fracture stage design, evaluating innovative stage spacing and cluster density practices to optimize recovery efficiency. The team will use a data driven approach to integrate geophysical, fluid flow and mechanical properties logs, microseismic and core data to better to characterize subsurface rock properties, faults and fracture systems to model and identify the best practices for field implementation, and assess potential methods that could enhance shale gas recovery through experimental and numerical studies integrated with the results of the production wells at the MSEEL site.

Permeability measurement experiments for additional core plugs from the science are underway.

Results and Discussion

Core Plugs

The core plugs exhibited similar permeability values as the previous samples. Some of the samples appeared to be fractured and exhibited permeability values in micro darcy range. The permeability measurements performed at high pore pressures revealed that the modified Klinkenberg correction is required up to pore pressure of 900 psia.

The analysis of the production and stimulation data from the existing horizontal wells at the MIP site as well as other horizontal Marcellus shale wells in the region has been completed, and additional modeling studies are being performed to determine the optimum well spacing. The analysis of the wireline and drilling continued on the methods for overburden stress prediction with recorded data. Also, spinner data is currently being analyzed for correlation with production features of the wellbore.

The analysis of the core plug permeability results indicated that for pore pressures below 900 psia, the flow regime is transition flow, and modified Klinkenberg correction is necessary to determine the absolute permeability. For pore pressure above 1000 psia, the flow regime appears to be slip flow, and Klinkenberg correction is sufficient to determine the absolute permeability.

Production Logging

This quarter, field work focused on undertaking production logging at the MIP-3H well. Logging was delayed from January into early March due to unseasonably warm weather during early February and also to issues cleaning out the lateral. Additional time was required in tractoring for the cleanout of MIP3H. Logging was completed and the well turned back to regular production on in the second week of March. Upon initial review, the data looks very good.

To interpret the production log data of the MIP 3H well, numerous down and up passes of the 1 11/16-inch Flow Scanner Logging Tool were undertaken (Figure 1.1). The tool contains 5 Mini-Spinners, 6 Water Holdup Measurements, 6 Gas Holdup Measurements, Relative Bearing, Deviation, Caliper, Pressure, and Temperature measurements that were recorded at various cable speeds to resolve the contribution to total well flow from each of the perforated intervals, as well as gas and water contribution from each of the perforated intervals.

Products

A preliminary data Flow Scanner Log Advisor (FSI) data set was delivered on 3/27/2017 and a final report is expected in early April. All the data look good and are being evaluated. The data will permit a thorough evaluation of different completion strategies, stages and clusters, and will be the final input to flow simulation.
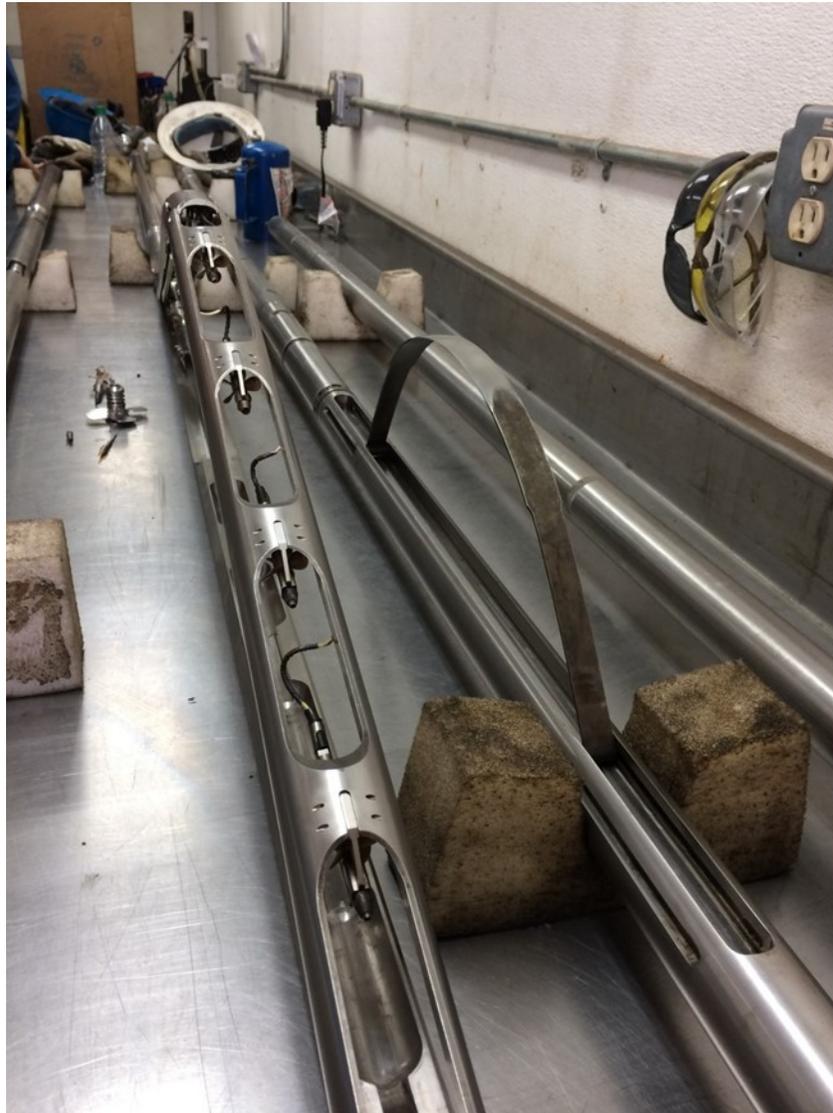

Figure 1.1, Schlumberger's Flow Scanner logging tool before deployment in the MIP 3H showing spinners and other tool components. Tool expands to measure flow at different level in the lateral.

Plan for Next Quarter

The permeability and porosity measurements on additional core plugs will be undertaken.

Topic 2 – Geophysical & Geomechanical

Approach

Wilson's effort this past quarter concentrated on: 1) analysis of geomechanical properties; and 2) preparation of an SEG Expanded Abstract. Siriwardane investigated the influence of a natural discrete fracture network on the growth of hydraulic fractures through the use of numerical modeling simulations. A literature review was performed to determine ranges for J1 and J2 natural fracture parameters. These parameters include fracture aperture and fracture spacing.

Project effort FY15 through March FY17: 4.5 FTE months.

Results & Discussion

Geophysical

Analysis of geomechanical properties

Inversion of 3D-3C data yields P- and S-acoustic impedances that can be combined to yield $\lambda\rho$ and $\mu\rho$ (e.g. Goodway et al., 1997; Hampson et al. , 2005; Russell, 2014; Sayers et al., 2015). λ and μ, Lamè's parameters, represent incompressibility and shear modulus, respectively. Interpretation of $\lambda\rho$-$\mu\rho$ volumes has been used recently to evaluate unconventional oil and gas shale reservoirs (see Alzate, 2012; Alzate and Devegowda, 2013; and Perez and Marfurt, 2014 and 2015). Alzate and Devegowda (2013) use $\lambda\rho$-$\mu\rho$ crossplots to identify organic rich and brittle sweet spots. They also associate lower Young's modulus with more organic rich intervals and lower Poisson's ratio with more brittle intervals.

In this study, the team computes $\lambda\rho$-$\mu\rho$ from log data for the Middle Devonian Hamilton Group and bounding Tully and Onondaga limestones taken from the vertical pilot well (Figure 2.1) drilled by Northeast Natural Energy, LLC on their Morgantown, WV well pad. They also compute brittleness using approaches proposed by Greiser and Bray (2007), Jarvie et al. (2007) and Wang and Gale (2009). The team then notes the results of a stimulation test and consider hydraulic fracture development within the context of these log derived parameters and mechanical properties. The stimulation tests are conducted using a geomechanical model developed from a comprehensive suite of logs collected in the vertical pilot well by Schlumberger (see Wilson et al., 2016).

Results indicate that the TOC (total organic carbon) rich Marcellus Shale is associated with lower Young's modulus, Poisson's ratio and lower values of $\lambda\rho$ and $\mu\rho$. High TOC intervals tend to be more brittle using both the Jarvie et al. (2007) and Wang and Gale (2009) approaches; however, brittle intervals are not confined to TOC rich zones. Model hydraulic fractures are, however, generally confined to TOC rich strata, while microseismic activity associated with shear failure of pre-existing natural fractures during treatment is distributed through the Hamilton Group.

Submission of Abstract for the 2017 Annual International SEG meeting (attached to the January through March 2017 Quarterly report):

The paper titled **"Relationships of $\lambda\rho$, $\mu\rho$, brittleness index, Young's modulus, Poisson's ratio and high TOC for the Marcellus Shale, Morgantown, West Virginia"** by *Thomas H. Wilson[*], Payam Kavousi, Tim Carr, West Virginia University; B. J. Carney, Northeast Natural Energy LLC; Natalie Uschner, Oluwaseun Magbagbeola and Lili Xu, Schlumberger,* was submitted to SEG for consideration.

The main conclusions of the paper are that in general, the TOC-rich lower Marcellus Shale is associated with the lower range of $\lambda\rho$, $\mu\rho$, a range that could be targeted in 3D-3C seismic data. Although the higher TOC zone is associated with higher brittleness index, it is not uniquely defined by it.

A specified range of $\lambda\rho$ and $\mu\rho$ parameters is often targeted as the sweet spot zone in 3D-3C seismic data sets (e.g. Alzate and Devegowda, 2013; Perez and Marfurt, 2015). Lower $\lambda\rho$ and $\mu\rho$ regions of unconventional shale reservoirs are generally thought to be more brittle and likely to provide enhanced permeability in response to hydraulic fracture treatment. In this study, the team examines the relationship of $\lambda\rho$ and $\mu\rho$ to brittleness and TOC. Comparison of the brittleness indices of Jarvie et al. (2007) and Wang and Gale (2009) suggest that the Jarvie et al. (2009) brittleness index is slightly higher than the Wang and Gale (2009) brittleness index in higher TOC lower Marcellus Shale. The lower $\lambda\rho$-$\mu\rho$ region is associated with the higher TOC lower Marcellus Shale, which also tends to be more brittle. The high TOC Marcellus Shale intervals in the Morgantown, WV area were confined to values of $\lambda\rho$ in the range of 12-25 GPa-g/cm3 and $\mu\rho$ in the range of 20-35 GPa-g/cm3 and to Young's moduli in the range of approximately 20-35GPa with Poisson's ratios varying approximately from 0.15 to 0.23.

The study also highlights that additional consideration should be given to the lower resolution seismic derived values of $\lambda\rho$ and $\mu\rho$. Smoothing of the $\lambda\rho$ and $\mu\rho$ values to approximate the loss in vertical resolution emphasizes that high TOC $\lambda\rho$-$\mu\rho$ regions extracted from 3D-3C seismic data will be less distinct than those indicated by finely sampled log data.

Stimulation tests indicate that hydraulic fractures are generally confined to the higher TOC Marcellus Shale, while microseismic monitoring during treatment revealed that microseismic events associated with shear failure of pre-existing natural fractures are distributed through the Hamilton Group and are largely limited in upward and downward growth by the Tully and Onondaga Limestones, respectively (see figures 2.1 and 2.2). The brittleness index (Grieser and Bray, (2007), not shown) indicates the Upper Hamilton Group is brittle as well, so rupture of natural fractures in this interval is expected.

Geomechanical

A parametric analysis on the effects of varying discrete fracture network aperture and spacing was performed. Based on the results from this analysis, the J1 fracture spacing (major axis) was chosen as 45 feet, and the J2 fracture spacing (minor axis) was chosen as 15 feet. The J1 and J2 fracture apertures were chosen as 0.2 mm and 0.14 mm, respectively. All of these values are within the ranges seen in the literature and allow for fracture growth closest to what has been reported in the microseismic data.

