Geochemical Evolution of Hydraulically-Fractured Shales

NETL Research and Innovation Center
Onshore Unconventional Resources Portfolio FY16
Task 5: Water and Geochemistry

Alexandra Hakala
National Energy Technology Laboratory
Presentation Outline

- FY16 Onshore Unconventional Resources Overview
- Task 5 Overview – Program Benefits, Project Objectives and Goals
- Technical Detail: Subsurface Geochemical Reactions
FY16 R&IC Onshore Unconventional Resources Portfolio

- Task 1: Project management
- Task 2: Induced Seismicity and Geomechanics (Lead: Dustin Crandall)
- Task 3: Field Geophysics (Lead: Rick Hammack)
- Task 4: Air Quality (Lead: Natalie Pekney)
- Task 5: Water and Geochemistry (Lead: Alexandra Hakala)
Benefit to the Program

- Facilitating a safe and environmentally sustainable supply of natural gas
  - Efficient resource development and associated footprint reduction
  - Subsurface science in the context of understanding the reservoir
  - Water quality and availability

- Research projects within Task 5: Water and Geochemistry will result in the following benefits:
  - Improved understanding of hydraulically-fractured reservoirs:
    - Characterize fluid-shale reactions that affect the reservoir and produced water composition
    - Identify microbiological populations present in hydraulically-fractured shales that can affect reservoir processes and well integrity
  - Ensuring protection of surface waters and shallow groundwaters (Water Quality):
    - Evaluate changes to well cement integrity in the presence of reactive geologic fluids and methods for monitoring well integrity
    - Identify best practices for waste disposal to minimize environmental impact
1. Understand effects of biological and chemical processes on unconventional oil and gas reservoir performance.

2. Develop tools for detection of chemical changes in the hydrocarbon reservoir and shallow receptors of released fluids and gas.

**Surface System Responses**

*Identify best practices for waste disposal to minimize environmental impact*

**Gas Well Cement Integrity**

*Evaluate changes to well cement integrity in the presence of reactive geologic fluids*

**Subsurface Geochemical Reactions**

*Characterize fluid-shale reactions that affect the reservoir and produced water composition*

**Microbial Communities and Biocides**

*Identify microbiological populations and biocide reactions in fractured shales*

**Sensors for In Situ Measurements**

*Develop sensors for monitoring well integrity*
How do we characterize and monitor the mineral reactions that could affect flow in fractured shales?

• Evaluate the shut-in period
• Compare chemical changes in the presence and absence of fracturing chemicals
  – Mineral Reactions – could these affect flow?
  – Changes in Fluid Chemistry – what needs to be monitored for water treatment design, and to tell us what’s happening downhole?

• Apply NETL’s experimental and analytical geochemistry capabilities to evaluate how fracturing chemicals react with shale
Mineral reactions and organic geochemical changes observed in lab-scale experiments

- Mineral reactions observed and modeled:
  - Calcite dissolution
  - Barite, gypsum, anhydrite, secondary smectite and carbonate precipitation
- Trace metal chemistry is controlled by secondary mineral precipitation
- Shale reactions with frac fluids result in changes to fluid and solid phase organic chemistry
- Geochemical tracers provide excellent signals for differences between formations
  - Ability to track fracture-scale reactions may be limited
Application of NETL R&IC’s experimental and analytical geochemistry capabilities to evaluate frac chemical-shale reactions

High-pressure, high-temperature Static and Flow-through reactor systems (Geological and Environmental Systems Directorate, GES)

Analytical geochemistry & geochemical modeling (GES) and characterization (Materials Engineering and Manufacturing Directorate, MEMD)

- Metal isotopes: Multicollector ICP-MS
- Organic geochemistry: LC-QTOF-MS, IC, GC-MS
- Visualization: environmental SEM, CT scanning
Static autoclave experiments to evaluate changes in shale after exposure to high-TDS frac fluids – 1 of 2

Static autoclave, polished Marcellus Shale before and after exposure to synthetic high-TDS fluid. Reacted at 77°C and 4000 psi for 6 days.

