Geochemistry and Environmental Problems of Flowback Water from Marcellus Wells in Pennsylvania

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Topics

- Flowback
- Chemistry of flowback
- Source of flowback brine
- Environmental Problems
ACKNOWLEDGEMENTS

- Evan Dresel  MS 1985  Conventional brines, recognition of evaporated seawater origin
- Lara Haluszczak  BS 2011  Marcellus data
- PA DEP  Marcellus data
Typical Marcellus Well

Cross-Section of Typical Horizontal Marcellus Well

24° conductor casing (brown) is installed up to 50 feet deep and cemented (grey) to the surface.

20° casing is installed through the 24° casing and continuing up to 500 feet deep. This casing is cemented to surface to isolate and protect near-surface groundwater.

13 3/8° casing is installed through the 20° casing and continuing up to 1000 feet deep. This casing is also cemented to the surface to protect the groundwater aquifer from the gas well.

5 1/2° casing continues down and is turned laterally into the Marcellus formation at a depth of 5000 to 9000+ feet below the surface.

Horizontal “lateral” portion of well extends from 3,000 to over 10,000 feet within Marcellus formation.

Kick off point for the bend from vertical to horizontal drilling.

Fresh groundwater zone up to 1000 feet deep

Vertical portion of well

Marcellus Center
For Outreach and Research
www.marcellus.psu.edu
Flowback Water

- 3 to 5 million gallons of water with additives are injected into an unconventional horizontal well during fracking.
- 10 to 20% of this water commonly flows back on release of pressure, by day 14.
- This water contains the additives, and in PA much of it has extremely high salinity and high contents of many elements.
- Water after day 14 is called “production water” but typically has similar chemistry.
Questions on Flowback Water

- What constituents are present in hazardous amounts?
- What to do with this water?
- What is the origin of the high salinity and related constituents?
- Is the brine actually coming from the Marcellus?
Sources of Data

- Dresel, E. and Rose, A.W., 2010, PA Geol. Survey, OFOG 10–01.0, 40 conventional oil and gas wells.
- PA DEP, 2011, data for 22 Marcellus wells, analyses in Haluszczak et al., 2013.
Wells Providing Chemical Data

Legend
Well Data Source

- ChiefOG
- DEP BOGM
- DRESEL
- GTI

0 25 50 100 Kilometers
Cl in flowback vs. days after fracking (GTI study)
Cl vs. Flow

Fig. 3—Marcellus Shale Well A flowback analysis—anion trend.
Ca vs. days after Fracking

![Graph showing Ca vs. days after Fracking](image-url)
# Chemistry—Injected Water and Day 14 Flowback Medians, GTI study, 7 wells, mg/L

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Injected Fluid</th>
<th>Flowback Day 14</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.0</td>
<td>6.2</td>
<td>~8</td>
</tr>
<tr>
<td>Cl</td>
<td>82</td>
<td>98,300</td>
<td>19,400</td>
</tr>
<tr>
<td>Br</td>
<td>&lt;10</td>
<td>872</td>
<td>67</td>
</tr>
<tr>
<td>SO4</td>
<td>59</td>
<td>&lt;50</td>
<td>2700</td>
</tr>
<tr>
<td>Ca</td>
<td>32</td>
<td>11,200</td>
<td>410</td>
</tr>
<tr>
<td>Mg</td>
<td>3.7</td>
<td>875</td>
<td>1290</td>
</tr>
<tr>
<td>Na</td>
<td>80</td>
<td>36,400</td>
<td>10,800</td>
</tr>
<tr>
<td>K</td>
<td>0.7</td>
<td>281</td>
<td>390</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;50</td>
<td>47</td>
<td>0.0034</td>
</tr>
</tbody>
</table>
# Chemistry – Minor Elements
Medians, mg/L, GTI Study, 7 samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Injected fluid</th>
<th>Flowback, Day 14</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>14</td>
<td>140</td>
<td>15</td>
</tr>
<tr>
<td>P</td>
<td>0.36</td>
<td>0.55</td>
<td>0.09</td>
</tr>
<tr>
<td>Al</td>
<td>0.3</td>
<td>0.5</td>
<td>0.001</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>20</td>
<td>4.4</td>
</tr>
<tr>
<td>Li</td>
<td>0.04</td>
<td>95</td>
<td>0.17</td>
</tr>
<tr>
<td>Sr</td>
<td>0.82</td>
<td>2330</td>
<td>8.1</td>
</tr>
<tr>
<td>Ba</td>
<td>0.6</td>
<td>1990</td>
<td>0.021</td>
</tr>
<tr>
<td>Mn</td>
<td>0.07</td>
<td>5.6</td>
<td>0.0004</td>
</tr>
<tr>
<td>Zn</td>
<td>0.08</td>
<td>0.09</td>
<td>0.005</td>
</tr>
<tr>
<td>Ra</td>
<td></td>
<td>2640 pCi/L*</td>
<td></td>
</tr>
</tbody>
</table>
Br/Cl indicates ancient brine