After establishing these parameters to ensure that the values were in ranges established in the literature, previous fracture propagation calculations were updated and new fracture geometries were obtained. Fracture propagation calculations were performed for a new stage, as well.

Table 2.1 shows the updated fracture geometries for MIP-3H stages 1 through 4. Figure 2.1 shows the fracture geometry for one of the primary induced hydraulic fractures in stage 4 of well MIP-3H. Figure 2 shows the cumulative proppant mass versus time (model vs measured), Figure 3 shows the slurry volume injected versus time (model vs measured), and Figure 2.4 shows the surface pressure versus time (model vs measured) for well MIP-3H. These figures show a good match between the numerical model and the reported data.

Table 2.1: Updated Fracture Geometries

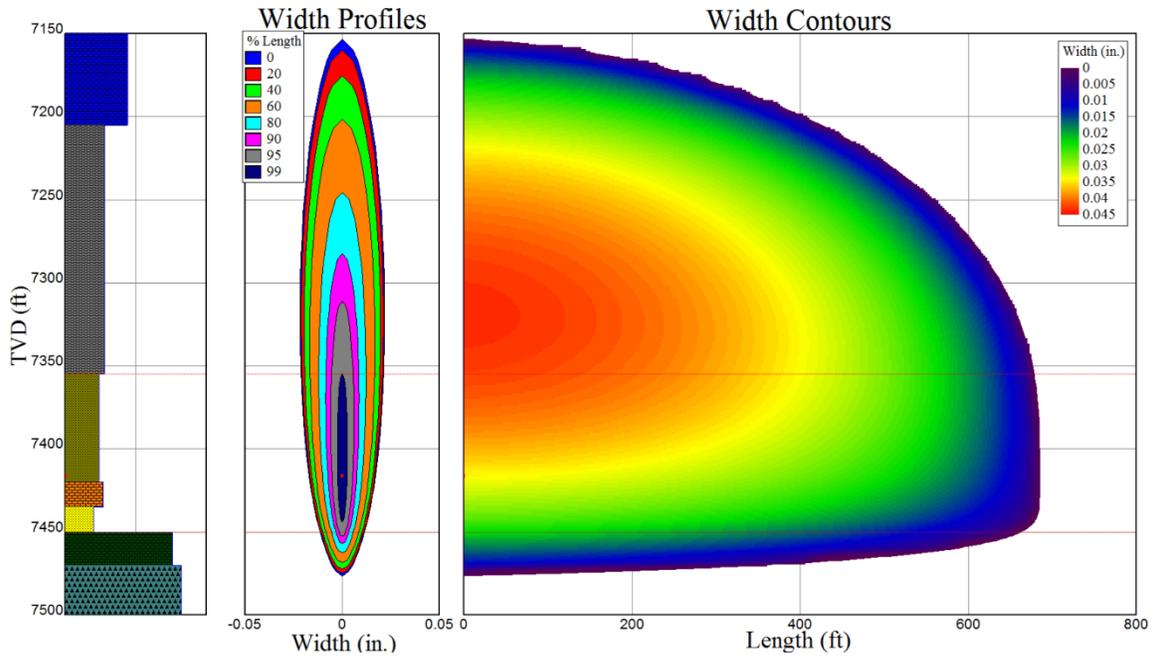| STAGE	Fracture Half-Length (ft)	Fracture Height (ft)	Average Fracture Width (in)
1	704.1	347.6	0.028428
2	664.2	329.8	0.028889
3	660.5	329.4	0.028885
4	685.7	325.2	0.026988

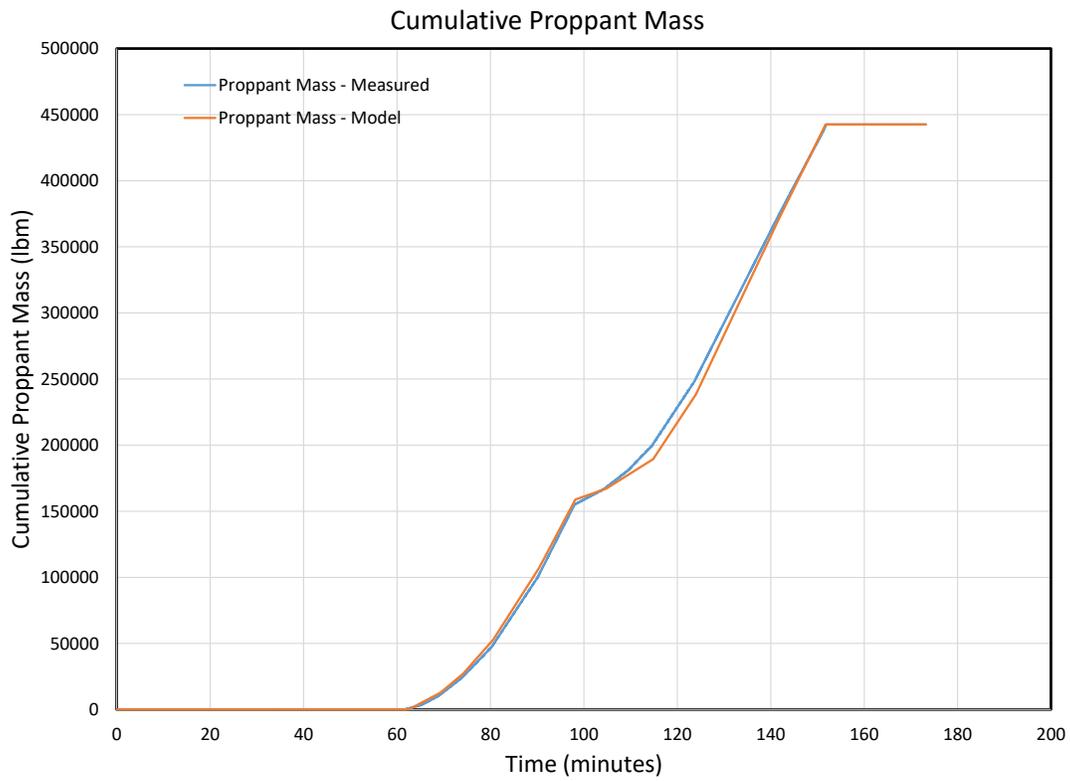**Figure 2.1: Fracture Geometry for Stage 4 - MIP 3H**

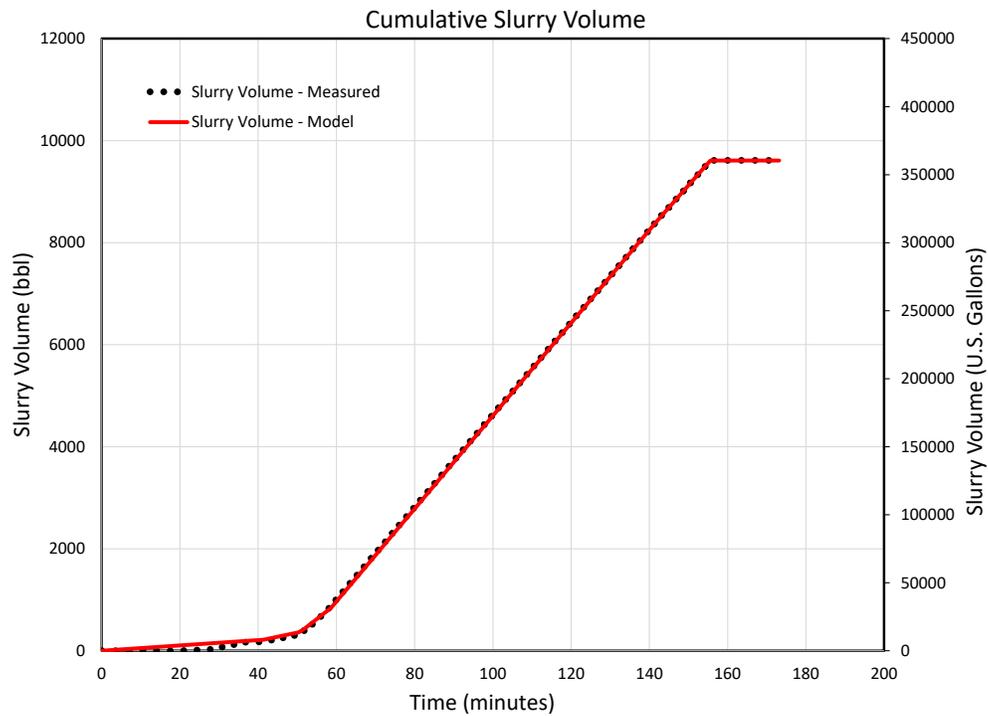**Figure 2.2: Cumulative Proppant Mass for Stage 4 - MIP 3H**

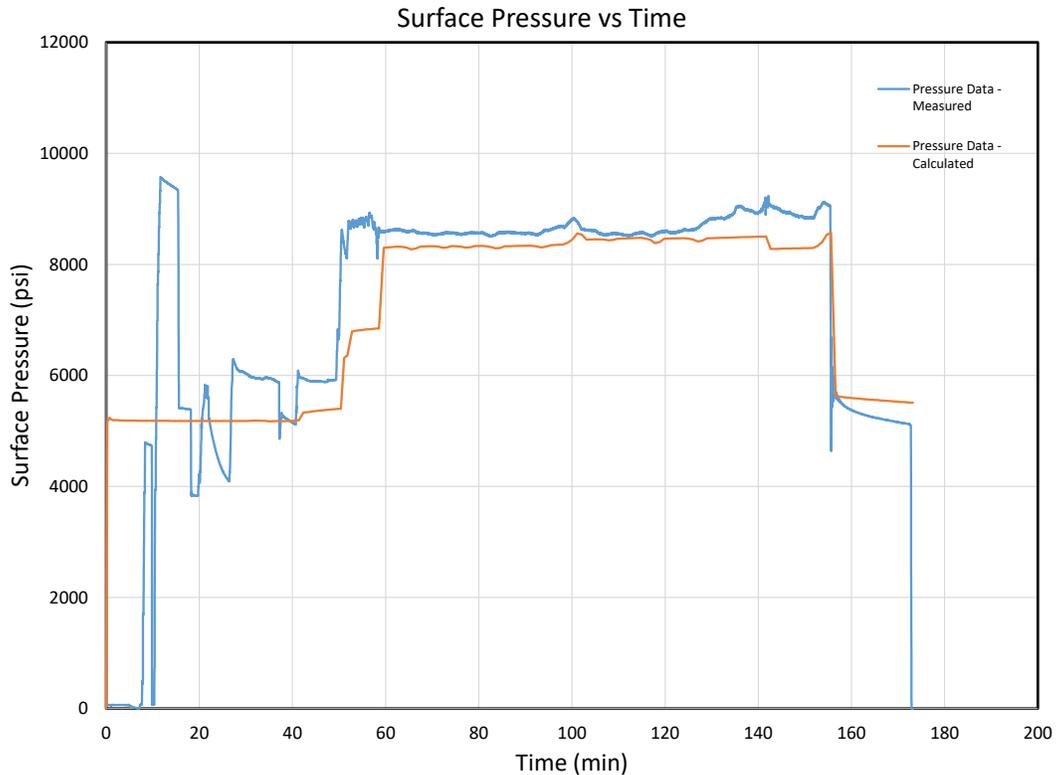**Figure 2.3: Cumulative Slurry Volume for Stage 4 - MIP 3H**

Figure 2.4: Surface Pressure versus Time for Stage 4 - MIP 3H

Products

Submission of Abstract for the 2017 Annual International SEG meeting:

The paper titled "Relationships of λρ, μρ, brittleness index, Young's modulus, Poisson's ratio and high TOC for the Marcellus Shale, Morgantown, West Virginia" by *Thomas H. Wilson[*], Payam Kavousi, Tim Carr, West Virginia University; B. J. Carney, Northeast Natural Energy LLC; Natalie Uschner, Oluwaseun Magbagbeola and Lili Xu, Schlumberger,* was submitted to SEG for consideration.