Post-exposure gypsum precipitation, calcite dissolution

Pre-exposure

Post-exposure

Post-exposure fracture growth

Pre-exposure

Post-exposure

1000x magnification

500x magnification

Dieterich, Kutchko, and Goodman (2016) Fuel
Static autoclave experiments to evaluate changes in shale after exposure to high-TDS frac fluids – 2 of 2

Static autoclave, polished Marcellus Shale after exposure to synthetic high-TDS fluid. Reacted at 85°C and 4000 psi for 5 days.

Barite and Sr-rich calcium carbonate observed on reacted shale surfaces
Mineral reactions and organic geochemical changes observed in lab-scale experiments

- Mineral reactions observed:
  - Calcite dissolution
  - Barite, gypsum, and carbonate precipitation
Experiment 1:
High-TDS Fluid + Shale

Fluid: 100% Synthetic Brine

Solid: Marcellus shale chips and powder (Greene County)

Water to Rock Ratio: 20.4 to 1

$pH_0$: 7.59 ± 0.1

Experiment 2:
High-TDS Fluid + Shale + Fracturing Chemicals

Fluid: 70% Synthetic Brine, 30% Fracturing Fluid

Solid: Marcellus shale chips and powder (Greene County)

Water to Rock Ratio: 18.6 to 1

$pH_0$: 1.83 ± 0.1

Analytical & Modeling Tools:
• ICP-OES, ICP-MS, IC, LC-QTOF, GC-MS
• Coulometry, SEM, XRD
• GWB for modeling

Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry
Most solution chemistry changes occur within 48 hours of bringing the experiment to elevated P,T.
Most elements show elevated concentrations in the experiment with fracturing chemicals after 16 d.

**Elements enriched in presence of fracturing fluids:**
Al*, As, B, Be, Cd, Co, Cr*, Cu, Fe*, Mn*, No, Ni, Pb, Sb, Sc, Sr, Ti, U*, V*, Y, Zn K*, Ca*, Mg*

**Elements enriched in absence of fracturing fluids:**
Ag, Ba, Th

* Denotes statistically significant enrichment based on Pearson correlation coefficients

* Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry
Evidence for significant carbonate dissolution in experiments containing fracturing fluids

<table>
<thead>
<tr>
<th>Inorganic Carbon (% carbon)</th>
<th>Supported by XRD patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted</td>
<td>0.528 ± 0.002</td>
</tr>
<tr>
<td>Brine + Shale</td>
<td>0.457 ± 0.002</td>
</tr>
<tr>
<td>Brine + Shale + Frac Fluid</td>
<td>0.208 ± 0.004</td>
</tr>
</tbody>
</table>

Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry
Evidence for secondary precipitation of carbonates and anhydrite

Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry
Redox changes, and may influence barite stability as observed by modeling fluid chemistry.
Changes in aqueous organic composition observed for the experiment containing frac fluids: LC-QTOF

Rocking autoclave, Marcellus Shale chips + powder, 15 d, 130°C, 4000 psi
BRINE-1: synthetic brine, BRINE-2: Fracturing fluid + synthetic brine

Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry
Changes in aqueous organic composition observed for the experiment containing frac fluids: GC-MS

Rocking autoclave, Marcellus Shale chips + powder, Fracturing fluid + synthetic brine, 15 d, 130°C, 4000 psi

Table 9: Aqueous organic composition of BRINE-2 as measured by GC-MS

<table>
<thead>
<tr>
<th>Reacted Samples</th>
<th>Time (days)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>9.8</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>4-Ethoxybenzoic Acid Ethyl Ester</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Benzene</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Dimethylbenzene</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Fural or 3-Furaldehyde</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>N,N-dimethyl-1-dodecanamine</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Napthalene</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Nonanol</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Tetrahydronaphthalene</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Toluene</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Trimethylbenzene</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Mineral reactions and organic geochemical changes observed in lab-scale experiments