![Graph showing Br/Cl ratios for different types of dilution and dissolution processes.]

- **Fresh water dilution**
- **Sea water dilution**
- **Halite dissolution**
- **GTI**
- **BOGM**
- **Dresel**
- **Chief**
- **SW Evap**
- **SW**

The graph illustrates the log concentration of Br vs. Cl for various dilution and dissolution scenarios.
Alternatives – Dissolution of halite or acid attack?

- Blauch et al. (2010) suggest that the high NaCl comes from dissolution of halite (NaCl)
- But Br/Cl would be much lower.
- GTI data does not show acid in the injected water – pH is near-neutral in both input and flowback.
Ca is enriched over evaporated seawater
Mg is depleted from evaporated seawater – dolomitization
Origin – Step 1

- Evaporation of seawater through gypsum precipitation into halite precipitation
- Probable timing and locale – Silurian Salina formation
- Step 2 – dolomitization (CaMg(CO$_3$)$_2$
- Other Steps
  - Mobilization out of Salina Fm. into overlying and underlying sediments (Ord. to Miss.)
  - Dilution with connate seawater in other formations, fresh water, injected water
  - Sulfate reduction and pyrite oxidation
Stratigraphy in SW PA

16,000 ft of sed. rock

Figure 2. Generalized stratigraphic column of rocks in southwestern Pennsylvania. Numbers indicate geologic units referred to in this article: 1, Pennsylvanian and Permian coal beds; 2, Pottsville Formation Salt sands; 3, Venango Group oil sands; 4, Huron Shale; 5, Rhinestreet Shale; 6, Marcellus Formation; 7, Oriskany Sandstone; 8, Lockport Dolomite; 9, Medina Group and equivalent Tuscarora Formation; 10, Utica Shale; 11, Gatesburg Formation sandstones; and 12, Potsdam Sandstone.
SO4 vs. Br – No pattern
SO$_4$ vs Br – Major S loss
# Ra and Ba Problems

<table>
<thead>
<tr>
<th>Element</th>
<th>Flowback</th>
<th>Drinking water Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba (mg/L)</td>
<td>1990* (Day 14)</td>
<td>2</td>
</tr>
<tr>
<td>Ra (pCi/L)#</td>
<td>2460*</td>
<td>5</td>
</tr>
</tbody>
</table>

*Median

#Rowan et al., 2011
Ra vs. Cl

Ra-226 (pCi/L) vs. Cl (mg/L)

- BOGM
- Dresel
Host for concentrated brine entering Marcellus wells?

- Marcellus Formation?  But this is a relatively impermeable tight shale.  Little pore space. Electric logs suggest essentially no saline pore fluid.  Fractures?