Plan for Next Quarter

Geophysical

With 4.5 FTE months invested in the project, the remaining effort will include examination of the influence of stress gradients inferred from the unconventional fracture model stimulation tests (Wilson et al., 2016 [see http://library.seg.org/doi/pdf/10.1190/segam2016-13866107.1] and Wilson et al., submitted). This effort was interrupted by the need to undertake a detailed consideration of geomechanical properties noted above. With limited remaining time, we will continue to explore how the hydraulic fractures behave across the interpreted zone of mechanical weakness between the 3H and 5H wells. The limited height growth observed in the hydraulic

fracture simulations will also be examined. Variations in model geomechanical properties will be explored to determine their effect on height growth and half length.

Geomechanical

The modeling study will continue with the use of assumed natural discrete fracture network, which was presented in this report to investigate other stimulation stages at well MIP 3H through the use of available information on the hydraulic fracturing field parameters (fluid volumes, pumping rate, proppant schedule, and geophysical data). Results presented in this report show that the computed fracture heights are higher than those which were computed without discrete fracture networks and are closer to the height of the microseismic data cloud. The analysis of microseismic data will be continued and a comparison of fracture geometries will be made with available microseismic data.

Topic 3 – Deep Subsurface Rock, Fluids, & Gas

Approach

The main focus of the subsurface team led by Sharma this quarter was to analyze core, fluid and gas samples collected from the MSEEL site. Members of Sharma's lab group (Dr. Warrier and Mr. Wilson) and Dr. Hanson from Mouser's lab group continue to coordinate and supervise all sample collection. Samples were also distributed to research team at OSU and NETL for analysis under different sub-tasks. Several talks and presentations were given at local and regional conferences /universities.

Results & Discussion

Progress on Sidewall Core, Vertical Core & Cutting Aanalysis

The sidewall cores are curated at OSU and WVU. Based on the geophysical logs, eight samples were selected from different lithologies, i.e. zones where we expect to see maximum biogeochemical variations. Samples were homogenized and distributed among different PI's, and are currently being processed for biomarker, isotope analysis, elemental analysis, porosity/pore structure, and noble gas analysis. For whole core analysis, cores were taken from 1-foot intervals through the 111 feet of whole vertical core. Samples were ground homogenized and distributed to different groups at WVU, OSU and NETL for different analysis.

In **Sharma's Lab** PhD. student Rawlings Akondi submitted a research paper summarizing the results of the optimized method developed to extract lipid biomarkers (indicative of live and dead microbes) from deep shales, and worked on the reviewer's comments on the paper. These methodological improvements would be very useful for recovering a diverse lipid pool from pristine deep shale cores. Another PhD. student of Sharma, Vikas Agrawal, developed an improved method for isolating kerogen from shales. The goal was to standardize the kerogen isolation procedure to extract the maximum amount of unaltered kerogen with effective removal of soluble organic matter, carbonates, silicates and heavy minerals from sidewall cores of MIP 3H well from MSEEL. The major problems faced in kerogen isolation were low yield of kerogen, formation of neo-fluorides on reaction with HF, and ineffective dissolution of carbonate, silicates and heavy minerals (as shown by XPS survey spectra in Fig. 3.1). The solution in all the extraction steps was filtered using a Polypropylene (PP) filtration assembly for acidic solutions and glass filtration

assembly for organic solutions. Formation of neo-fluorides was due to prolonged treatment of shale samples with HF. To overcome this limitation, HF reactions were carried out multiple times for shorter durations at higher temperatures. Additionally, after each reaction, the solution was then neutralized using NH_4OH and rinsed multiple times with DI water to remove all the fluorides. It was also discovered that some amount of carbonate minerals were bound to silicate minerals, leading to ineffective removal of carbonate minerals. To overcome this step, after the HF step, shale residue were treated again with HCl. for effective removal. To maximize the yield of kerogen and for the effective removal of heavy minerals (including pyrite), a physical separation step was standardized by varying the density of $ZnBr_2$ solution. After this modification, the yield of kerogen and purity of kerogen changes drastically, as shown in Figure 3.1. The pure kerogen will now be studied using ^{13}C NMR, XPS and FTIR to understand physical and molecular characterization of kerogen needed for flow/resistivity models and better estimation of gas in place and hydrocarbon potential.
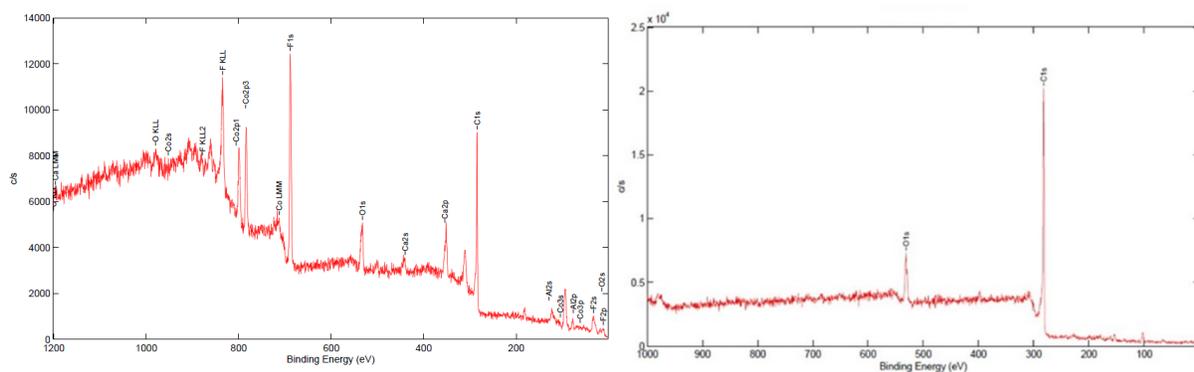

Figure 3.1a.XPS survey spectra of kerogen from Marcellus shale showing peaks of fluoride, calcium, heavy metal cobalt and aluminum. It shows formation of neo-fluorides and ineffective isolation of kerogen and **1b)** XPS survey spectra of kerogen after using the new method. Note all other minerals except kerogen has been removed from shale matrix

In **Cole's Lab,** large field backscattered electron (BSE) maps have been acquired for polished thick sections of core samples TL 36 (Tully Limestone, depth 7200') and MT 16 (Upper Marcellus, depth 7543.0'). These data provide a large-area mineralogy/fabric analyses of core samples viewed perpendicular to bedding. QEMSCAN mineral maps (several 1 mm^2 fields) also have been measured from polished thick sections of OM-rich samples MT 25 (Marcellus Top, depth 7451.5') and ML 10 (Lower Marcellus, depth 7543.0'), allowing quantification of modal (volume percent) mineralogy and large OM features (Figures 3.2 a and 2b).
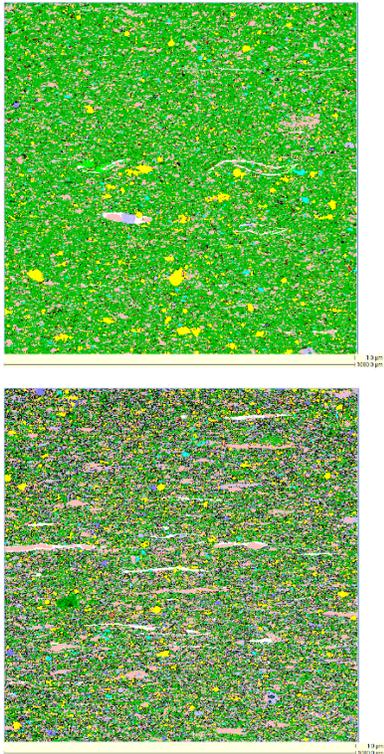
Figure 3.2a. QEMSCAN mineral map of 1 mm² region of **MT 25** (Marcellus Top, depth 7451.5'). Green matrix is composed mainly of illitic clay (63.2 %); pink is quartz (21.5 %); yellow is pyrite (5.8 %); cyan is albite (1.8 %); mica (2 %) as biotite (brown), muscovite and glauconite (dark green); OM is white (1.2 %), light green is Fe-chlorite (0.6 %), red is titania (0.5 %); lavender is calcite (0.3 %) unclassified mixed pixels are black (4.1 %). Remaining < 1% includes Ca-phosphate, dolomite, K-feldspar, gypsum/anhydrite. Some of the titania (anatase or rutile) will require cross-checking for barium (barite), as there is overlap of EDXS spectral lines for barium and titanium. **2b)** QEMSCAN mineral map of 1 mm² region of **ML 10** (Lower Marcellus, depth 7543.0'). Compared to Marcellus Top, this hydraulic fracturing target is very different in mineral composition and texture. Same color scheme for minerals as in **Figure 3.1,** including illitic clay (25.7 %); quartz (25.2 %); unclassified mixed pixels (22.5 %); calcite (10.3 %); pyrite (8.8 %); albite (1.6 %); OM (3.4 %), gypsum/anhydrite is purple (1 %), dolomite (0.7 %). Remaining < 1% includes small quantities of mica as biotite, muscovite and glauconite; titania; Ca-phosphate, and K-feldspar. Some of the titania pixels (anatase or rutile) will require cross-checking for barium (barite), as there is overlap of EDXS spectral lines for barium and titanium. Work also remains to decipher the large number of unclassified mixed pixels for this sample.

In **Mouser's Lab** Andrea participated in sampling the biomass and lipids from several sections of the liner during production logging that occurred this quarter. Those samples were distributed to Mike and Kelly, and will be extracted for intact lipids. Andrea also collected samples from MSEEL wells (MIP 3H and 5H) before and after production logging, and ran the geochem on those samples and distributed them to the team. Andrea has made significant progress on LC-MS analysis of lipids from the cores and fluids. She has identified core archaeal lipids in the Tully shale, and intact lipids in drill muds and well fluids 200+ days post production. She will be returning to Germany to finalize her analysis in May 2017. They expect to wrap up a publication in early summer.

Wrighton's Lab received the sequencing data from pristine sidewall core samples and all sequencing data were quality checked, filtered and assembled. Comparison of core material samples to control samples did not show any clear genomic signatures for indigenous microbial life in the MIP3H well.

Progress on Produced Fluid and Gas Analysis

Produced water samples were collected in 5 gallon carboys every 6 weeks. The samples were then transported, filtered and processed in Sharma Laboratory at WVU. All water samples were collected in different containers using different methods/ preservatives etc. specified for different kinds of analysis. All PI's at OSU and NETL provided their detailed sampling instructions. Dr. Warrier and Dr. Wilson from WVU, and Hanson from OSU, were primarily in charge of sample collection and distribution among different PI's at WVU, OSU and NETL. The collected fluids are currtely being processsed for biomass, reactive chemistry, organic acids, and noble gas and stable isotope analysis at different institutes.