- Mineral reactions observed and modeled:
  - Calcite dissolution
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- Trace metal chemistry is controlled by secondary mineral precipitation
- Shale reactions with frac fluids result in changes to fluid and solid phase organic chemistry
Flow-through experiments to evaluate effects of flow on mineral dissolution and precipitation

- Are observations from static and rocking autoclave experiments consistent with a system under flow?
- Can geochemical tracers (metal isotopes) provide insight on mineral dissolution and precipitation?
Barite formation observed in flow-through experiment containing reused produced water + frac chemicals

Marcellus shale reacted with hydraulic fracturing fluid from reused produced water

X-ray computed tomography image

Scanning electron microscope image

Dissolved calcite precipitate barite
Fluid chemistry for flow-through control experiment also shows Ba and SO$_4^{2-}$ decrease

Implication: Scale inhibitor may not be performing as expected

Paukert, Hakala, Jarvis, AGU Fall Meeting, December 2015; in preparation
Minimal changes in Sr and Li isotope signatures observed for shale-frac fluid reactions

Implication: Although useful for monitoring basin-scale fluid mixing, Sr and Li isotopes show limited application as indicators for frac fluid shale interactions.

Phan, Paukert, Hakala, AGU Fall Meeting, December 2015; in preparation
Mineral reactions and organic geochemical changes observed in lab-scale experiments

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## Accomplishments to Date

### Onshore UCR Task 5: Water and Geochemistry

<table>
<thead>
<tr>
<th>Time Period</th>
<th>Accomplishments</th>
</tr>
</thead>
</table>
| **Historical - FY 15** | • Batch experiments showed that fracturing fluids affect shale mineral reactions through pH and redox based reactions  
                          • Fiber optic-based pH sensing applications developed for aqueous subsurface environments  
                          • Air drilling identified as a plausible cause for groundwater methane transport as shown through 3D TOUGH 2 modeling |
| **Current - FY 16** | • Fracturing fluid-shale mineral reactions observed to result in mineral dissolution and precipitation along fractures, however have a limited influence on produced water total dissolved solids  
                          • Completion of largest microbial characterization survey of hydraulically-fractured environments to date  
                          • Gas well cement mineralogy and structures are affected by coal mine water  
                          • Leaching of metals and salts from drill cuttings disposal sites can vary by drilling method, elements of interest, and disposal site geochemical conditions  
                          • New approaches were developed for surface water monitoring of produced water spills, and shallow groundwater monitoring of methane migration  
                          • Dissolved iron and pyrite influence the degradation rate of biocides introduced to shale formations during hydraulic fracturing |
| **Future - FY 17** | • Focus on water systems, continue with leaching studies and modeling; monitoring and geochemical analysis approaches  
                          • Add produced water treatment and planning, geospatial approach to establishing base of groundwater |
Synergy Opportunities

• Pore to Core Scale Processes in Shale
  – NETL, LANL, SSRL, LBNL, Sandia Collaborations – Meeting on July 14, 2016
  – Leveraging research across multiple portfolios (unconventional oil and gas resources; geologic CO₂ storage)
  – Focus on shales

• Coordinate experimental efforts with SSRL with a focus on organic geochemical reactions and barite geochemistry

• Other opportunities to be identified
Summary

Next steps for hydraulically-fractured reservoir shale geochemistry

- Evaluate secondary mineral precipitation along a fracture flow pathway – can precipitation benefit fracture propping?
- Cement reactions involving the near-wellbore environment?
- More in-depth investigation related to organic geochemistry and microbiology of these systems
Appendix
Organization Chart

• Describe project team, organization, and participants.
  – Link organizations, if more than one, to general project efforts (i.e. materials development, pilot unit operation, management, cost analysis, etc.).