- Adjacent formations?  But radium isotopes suggest Marcellus as host. Porosity/fractures in limestones and calcareous zones?
Vertical extent of fractures
Radium isotopes

238U

234U

230Th

226Ra

$T_{1/2} = 1500$ yr
Decay Series

232Th → 228Ra

$T_{1/2} = 6.7 \text{ yr}$
Radium in brine vs. host (Rowan, 2010)

**Diagram Description:**

- **Formation Age:**
  - Cambrian
  - Ordovician
  - Silurian
  - Devonian

- **Levels within Each Formation Age:**
  - Upper
  - Middle
  - Lower

- **Total Radium, in picocuries per liter:**
  - Range: 0 to 16,000

**Explanation of Symbols:**
- Upper Devonian sandstones
- Middle Devonian, Marcellus Shale
- Middle Devonian, Huntersville Chert
- Middle Devonian, Onondaga Limestone
- Lower Devonian, Oriskany/Ridgely Sandstone
- Lower Devonian, Heiderberg Limestone
- Upper Silurian, Bass Islands/Akron Dolomite
- Lower Silurian, Medina/Tuscarora Sandstone
- Upper Ordovician, Queenston Shale
- Ordovician, undifferentiated
- Upper Cambrian, Theresa Sandstone
- Unknown age
- Median

**Legend:**
- Symbols correspond to different geological layers and formations, illustrating radium presence and concentration.
**$^{228}\text{Ra} / ^{226}\text{Ra}$ in brine vs. host**

<table>
<thead>
<tr>
<th>Formation Age</th>
<th>Upper</th>
<th>Middle</th>
<th>Lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devonian</td>
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<td></td>
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</tr>
<tr>
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<td>[Data points]</td>
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<td></td>
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<tr>
<td></td>
<td>[Data points]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silurian</td>
<td></td>
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<td></td>
<td>[Data points]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Data points]</td>
<td></td>
<td></td>
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<tr>
<td>Ordovician</td>
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<td>[Data points]</td>
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<td></td>
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<td>[Data points]</td>
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<tr>
<td>Cambrian</td>
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<tr>
<td>Unknown</td>
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</tr>
</tbody>
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**EXPLANATION**
- Upper Devonian sandstones
- Middle Devonian, Marcellus Shale
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![Graph showing data points for different geological formations and age groups with various symbols for different rock types.](image-url)
Abundance of $^{226}$Ra vs $^{228}$Ra

- A typical shale has 10 ppm Th and 3.7 ppm U
- In radioactivity units, this translates to about 1.3 pCi/g of each parent.
- At radioactive equilibrium, amounts of $^{226}$Ra and $^{228}$Ra would be equal.
- Equal leaching of Ra isotopes would result in equal concentrations or $^{226}$Ra and $^{228}$Ra in solution.
- But $^{226}$Ra is far higher than $^{228}$Ra in brines.
- Implies U host is more abundant or more easily leached than Th host.
- $^{226}$Ra is from Marcellus with high U?
Removal/Disposal of Ra and Ba

- Sulfate precipitation – but 3 truckloads of sludge is lifetime Ra limit for a normal landfill.
- Release to streams- Probable adsorption on Fe oxides and uptake by biota.
- Ra and Rn hazards for workers.
- Coat wellbore and proppants w/ Ra-exchange resin (Ra in brine is a widespread problem).
- Re-use of flowback.
Water Supply and Disposal Solutions

- Re-use of prior flowback
- Use abandoned mine drainage (Effect of high sulfate?)
- Ship to deep injection wells (very few in PA, possible EQ triggering)
Leakage of brine

- Natural salt springs in deep valleys.
- Minor groundwater component in many valleys (Warner et al., 2012).
- Control by lineaments – deep fault zones.
- Possible contamination from depth by fracking??
Summary

- Extremely saline brine flows back from Marcellus wells, will be Production Water.
- Origin as evaporated seawater from Salina Salt Formation.
- Migration from Salina, extensive interaction with other rocks (dolomitization, S reduction)
- High levels of Ra, Ba greatly exceed drinking water standards.
- Lack of good disposal methods.
- Flowback may be derived largely from overlying and underlying formations rather than Marcellus.