Sharma Lab continues to analyze O, H, and C isotopic composition of produced fluids collected from 3H and 5H. In addition, 11 carbonate vein samples in and around the landing zone were

analyzed as a possible source of initial DIC enrichment seen in both wells, returning values less enriched than the produced water ruling out carbonate dissolution adjacent to the wellbore as a contributor to the DIC spike. Ongoing investigation includes sampling from microbial isolates with chemicals found in fracturing fluid provided by the Wrighton lab at OSU to determine microbial contribution to the DIC enrichment.
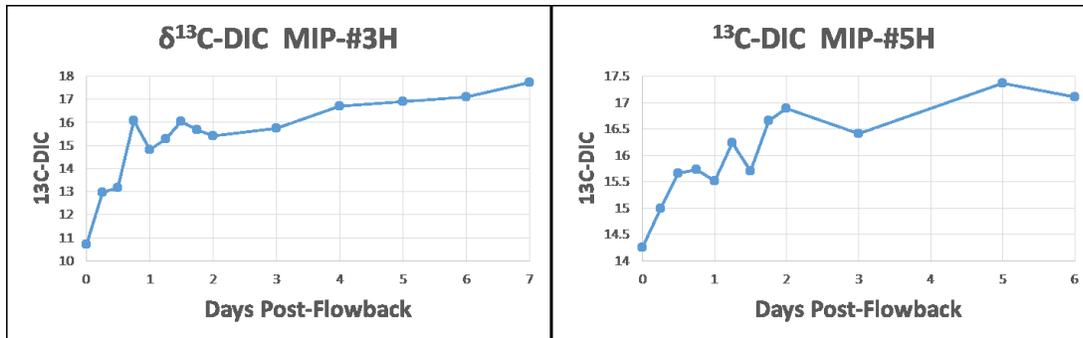

Figure 3.3 Graphs showing evolution of carbon isotopic composition of produced water in wells 3H and 5H.

18O/D analysis has been completed on all samples to date. Both 3H and 5H plot similar trends, showing an 18O shift to more enriched values from the Local Meteoric Water Line indicative of high temperature exchange within the formation. Molecular and isotopic composition of CH_4 and CO_2 of produced gas sampled concurrently with produced water is underway to constrain methanogenic pathways. Results to date were presented at GSA Joint Sectional Meeting in Pittsburgh, PA on March 19th.

Wrighton's Lab received metagenomic sequencing data for seven produced water samples from wells MIP3H and MIP5H. The data is currently being analyzed, and binned genomes are being compared to other wells in the database. Multiple publications based on these data are being prepared with submissions anticipated in the last half of 2017. The team selected 10 additional produced water samples (MIP3H, MIP5H) for metagenomic sequencing. DNA extractions are currently underway with data expected June 2017. Metabolite analyses from produced fluid samples (paired to metagenomic samples) were sent to Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory for NMR metabolite analysis. Data is expected in April 2017. They are currently testing the salinity tolerance of the dominant methane-producing microorganism (Methanohalophilus species) isolated from the MIP3H well. The genome of the isolate is being sequenced with data anticipated in May 2017.

Analysis of fluid samples from the MIP 3H and 5H wells continues in **Cole Lab**. Several of the samples were re-analyzed in duplicate at different dilutions to determine reproducibility of the analysis. The team has also tried to analyze some of the flowback fluids for other nitrogen compounds, however, results were inconclusive due to the complex chemistry of the fluids. Data reduction from samples analyzed by IC, ICP-MS continues. They have been reviewing the raw data, trying to identify and quantify trace species that are present in the flowback fluid. Several of the flowback filters from the 3H and 5H, as well as those from the 4H and 6H, were analyzed by SEM. Results show that microbial cells are present on the filters, although their distribution is sparse. Mineral precipitates on the filters are dominated by NaCl and $BaCl_2$, making it difficult to image cells. Analysis of filters that were rinsed more thoroughly still show some $BaCl_2$, suggesting that it may be present in suspension in the fluids.

Darrah's Lab continued time-series analysis of fluid samples collected monthly from the MIP 3H and 5H wells. Some initial graphs and results from Ne and Ar analysis are pasted below:
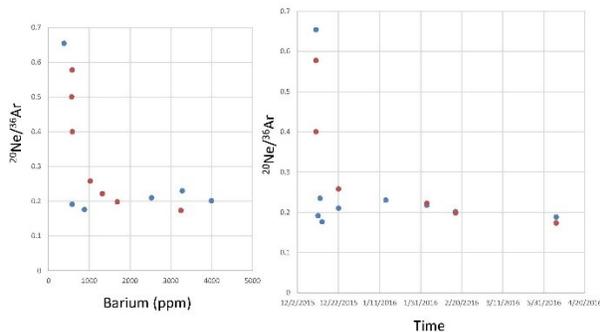

$^{20}Ne/^{36}Ar$ vs. Barium and time

Figure 3.4. 20Ne/36Ar vs. Barium (left) and Time (Right). The 20Ne/36Ar is a sensitive tracer of water contributions and gas-water interactions. The data demonstrate that within approximately one month of production, the atmospheric components have been removed from the system and that we are accessing natural gas derived from the shale gas reservoir. Ongoing numerical modelling is using these measurements to determine gas in place and gas-water interactions that occur in the Marcellus.

Products

1) Wilson T, and Sharma S. 2017. Inferring biogeochemical interactions in deep shale reservoirs at the Marcellus Shale Energy and Environment Laboratory (MSEEL). Joint 52nd northeastern annual section/ 51st north-central annual section meeting March 19-21, Pittsburgh, PA.

2) Akondi R, Trexler R, Pfiffner SM, Mouser PJ, Sharma S 2017. An Improved Lipid Extraction Method for Deep Subsurface Shale. Frontiers in Microbiology (in review)

Plan for Next Quarter

Sharma's Lab

The pure kerogen will now be studied using 13C NMR, XPS and FTIR to understand physical and molecular characterization of kerogen needed for flow/resistivity models and better estimation of gas in place and hydrocarbon potential.

Cole's Lab

Work will continue on the quantification of modal (volume percent) mineralogy and large OM features. Analysis of fluid samples from the MIP 3H and 5H wells continues.

Mouser's Lab

Andrea will be returning to Germany to finalize her LC-MS analysis of lipids from the cores and fluids in May 2017. They expect to wrap up a publication in early summer.

Wrighton's Lab

The team will continue analyzing metagenomic sequencing data, and binned genomes are being compared to other wells in the database. Multiple publications based on these data are being prepared with submissions anticipated in the last half of 2017. . DNA extractions are currently underway for 10 additional produced water samples (MIP3H, MIP5H) for metagenomic sequencing, with data expected June 2017.

Darrah's Lab

They will continue numerical modelling is using the measurements outlined above to determine gas in place and gas-water interactions that occur in the Marcellus.

Topic 4 – Environmental Monitoring – Surface Water & Sludge

Approach

The Marcellus Shale Energy and Environment Laboratory (MSEEL) is the first comprehensive field study, coupling same site environmental baseline, completion and production monitoring with environmental outcomes. One year into the post-completion part of the program, the water and solid waste component of MSEEL has systematically sampled flowback and produced water volumes, hydraulic fracturing fluid, flowback, produced water, drilling muds, drill cuttings and characterized their inorganic, organic and radio chemistries. In addition, surface water in the nearby Monongahela River was monitored upstream and downstream of the MSEEL drill pad. Toxicity testing per EPA method 1311 (TCLP) was conducted on drill cuttings in both the vertical and horizontal (Marcellus) sections to evaluate their toxicity potential.

Previous findings

The MSEEL wells used green completion strategy, including a synthetic-based drilling fluid (Bio-Base 365). All drill cutting samples fell below TCLP thresholds for organic and inorganic components, indicating that they are non-hazardous per the Resource Conservation and Recovery Act. Maximum specific isotopic activity in drill cuttings was recorded for ^{40}K, which was 28.32 pCi/g. Gross alpha accounted for the highest reading at 60 pCi/g. The maximum combined radium isotope values were 10.85 pCi/g. These radioactivity levels are within the background range for the region.

The composition of the hydraulic fracturing (HF) fluids in both wells was similar to the makeup water which was drawn from the Monongahela River. Its chemistry was typical of Monongahela River water. This is true of inorganics, organics and radio chemicals. Organic surrogate recoveries were in the range of 90 to 104%, indicating good quality control at the analytical laboratory. There was no evidence that Monongahela River quality was influenced by well development, completion or production at the MSEEL site.

Produced water is severely contaminated, indicating care in handling. Concentrations of all parameters increased through the flowback/produced water cycle. $^{226+228}$Ra reached 20,000 pCi/L at post completion day 251, indicating an important trend that will be carefully assessed in ongoing monitoring.

Methods

Table 4.1 summarizes the produced water sampling schedule for the quarter. Produced water samples were taken at the upstream end of each well's separator.

Table 4.1: Sampling schedule for the quarter.

	Freshwater		Aqueous/Solids: drilling/completion/production							Sampling Dates	Sampling Notes
	Mon River	Ground water	HF fluid makeup	HF fluids	flowback/ produced	drilling fluids	drilling cuttings/ muds	total aqueous	total solids		
Flowback @ 57 weeks - 3H					1			1		1/13/2017	one sample 3H
Flowback @ 57 weeks - 5H					0			0		-	no sample (5H not producing)
Flowback @ 215* Weeks - 4H					1			1		1/13/2017	one sample 4H
Flowback @ 215* Weeks - 6H					1			1		1/13/2017	one sample 6H
Flowback @ 61 weeks - 3H					1			1		2/14/2017	one sample 3H
Flowback @ 61 weeks - 5H					2			2		2/14/2017	two samples 5H
Flowback @ 219 weeks - 4H					1			1		2/14/2017	one sample 4H
Flowback @ 219 weeks - 6H					1			1		2/14/2017	one sample 6H
Flowback @ 65 weeks - 3H					1			1		3/13/2017	one sample 3H
Flowback @ 65 weeks - 5H					1			1		3/17/2017	one sample 5H
Flowback @ 223 weeks 4H					1			1		3/17/2017	one sample 4H
Flowback @ 223 weeks 6H					1			1		3/17/2017	one sample 6H

Analytical parameters

Analytical parameters are listed in tables 4.1 and 4.2.

Table 4.2: Aqueous analytical parameters

Aqueous chemistry parameters - HF fluids and FPW***						
Inorganics				Organics	Radionuclides	
	Anions	Cations*				
pH	Br	~~Ag~~	Mg	Benzene	α	
TDS	Cl	Al	Mn	Toluene	β	
TSS	SO_4	As	Na	Ethylbenzene	^{40}K	
Conductance	sulfides	Ba	Ni	Total xylene	^{226}Ra	
Alkalinity	nitrate	Ca	Pb	m,p-xylene	^{228}Ra	
Bicarbonate	nitrite	Cr	Se	o-xylene		
Carbonate		Fe	Sr	MBAS		
TP		K and Li	Zn	O&G		

Table 4.3: Analytical parameters drill cuttings and mud.