• Please limit company specific information to that relevant to achieving project goals and objectives.
### Organization Chart: R&IC Onshore UCR

<table>
<thead>
<tr>
<th>Technical Portfolio Lead (TPL)</th>
<th>FY 2016</th>
<th>FY 2017 and Future</th>
</tr>
</thead>
<tbody>
<tr>
<td>No TPL; Portfolio coordinated by TTCs</td>
<td>Task 1: Project Management – Alexandra Hakala</td>
<td>Alexandra Hakala</td>
</tr>
<tr>
<td></td>
<td>Task 2: Induced Seismicity and Geomechanics – Dustin Crandall</td>
<td>Task 1: Project Management – Alexandra Hakala</td>
</tr>
<tr>
<td></td>
<td>Task 4: Air Quality – Natalie Pekney</td>
<td>Task 3: Wellbore Issues – Barbara Kutchko</td>
</tr>
<tr>
<td></td>
<td>Task 5: Water and Geochemistry – Alexandra Hakala</td>
<td>Task 4: Seismicity Issues – Rick Hammack</td>
</tr>
<tr>
<td></td>
<td>Task 8: Systems Analysis for Onshore UCR – Donald Remson</td>
<td>Task 7: Hybrid Energy Systems – Mark McKoy</td>
</tr>
</tbody>
</table>

**Lead (TPL):** Alexandra Hakala

**Team Technical Coordinators (TTC):**

- No TPL; Portfolio coordinated by TTCs
- Task 1: Project Management – Alexandra Hakala
- Task 2: Induced Seismicity and Geomechanics – Dustin Crandall
- Task 3: Field Geophysics – Rick Hammack
- Task 4: Air Quality – Natalie Pekney
- Task 5: Water and Geochemistry – Alexandra Hakala
- Task 6: Air Quality Issues – Natalie Pekney
- Task 7: Hybrid Energy Systems – Mark McKoy
- Task 8: Systems Analysis for Onshore UCR – Donald Remson
FY 2016

Task 5: Water and Geochemistry, TTC: Alexandra Hakala

<table>
<thead>
<tr>
<th>Project</th>
<th>Principal Investigator</th>
<th>Team Members (NETL, ORISE, AECOM)</th>
<th>External Partners</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid and Solid Isotope Characterization at MSEEL</td>
<td>Alexandra Hakala</td>
<td>Thai Phan, Christina Lopano, Tracy Bank, Bill Garber</td>
<td>Shikha Sharma (WVU), Brian Stewart (Pitt)</td>
</tr>
<tr>
<td>Characterize chemistry of drill cuttings leachates</td>
<td>Christina Lopano</td>
<td>Mengling Stuckman, Alexandra Hakala</td>
<td></td>
</tr>
<tr>
<td>Comparison of microbial ecology in fractured shales</td>
<td>Djuna Gulliver</td>
<td>Daniel Lipus</td>
<td>Kyle Bibbey (Pitt)</td>
</tr>
<tr>
<td>Biocide effectiveness through reactivity with shale minerals</td>
<td>Alexandra Hakala</td>
<td>Jinesh Jain</td>
<td>Athanasios Karamalid, Nizette Edwards-Consolazio (CMU)</td>
</tr>
<tr>
<td>Sensor development for well corrosion monitoring</td>
<td>Paul Ohodnicki</td>
<td>Margaret Ziomonek-Moroz, Conjung Wang</td>
<td></td>
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<tr>
<td>Cement integrity affected by acid mine water</td>
<td>Barbara Kutchko</td>
<td>James Gardiner, Alexandra Hakala</td>
<td>PA Department of Environmental Protection</td>
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<tr>
<td>Methane and radon migration in shallow aquifers</td>
<td>Daniel Soeder</td>
<td>AECOM</td>
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</table>
Proposed FY 2017 Projects

Task 2: Reservoir Processes, TTC: Dustin Crandall

<table>
<thead>
<tr>
<th>Project</th>
<th>Principal Investigator</th>
</tr>
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<tbody>
<tr>
<td>Organic, inorganic and isotopic analysis of fracture permeability changes</td>
<td>Alexandra Hakala</td>
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<tr>
<td>Reactive fracture flow tests</td>
<td>Alexandra Hakala</td>
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<tr>
<td>Characterization of key elements for mineral dissolution and precipitation</td>
<td>Christina Lopano</td>
</tr>
<tr>
<td>Ba precipitation control and Ba isotope development</td>
<td>Christina Lopano</td>
</tr>
<tr>
<td>Evaluation of microbial populations</td>
<td>Djuna Gulliver</td>
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</table>