Solids chemistry parameters - Cuttings & Muds									
Inorganics				Organics	Radionuclides	TCLPs			
	Anions	Cations*							
alkalinity**	Br	Ag	Mg	Propane	α	Arsenic	1,4-Dichlorobenzene	Methly ethyl ketone	
conductance	Cl	Al	Mn	DRO	β	Barium	1,2-Dichloroethane	Nitrobenzene	
pH	SO_4	As	Na	ORO	^{40}K	Benzene	1,1-Dichloroethylene	Pentrachlorophenol	
bicarbonate**	sulfide	Ba	Ni	GRO	^{226}Ra	Cadmium	2,4-Dinitrotoluene	Pyridine	
carbonate**	nitrate	Ca	Pb	Ethylbenzene	^{228}Ra	Carbon tetrachloride	Endrin	Selenium	
TP	nitrite	Cr	Se	m,p-xylene		Chlordane	Heptachlor	Silver	
		Fe	Sr	o-xylene		Chlorobenzene	Heptachlor epoxide	Tetrachloroethene	
		K	Zn	Styrene		Chloroform	Hexachlorobenzene	Toxaphene	
				Toluene		Chromium	Hexachlorobutadiene	Trichloroethylene	
				Total xylenes		o-Cresol	Hexachlororethane	2,4,5-Trichlorophenol	
				TOC		m-Cresol	Lead	2,4,6-Trichlorophenol	
				COD		p-Cresol	Lindane	2,4,5-TP (Silvex)	
				O&G		Cresol	Mercury	Vinyl chloride	
						2,4-D	Methoxychlor		

Results & Discussion

Produced water volume trends in wells MIP 3,5H and MIP 4,6H.

NNE's water production logs were used to estimate produced water volumes. While water production rates were similar in the first two months post completion, cumulative water production rates soon diverged, yielding very different curves for each well (figure 4.1). It is noted that the older wells (4H, 6H) were shut in between 12 Dec 15 and 17 Oct 16, an interval of 315 days.

The proportion of hydrofrac fluid returned as produced water, even after 1844 days (5 years) was only 12% at MIP 4H and 7.5% at MIP 6H (Table 4.4). The reason for the variation among wells, respective to both cumulative and proportional produced water returns, remains an unanswered question.
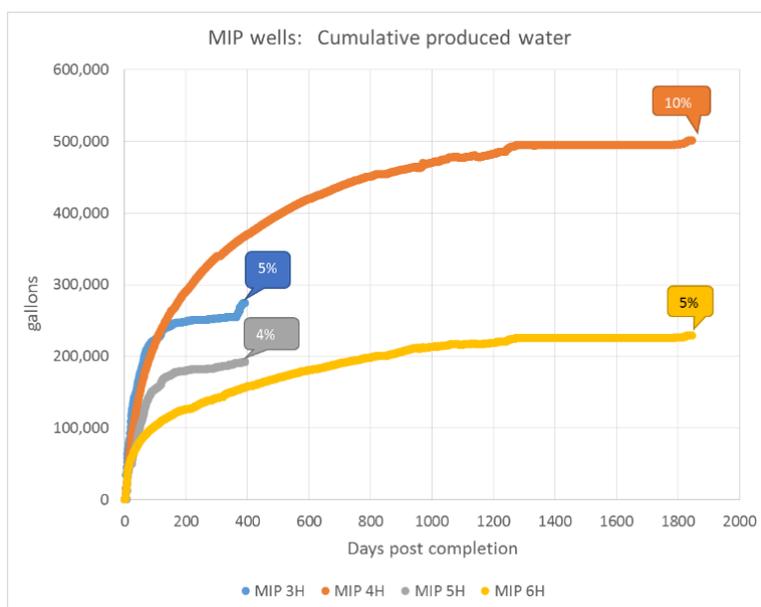

Figure 4.2: Cumulative water production at the four MSEEL wells. The estimated proportion of produced water to HF fluids are shown in the callouts.

Table 4.4: Produced water volumes relative to injected HF fluid for each MSEEL well.

	days post completion	cumulative produced water		HF injected
		gal	% injected	gal
MIP 3H	392	274,102	2.6%	10,404,198
MIP 5H	392	192,134	2.0%	9,687,888
MIP 4H	1844	501,396	12.0%	4,160,982
MIP 6H	1844	229,183	7.5%	3,042,396

Trends in produced water chemistry

Major ions

While makeup water was characterized by low TDS (total dissolved solids) and a dominance of calcium and sulfate ions, produced water from initial flowback is essentially a sodium/calcium chloride water (figure 4.2). Other than slight increases in the proportion of barium and

strontium, the ionic composition of produced changed very little through 314 days post completion.
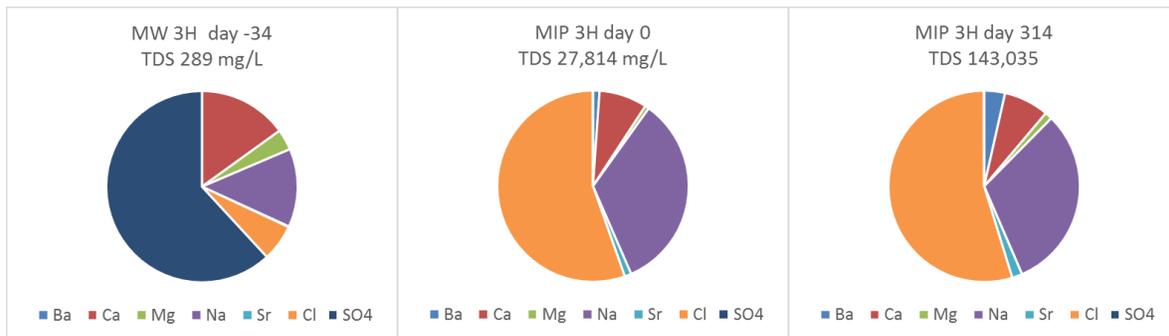

Figure 4.3: Changes in major ion concentrations in produced water from well MIP 3H. From left to right the charts represent makeup water from the Monongahela River, produced water on the first day of flowback and produced water on the 314th day post completion.

In fact, after 1858 days ionic composition remained nearly identical to the initial produced water (figure 4.3).
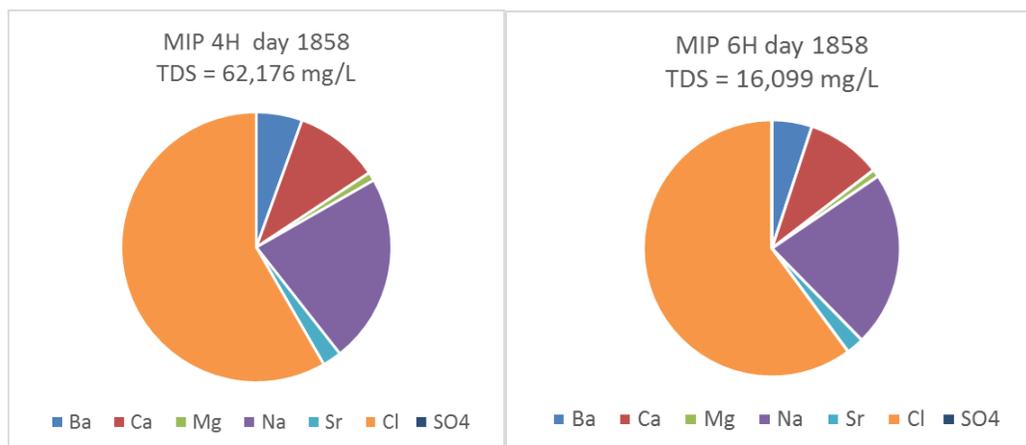

Figure 4.4: Major ion composition of wells MIP 4H and 6H 1858 days after completion.

While TDS increased rapidly over the initial 90 days post completion, it appears to have levelled off between 100,000 and 150,000 mg/L (figure 4.4). The older 4H and 6H wells offer insight into the longer term TDS trend. Those wells only came back on line during this quarter after a shut in period of 315 days. Those results vary but they are much lower than the current values for wells MIP 3H and 5H.
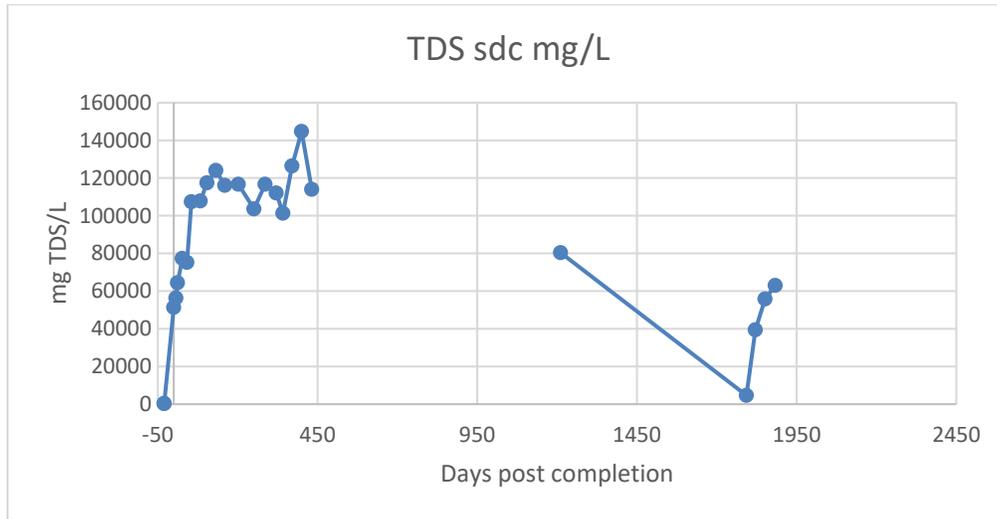
Figure 4.5: Changes in produced water TDS sdc (sum of dissolved constituents) through the first 432 days post completion (3,5H) and days 1211 through 1883 (4,6H).

Water soluble organics

The water soluble aromatic compounds in produced water: benzene, toluene, ethylbenzene and xylene were never high. With one exception at post completion day 321, benzene has remained below 30 µg/L (figure 4.5). This seems to be a characteristic of dry gas geologic units. After five years, benzene has declined below the drinking water standard of 5 µg/L.
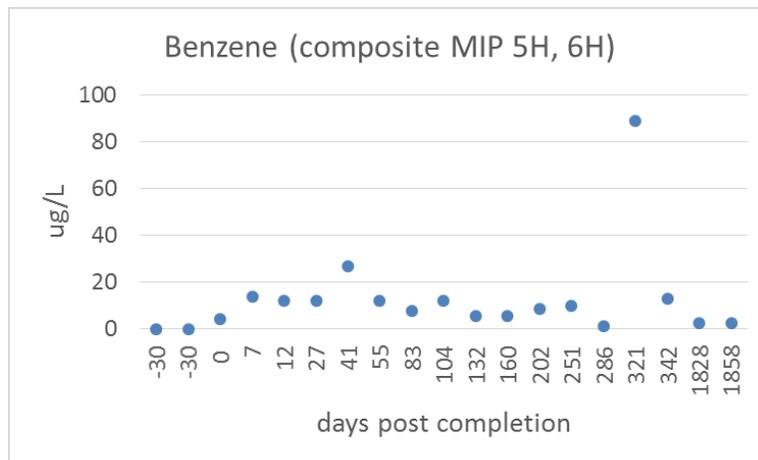

Figure 4.6: Changes in benzene concentration. The figure shows data from well 5H through the first 342 days post completion, followed by results from well 6H.

Radium isotopes

Radioactivity in produced water

Radium concentrations generally increaseded over the 314 days post completion at wells MIP 3H and 5H. Maximum levels of the radium isotopes reached about 20,000 pCi/L at the unchoked 3H well and about half that amount at 5H.
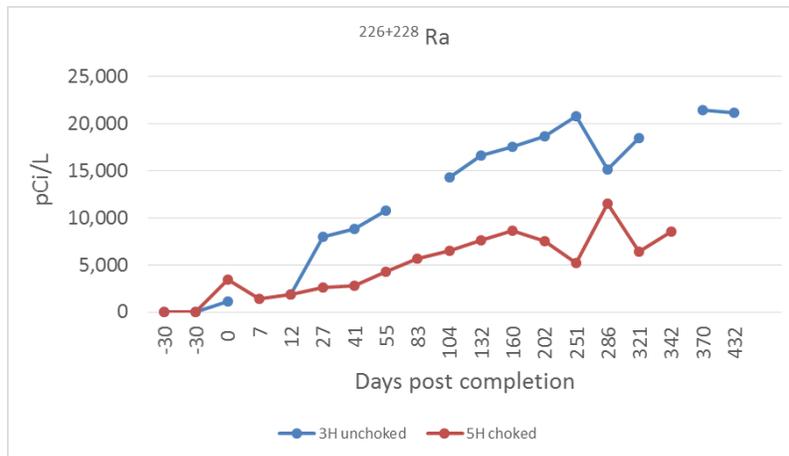
Figure 4.7: The radium isotopes are plotted against days post well completion. Well 5H was choked periodically. It produced less water and lower concentrations of radium.

At the older wells MIP 4H and 6H, all isotope concentrations declined to low levels, often below the MDC (minimum detectable concentration) (table 4.5). This, like the apparent decline in TDS at the older wells is an interesting result and, if sustained by future sampling, would suggest exhaustion of contaminant reserves within the fracture field.

Table 4.5: Radiochemistry of the older wells 4H and 6H at 1828 (5 years) days post completion.

		16-Nov-16 MIP 4H days post completion: 1828			16-Nov-16 MIP 6H days post completion: 1828		
		act[1]	unc[2]	mdc[3]	act[1]	unc[2]	mdc[3]
α	pCi/L	228.0	53.6	27.2	57.7	10.9	1.6
β	pCi/L	48.7	20.1	29.2	7.4	1.6	0.8
^{226}Ra	pCi/L	353.3	260.6	309.2	199.3	333.5	390.3
^{228}Ra	pCi/L	31.1	31.9	48.6	0.0	20.9	54.6
^{40}K	pCi/L	49.7	95.5	102.7	0.0	21.9	151.4

[1] activity

[2] +/- uncertainty

[3] minimum detectable concentration

<u>Solid waste</u>

The TCLP (toxicity characteristics leaching procedure) or USEPA method 1311 is prescribed under the Resources Conservation and Recovery Act (RCRA) to identify hazardous solid waste. TCLP was applied to thirteen drill cutting samples, twelve from MIP 3H and 5H and one from another well in western Monongalia County. All three wells had been developed using green, synthetic drilling fluid. All samples fell below the TCLP criteria for hazardous waste and would be classified under RCRA subtitle D. Bio-Base 365 drilling fluid (Shrieve Chemical Products,

Inc.) had been used at the MSEEL wells and ABS 40 (AES Drilling Fluids Inc.) was used at the other well.

Products

Plan for Next Quarter

The team will continue to sample and analyze flowback/produced water (FPW) from wells MIP 3H, 4H, 5H and 6H. With the older wells (4H, 6H) back on line we will use their produced water to extent the prediction range of the newer wells (3H, 5H). This will allow them to focus on long term trends, geochemical analysis and generation of journal publications.

Topic 5 – Environmental Monitoring: Air & Vehicular

Approach

This quarter, the results from the trace metals analysis were presented as a poster entered in the Van Liere poster competition sponsored by the WVU Health Sciences Center. The poster won in its category of Community and Translational Sciences. A synopsis of the poster, titled Use of Trace Elements for Estimating Community Exposure to Marcellus Shale Development Operations by Maya Nye, Michael McCawley, Alex Dzomba and Travis Knuckles of WVU and James Ross, of Columbia University, is included.

Results & Discussion

Synopsis

Since 2009, unconventional natural gas drilling (UNGD) has significantly increased in the Appalachian region of the United States with the exploration of the Marcellus Shale gas formation. Elevated concentrations of particulate matter <2.5 μm (PM2.5), have been documented in areas surrounding drilling operations during well stimulation (otherwise known as hydraulic fracturing or "fracking"). As such, many Appalachian communities are experiencing increased industrial activities and possible air pollutant exposures from nearby shale gas extraction activities. Recent epidemiological studies have associated emissions from UNGD with health effects based on distances from the well pads though little progress has been made in targeting the exposure agent(s). In this study, we collected samples of PM2.5 on PTFE filters at three points downwind (1, 2 and 7 km) of a Marcellus Shale gas well pad in Morgantown, West Virginia during an 8-day hydraulic fracturing stimulation process. The filters were analyzed for trace elemental content via inductively coupled plasma mass spectrometry (ICP-MS). Further analysis was conducted using an experimental model incorporating wind patterns to determine which elements could be traced downwind of the UNGD site. Previous studies of UNGD operations indicated that 1km might be the extent of measurable emissions from the well pad. Results of this study seem to indicate that well pad emissions may be measurable at distances of at least 7 km. Magnesium (Mg) concentrations, in correspondence with wind patterns, were consistently proportional to other elements (barium, strontium, vanadium) at each sampling site. These data suggest that Mg may be a good trace element to detect the reach of emissions from

UNGD point sources in the Marcellus Shale region, allowing even complex topographic and meteorological conditions to be modeled and confounding sources of similar emissions to be discounted. Additionally, the data appear to lend credence to recent epidemiological studies showing effects of UNGD as far out as 15 km and suggest that UNGD air emissions may be an exposure agent to communities living even some distance from UNGD facilities. Future studies are needed to further explain the off-site reach of UNGD emissions and to characterize their potential toxicity.

Conclusions presented on poster

1. Mg may serve as a good trace element to detect the reach of emissions from UNGD point sources in the Marcellus Shale region allowing even complex topographic and meteorological conditions to be modeled and confounding sources of similar emissions discounted. Magnesium (Mg) concentrations were consistently proportional to other elements (Ba, Co, Sr, V) at each sampling site for included sample periods.

2. The data appear to lend credence to recent epidemiological studies showing effects of UNGD as far out as 15 km and suggest that UNGD air emissions may be an exposure agent to communities living even some distance from UNGD facilities.

3. Future studies are needed to further explain the off-site reach of UNGD emissions.

Products

McCawley M, Dzomba A, Knuckles T, and Nye M. 2017. Use of trace elements for estimating community exposure to Marcellus shale development eperations. Poster presented at: Van Liere Poster Competition. WVU Health Sciences Center; 2017; Morgantown, WV.

Plan for Next Quarter

Topic 6 – Water Treatment

Approach

The team's first research activity of produced water treatment focuses on developing an (bio)electrochemical method to remove scale-forming cations as a pre-treatment system for produced water treatment. A two-chamber bioelectrochemical system used in this study contained an anode and cathode chambers separated by a cation exchange membrane. Each chamber contained graphite woven felt electrodes. An electric current was used to create a pH unbalance between the anode and cathode. The high-pH cathlyte was then used to treat raw produced water to remove multi-valent cations as a softening process. Produced water sample was collected at the MSEEL site and used in the study. The treatment method was shown to be effective in removing scale-forming cations.

From January to March 2017, the water treatment team tested anolyte and catholyte in continuous mode with a CMI-7000 cation exchange membrane (CEM) and Nafion-115 CEM using different currents of 300 mA to 900 mA.

Results & Discussion

Electrolytic production of high-pH catholyte for produced water softening

A two-chamber electrolysis cell design was tested in this task (Figure 6.1). It consisted of anode and cathode chambers separated by a cation exchange membrane (CMI-7000, Membrane International Inc., Ringwood, USA). The anode and cathode chambers contained a dimensionally stable anode (DSA) electrode (geometric dimension of 5.5 x 5.5 cm^2, 0.1 cm thick, Edgetech Industries LLC., Medley, FL, USA) and a stainless steel mesh electrode (geometric dimension of 5.5 x 5.5 cm^2, 0.1 cm thick, McMaster-Carr., Elmhurst, IL, USA), respectively. The anode and cathode chambers each had a working volume of 170 mL. A 0.222 M NaCl solution was pumped continuously into the anode and cathode compartments with different pump speeds (5 rpm = 2.4 mL/min, 15 rpm = 7.5 mL/min, 25 rpm = 12.5 mL/min, and 50 rpm = 26 mL/min). An electric current 300 mA was applied to drive the electrolysis using a potentiostat/galvanostat (Gamry Reference 3000). Results of the catholyte and anolyte pH are shown in Figure 6.2. Some experiments were done using distilled ionized (DI) water as the catholyte and NaCl as the anolyte but the results were not better than those where NaCl was used as both the anolyte and catholyte. As depicted in the graph, different pump speeds do not make any significant difference in results. Also, within the first 10 minutes for all conditions, the catholyte reached a pH above 11.
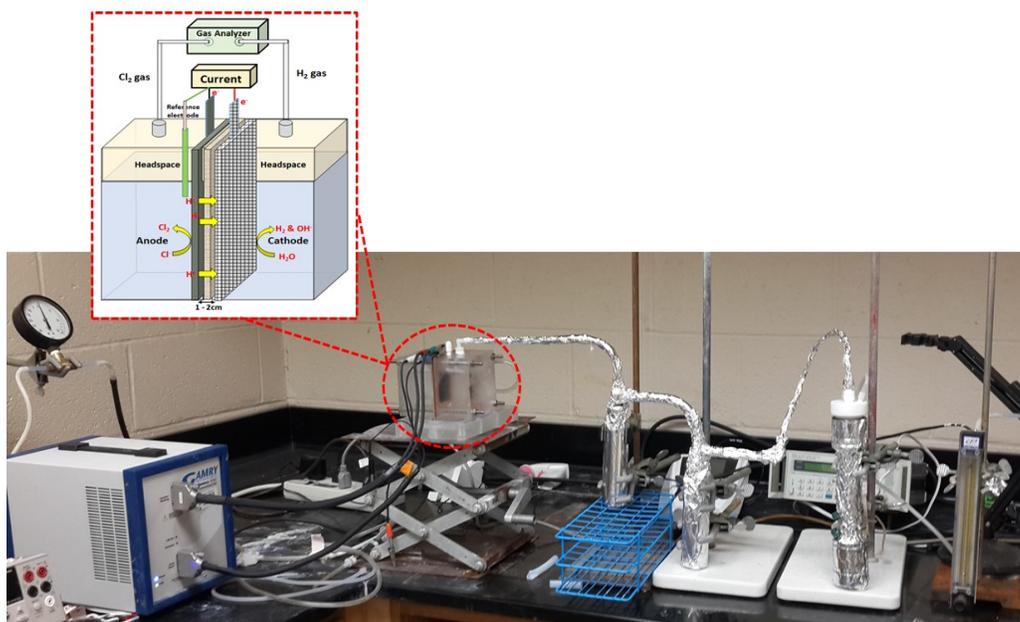

Figure 6.1: The two-chambered electrolysis system for water softening treatment.
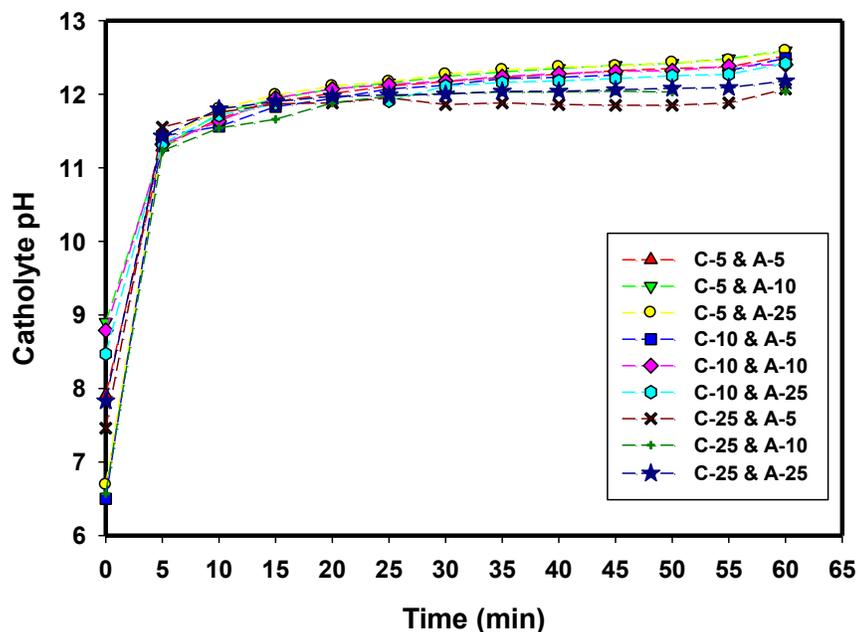
Figure 6.2: Catholyte pH in continuous mode with different pump speeds for anode and cathode (C represents catholyte and A for anolyte. Numbers refer to the pump speed so C-5, A-5 means catholyte 5 rpm and anolyte 5 rpm).