Task 3: Wellbore Issues, TTC: Barbara Kutchko

<table>
<thead>
<tr>
<th>Project</th>
<th>Principal Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaluate cement samples from wellbore-acid mine water field scenarios</td>
<td>Barbara Kutchko</td>
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<tr>
<td>Synchrotron analysis of cement samples</td>
<td>Christina Lopano</td>
</tr>
<tr>
<td>Corrosion and stress wellbore sensor development</td>
<td>Paul Ohodnicki</td>
</tr>
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Task 5: Water Issues, TTC: Alexandra Hakala

<table>
<thead>
<tr>
<th>Project</th>
<th>Principal Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development of new isotope systems for fluid analysis</td>
<td>Alexandra Hakala</td>
</tr>
<tr>
<td>Electrochemistry-based techniques for trace metal determination in brines</td>
<td>Alexandra Hakala</td>
</tr>
<tr>
<td>Geochemical studies with drill cuttings</td>
<td>Christina Lopano</td>
</tr>
<tr>
<td>Modeling fate of drill cuttings leachate</td>
<td>Daniel Soeder</td>
</tr>
<tr>
<td>Geochemical testing and modeling of established isotope tracers in UOG basins</td>
<td>Alexandra Hakala</td>
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<tr>
<td>Water treatment for produced waters</td>
<td>Nicholas Siefert</td>
</tr>
<tr>
<td>Establish base to groundwater in U.S. shale basins</td>
<td>Kelly Rose</td>
</tr>
<tr>
<td>Produced water supply chain modeling</td>
<td>Robert Dilmore</td>
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### Gantt Chart

<table>
<thead>
<tr>
<th>Task/Subtask</th>
<th>Start</th>
<th>Finish</th>
<th>FY16</th>
</tr>
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<tbody>
<tr>
<td><strong>5. Water and Geochemistry</strong></td>
<td></td>
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<tr>
<td>5.1 Field Laboratories</td>
<td>10/01/2015</td>
<td>09/30/2020</td>
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<tr>
<td>5.1.1 Fluid and solid isotope characterization at MSEEL</td>
<td>10/01/2015</td>
<td>09/30/2016</td>
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<tr>
<td>5.1.2 Characterize chemistry of leachates from solid wastes when disposed under various conditions</td>
<td>10/01/2015</td>
<td>09/30/2016</td>
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<tr>
<td>5.2 Fundamentals of Unconventional Oil and Gas Reservoirs</td>
<td>10/01/2015</td>
<td>09/30/2020</td>
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<tr>
<td>5.2.1 Comparison of microbial ecology in Marcellus (dry gas) reservoir and the Bakken Petroleum System (oil, NGL, and gas)</td>
<td>10/01/2015</td>
<td>09/30/2016</td>
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<tr>
<td>5.2.2 Biocide effectiveness through reactivity with shale minerals</td>
<td>10/01/2015</td>
<td>09/30/2016</td>
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<tr>
<td>5.3 Wellbore Integrity</td>
<td>10/01/2015</td>
<td>09/30/2020</td>
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<tr>
<td>5.3.2 Sensor development – monitor potential casing corrosion downhole</td>
<td>10/01/2015</td>
<td>09/30/2016</td>
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</tr>
<tr>
<td>5.3.3 Evaluate effect of acidic, metal-laden mine waters on well casing and cement</td>
<td>10/01/2015</td>
<td>09/30/2016</td>
<td></td>
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<tr>
<td><strong>5.4 Protecting Water Resources</strong></td>
<td>10/01/2015</td>
<td>09/30/2020</td>
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<tr>
<td>5.4.1 Methane and radon migration in shallow aquifers as a site is developed</td>
<td>10/01/2015</td>
<td>09/30/2016</td>
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</table>
Journal Publications:

Additional Tech Transfer (details available upon request):
- Conference Papers: 1
- Inventions, Patent Applications, Licenses: 1
- Presentations: 14
- Publications (including in preparation): 18