Electrolysis under different currents with CMI-7000 cation exchange membrane
To study how current affects the efficiency of the cell for high catholyte pH generation, different currents ranging from 300 to 900 mA were tested in batch mode. The following graphs and table show the results of catholyte and anolyte pH. (Table 6.1 and Figure 6.3).

Table 6.1: Catholyte and anolyte pH with different applied currents in batch mode

(CMI-7000 membrane was used).

Time	300 mA		500 mA		700 mA		900 mA	
(min)	Cathode	Anode	Cathode	Anode	Cathode	Anode	Cathode	Anode
0	4.92	4.04	5.92	5.12	6.43	4.28	4.29	3.92
5	11.53	2.68	11.44	2.68	11.72	2.49	11.97	2.4
10	11.91	2.46	11.9	2.44	12.09	2.3	12.24	2.23
15	12.13	2.35	12.11	2.33	12.29	2.2	12.41	2.14
20	12.25	2.27	12.24	2.25	12.42	2.14	12.53	2.09
25	12.36	2.22	12.34	2.2	12.51	2.1	12.63	2.06
30	12.43	2.18	12.43	2.2	12.58	2.08	12.68	2.03
35	12.48	2.15	12.5	2.12	12.62	2.07	12.77	2.02
40	12.53	2.12	12.56	2.09	12.65	2.05	12.82	2

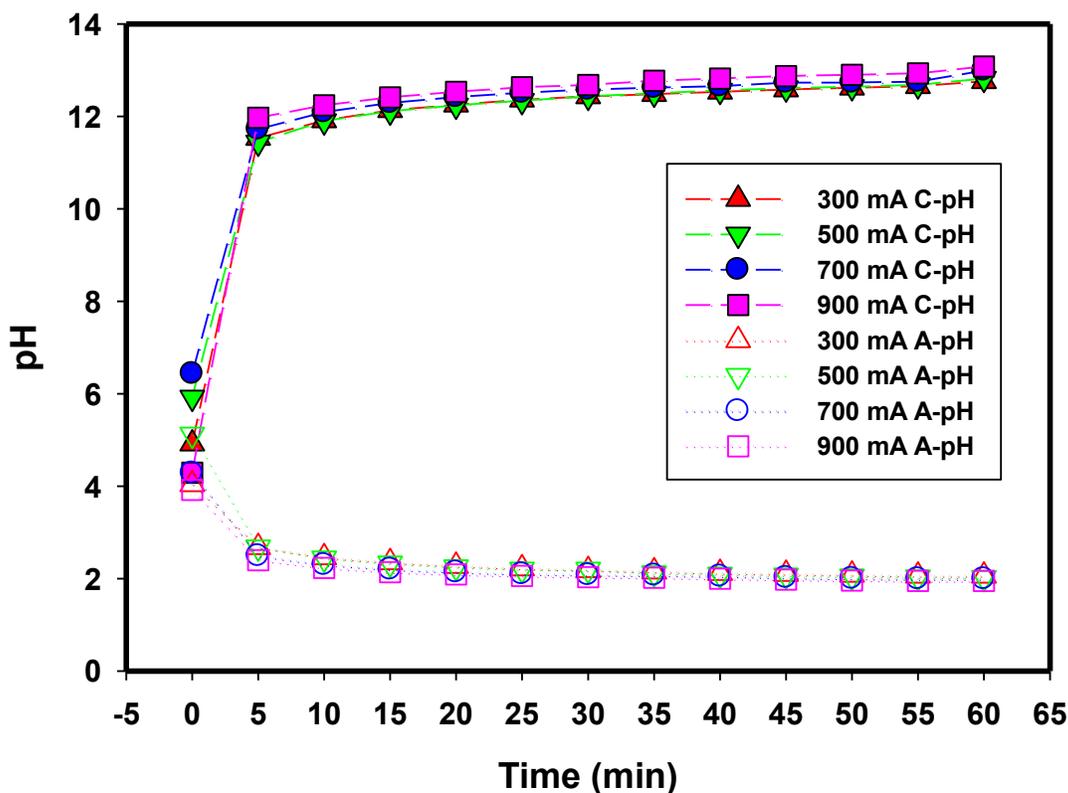| 45	12.58	2.1	12.61	2.07	12.73	2.02	12.87	1.98
50	12.62	2.08	12.64	2.05	12.73	2	12.9	1.96
55	12.65	2.06	12.68	2.03	12.75	1.99	12.93	1.95
60	12.76	2.06	12.82	2.02	12.99	1.99	13.08	1.95

Figure 6.3: Catholyte pH and anolyte with different applied currents in batch mode (CMI-7000 membrane was used).

Electrolysis with Nafion 115 cation exchange membrane

Nafion 115, a type of cations exchange membrane, was used in batch mode with different currents to test whether or not the pH could be improved. Results are provided in the following Table 2 and Figure 6.4. Comparing CMI-7000 with the Nafion 115 in batch mode, there is almost no difference between results. A chloride analysis and a metal test for sodium were performed on samples from both membranes to better compare results.

Table 6.2: Catholyte and anolyte pH with different applied current in batch mode

(Nafion 115 membrane was used).

Time	300 mA		500 mA		700 mA		900 mA	
(min)	Cathode	Anode	Cathode	Anode	Cathode	Anode	Cathode	Anode

| 0	4.65	3.62	4.21	3.41	4.92	3.95	4.17	4.01
5	11.59	2.59	11.70	2.54	11.76	3.57	11.68	2.37
10	11.94	2.36	12.05	2.35	12.12	3.38	12.07	2.19
15	12.11	2.27	12.25	2.26	12.33	2.98	12.26	2.09
20	12.21	2.18	12.40	2.19	12.41	2.66	12.40	2.03
25	12.29	2.14	12.50	2.14	12.51	2.48	12.53	1.99
30	12.37	2.09	12.58	2.10	12.59	2.33	12.63	1.96
35	12.43	2.06	12.65	2.07	12.68	2.27	12.70	1.94
40	12.49	2.03	12.71	2.04	12.74	2.08	12.76	1.92
45	12.54	2.00	12.76	2.02	12.78	2.01	12.80	1.90
50	12.58	1.98	12.81	1.99	12.83	1.89	12.83	1.87
55	12.62	1.97	12.83	1.97	12.86	1.87	12.88	1.84
60	12.74	1.97	12.92	1.95	12.95	1.85	13.09	1.80
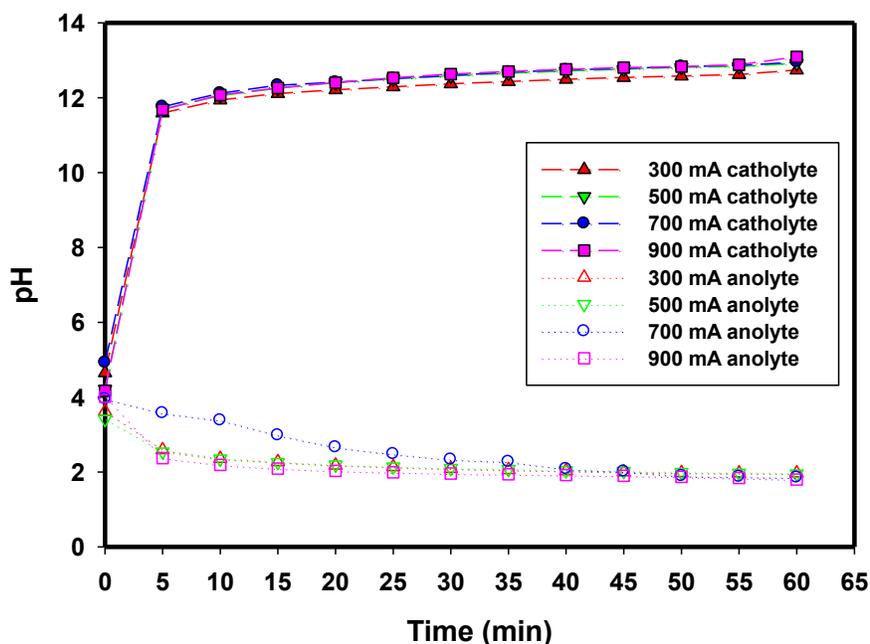
Figure 6.4: Catholyte pH and anolyte pH with different applied current in batch mode

(Nafion 115 membrane was used).

Chloride and metals with the Nafion 115 and CMI-7000 cation exchange membranes
Due to the use of a cation exchange membrane, it is expected that only cations pass through the membrane from anode to cathode. However, based on chloride data it can be seen that some anions (chloride) passed from the cathode to anode. The decrease in chloride concentration in the anode

is because of chloride oxidation to chlorine gas, but the decrease of chloride concentration in the cathode is not expected. However, comparing chloride data between the CMI-7000 (Figure 6.5) and Nafion 115 cation exchange membranes (Figure 6.6), it can be seen that chloride concentration in the cathode is more stable with the Nafion 115 than the CMI-7000. The only cation existing in the solution is sodium (Na), which passes through the membrane during the process. Thus, sodium concentration decreases in the anode and increases in the cathode. Sodium analysis on samples from both the Nafion 115 and CMI-7000 confirm this expectation (Figure 6.7 and Figure 6.8). However, by comparing data of the two membranes it can be understood that the Nafion 115 has a better performance in allowing sodium ions to pass through. Based on the entire data, the Nafion 115 will be used for further experiments.
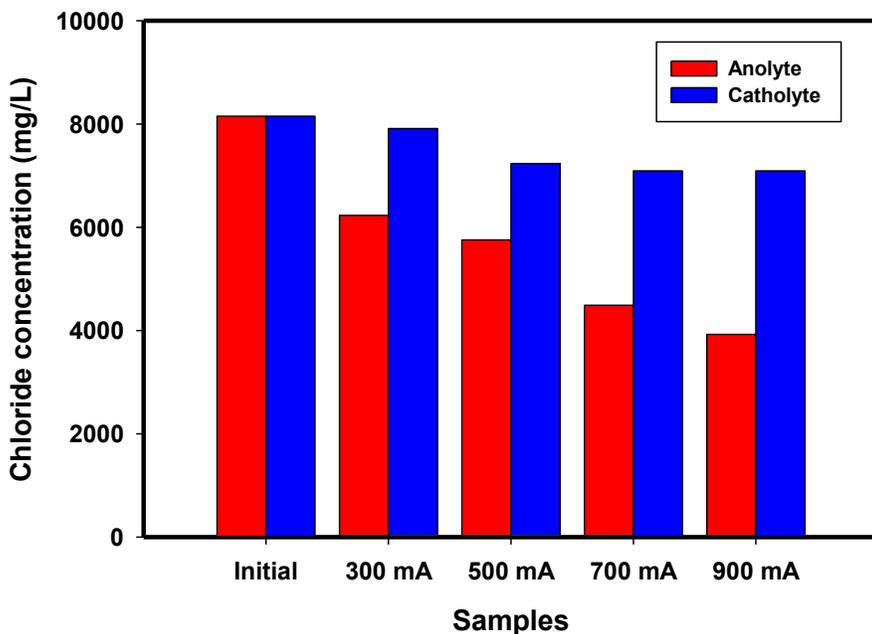

Figure 6.5: Chloride concentration of anolyte and catholyte under different applied currents with CMI-7000 cation exchange membrane.
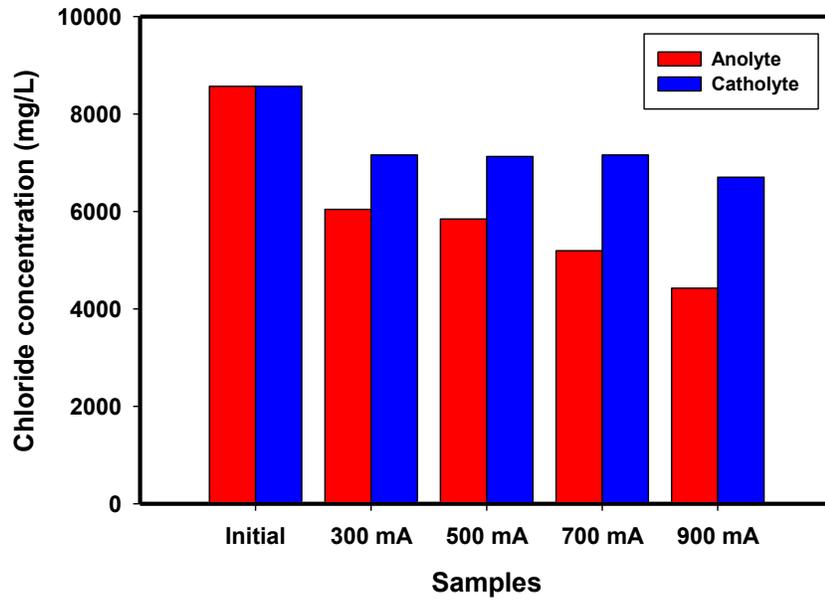
Figure 6.6: Chloride concentration of anolyte and catholyte under different applied currents with Nafion-115 cation exchange membrane.
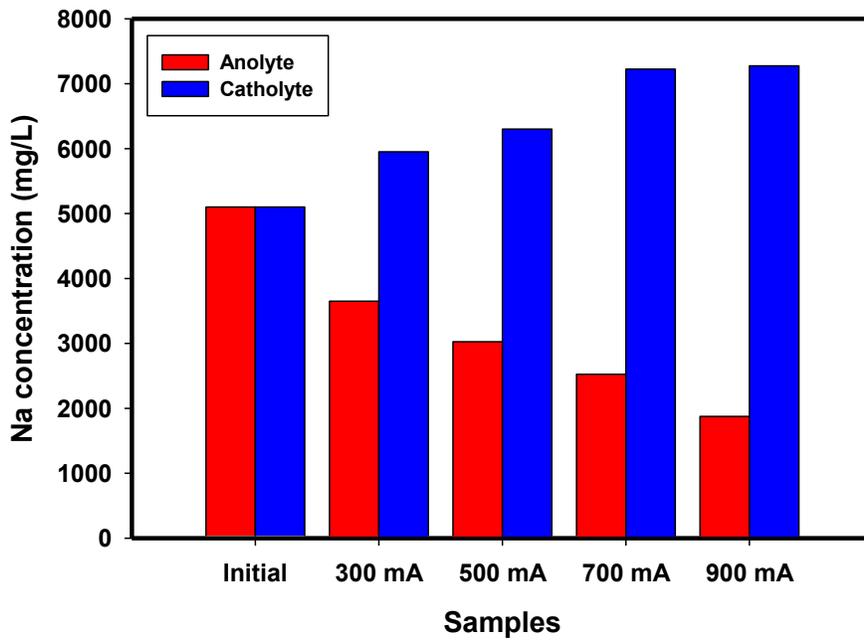

Figure 6.7: Sodium concentration of anolyte and catholyte under different applied currents in batch mode with the CMI-7000 membrane.
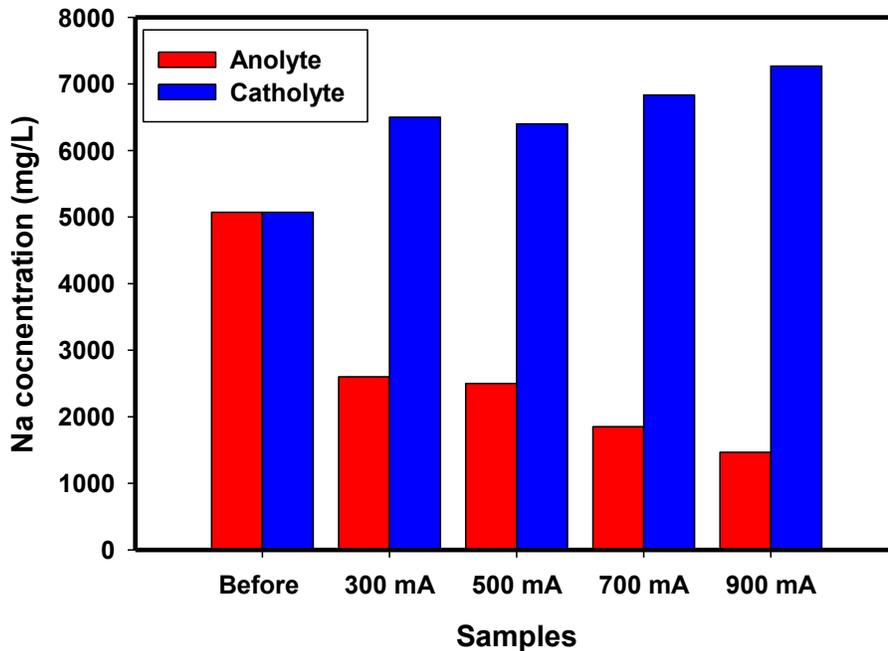
Figure 6.8: Sodium concentration of anolyte and catholyte under different applied currents in batch mode with the Nafion 115 membrane.

Products

Khajouei Golnoosh, Hoil Park, Jenna Henry, Harry Finklea, Lian-Shin Lin. *Produced water treatment using electrochemical softening system*. Institute of Water Security and Science (IWSS) symposium, February 28, Morgantown, West Virginia.

Plan for Next Quarter

Future work will be to conduct to use the high-pH catholyte for produced water softening. Specifically, softening effectiveness under different ratios of the produced water and the alkaline catholyte will be quantified and optimal condition characterized.

Topic 7 – Database Development

Approach

The team will use CKAN, open source data portal software (www.ckan.org). This platform is used by NETL-EDX and Data.gov among other organizations and agencies. The team will use this platform to store, manage, publish and find datasets.

Results & Discussion

There are no updates for this quarter.

Products

Plan for Next Quarter

Topic 8 – Economic and Societal

Approach

The lead on the political and societal project will work to identify and evaluate the factors shaping the policymaking response of local political actors. Included in this assessment will be an accounting, past and present, of the actions of public and private individuals and groups acting in favor of or opposed to shale gas drilling at the MSEEL site.

First year activity includes developing, distributing, collecting and compiling the responses from a worker survey and a vendor survey. The worker survey will address job characteristics and offsite expenditures. The vendor survey will help to identify per-well cost structures.

Results & Discussion

The team completed work this quarter, documenting the state of the region at the initiation of the Marcellus shale experimental well-drilling project. The document, titled "MSEEL Project Context: State of the Region (2001-2014)", is published as an on-line report accessible from the WVU Regional Research Institute website at http://rri.wvu.edu/resource-documents/. The report, which describes the socioeconomic context for the MSEEL well, provides socioeconomic trends leading up to the project, and includes data on gas drilling and production trends.

The second activity draws on collaboration with NNE on a model for providing generalizable costs for future shale gas development impacts assessments. A technical document describing this model is in progress and should be completed and posted to the RRI website by summer 2017.

Pending the completion of this final technical document for the model, this task is complete and will not be updated in future reports.

Products

Plan for Next Quarter

Cost Status

Year 1

Start: 10/01/2014 End: 09/30/2017

Baseline Reporting Quarter

	Q1 (12/31/14)	Q2 (3/30/15)	Q3 (6/30/15)	Q4 (9/30/15)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share	$549,000		$3,549,000	
Non-Federal Share	$0.00		$0.00	
Total Planned (Federal and Non-Federal)	$549,000		$3,549,000	
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$0.00	$14,760.39	$237,451.36	$300,925.66
Non-Federal Share	$0.00	$0.00	$0.00	$0.00
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$0.00	$14,760.39	$237,451.36	$300,925.66
Cumulative Incurred Costs	$0.00	$14,760.39	$252,211.75	$553,137.41
Uncosted				
Federal Share	$549,000	$534,239.61	$3,296,788.25	$2,995,862.59
Non-Federal Share	$0.00	$0.00	$2,814,930.00	$2,814,930.00
Total Uncosted - Quarterly (Federal and Non-Federal)	$549,000	$534,239.61	$6,111,718.25	$5,810,792.59

Start: 10/01/2014 End: 09/30/2017

Baseline Reporting Quarter

	Q5 (12/31/15)	Q6 (3/30/16)	Q7 (6/30/16)	Q8 (9/30/16)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share	$6,247,367		$7,297,926	
Non-Federal Share	2,814,930		$4,342,480	
Total Planned (Federal and Non-Federal)	$9,062,297	$9,062,297.00	$11,640,406	
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$577,065.91	$4,480,939.42	$845,967.23	$556,511.68
Non-Federal Share	$0.00	$2,189,863.30	$2,154,120.23	$0.00
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$577,065.91	$6,670,802.72	$3,000,087.46	$556,551.68
Cumulative Incurred Costs	$1,130,203.32	$7,801,006.04	$10,637,732.23	$11,194,243.91
Uncosted				
Federal Share	$5,117,163.68	$636,224.26	$1,004,177.30	$447,665.62
Non-Federal Share	$2,814,930.00	$625,066.70	($1,503.53)	($1,503.53)
Total Uncosted - Quarterly (Federal and Non-Federal)	$2,418,796.68	$1,261,290.96	$1,002,673.77	$446,162.09

Start: 10/01/2014 End: 09/30/2017

Baseline Reporting Quarter

	Q9 (12/31/16)	Q10 (3/30/17)	Q11 (6/30/17)	Q12 (9/30/17)
Baseline Cost Plan	(From 424A, Sec. D)			
(from SF-424A)				
Federal Share				
Non-Federal Share				
Total Planned (Federal and Non-Federal)				
Cumulative Baseline Costs				
Actual Incurred Costs				
Federal Share	$113,223.71	$196,266.36		
Non-Federal Share	$0	$0		
Total Incurred Costs - Quarterly (Federal and Non-Federal)	$113,223.71	$$196,266.36		
Cumulative Incurred Costs	$11,307,467.62	$11,503,733.98		
Uncosted				
Federal Share	$334,441.91	$138,175.55		
Non-Federal Share	($1,503.53)	($1,503.53)		
Total Uncosted - Quarterly (Federal and Non-Federal)	$332,938.38	$136,672.02		

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