Approaches with Recycle, Treatment, and Disposal of Flowback and Produced Water and the ABCs of Managing NORM in the Marcellus Shale Region

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Safety Moment – Working at a Wastewater Treatment Locations

- When handling treatment chemicals, wear proper PPE protection – safety eye glasses, gloves

- Always be aware where the safety eyewash water bottles and or shower are located

- Wear a face mask when handling chemicals that generate dust
Current Recycle Treatment Challenges

- Current Operator recycle/reuse approaches varies
- Flowback and produced water chemistry varies
- Frac water chemistry requirement varies
- Cost of treatment – AFE and LOE budgets
- Cost of water transfer
- Drilling and completion logistics
- Regulatory considerations
Water inputs and outputs change throughout life cycle of each gas well
- Mud drilling water
- Top hole water
- Flowback water
- Produced water
- Storm water

Operators in Marcellus and Utica are using varied recycle treatment approaches.
Flowback and Produced Water Handling

- Blend untreated flowback and produced water with fresh water
- Treat flowback and produced water to make a clean brine and blend with fresh water
- Add friction reducers, anti-scalant and biocides for hydraulic fracture water makeup
- Transfer flowback and produced water to permitted central treatment facilities for recycle and reuse
- Transfer flowback and produced water to permitted brine disposal wells
Recycle Flowback and Produced Water – Many Treatment Approaches

- Flowback water – water that returns to surface via wellbore after the fracturing treatment is complete

- Produced water – water produced along with oil and gas

<table>
<thead>
<tr>
<th>Parameter (mg/L or ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Suspended Solids (TSS)</td>
</tr>
<tr>
<td>Bacteria - SRB and APB</td>
</tr>
<tr>
<td>Iron (Fe²⁺)</td>
</tr>
<tr>
<td>Barium</td>
</tr>
<tr>
<td>Strontium</td>
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<tr>
<td>Calcium</td>
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<tr>
<td>Total Dissolved Solids (TDS)</td>
</tr>
<tr>
<td>Sulfates</td>
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<tr>
<td>Chlorides</td>
</tr>
</tbody>
</table>
Key Hydraulic Fracture Water Fluid Properties

- Low viscosity
- Non-reactive
- Non-flammatory
- Minimal residuals
- Minimal potential for scale & corrosion
- Low entrained solids
- Around Neutral pH (6.5 to 7.5)
Water Impurities of Concern

- Scale Forming Constituents
- High Dissolved Solids (Chlorides, Sulfates & Calcium)
- Bacteria: Acid Producing (APB) and Sulfate Reducing Bacteria (SRB)
- Suspended Solids
- Hydrocarbons
- Acid Gases (CO₂ & H₂S)
- Friction Reducers
- Warmer season odor
## Recycle Treatment Options

<table>
<thead>
<tr>
<th>Technology</th>
<th>Bag Filtration</th>
<th>Physical/Chemical Separation</th>
<th>Electro-Coagulation</th>
<th>Chlorine Dioxide Treatment</th>
<th>Evaporation/Distillation (MVR)</th>
<th>Crystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Suspended Solids (TSS)</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>× With pretreatment</td>
<td>×</td>
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<tr>
<td>Metals</td>
<td>×</td>
<td></td>
<td>×</td>
<td>×</td>
<td>× With pretreatment</td>
<td>×</td>
</tr>
<tr>
<td>Bacteria</td>
<td>×</td>
<td></td>
<td></td>
<td>×</td>
<td>× With pretreatment</td>
<td>×</td>
</tr>
<tr>
<td>Barium</td>
<td>×</td>
<td></td>
<td></td>
<td>×</td>
<td>× With pretreatment</td>
<td>×</td>
</tr>
<tr>
<td>Hardness (Ca)</td>
<td></td>
<td></td>
<td></td>
<td>×</td>
<td>× With pretreatment</td>
<td>×</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td></td>
<td></td>
<td></td>
<td>×</td>
<td>× With pretreatment</td>
<td>×</td>
</tr>
</tbody>
</table>

**Limitations**
- Disposing of spent filter bags. Can be costly.
- Can have large chemical usage and solids processing / landfilling.
- Requires very consistent/stable raw water quality. Can have high ($) electrical requirements.
- Danger handling and generating chlorine dioxide. Can be costly. Have to pay close attention to system performance.
Recycle Treatment Approaches

- No Treatment
- Bag Filtration
- Biocide Treatment
- Physical/Chemical
- Electrocoagulation
- Evaporation
Sludge Handling and Disposal

- Metal hydroxide sludge – non hazardous can be disposed at permitted landfills

- Depending on the water treatment process, sludge can contain elevated levels of naturally-occurring radioactive material (NORM) that may require management and additional disposal methods.

**Good Management Of NORM/TENORM Must Begin With A Good Understanding Of Radioactivity**
Radiation

- **Energy** released from unstable atoms
- Radiation can have the form of
  - rays (electromagnetic waves) or
  - high-speed particles
Radioactive Decay

- The process in which a radioactive atom releases some excess energy (in the form of radiation)

Large, unstable nucleus

Alpha

Beta

Gamma

Neutron

Ionizing Radiation
Radioactivity

- The rate of the radioactive decay process.
- Measured in units of decays (nuclear disintegrations) per unit time.
  - dpm (disintegrations per minute)
  - dps (disintegrations per second; 1 dps = 60 dpm)
  - Curies (3.7 x 10^{10} dps)
    - 1 Curie = 1 g Ra-226
  - Becquerel (1 dps)
- Environmental applications commonly measure radioactivity in units of pico-Curies (pCi)
  - 1 pCi = 2.22 dpm
Isotopes are atoms of the same element (the same number of protons) but a different number of neutrons.

Isotopes have the same chemical properties; however, the nuclear properties can be quite different.
Radiation Dose:

- **Rem (US Unit)**
  - **Roentgen Equivalent Man**
  - Unit for measuring dose equivalence
  - Takes into account the energy absorbed (dose) and the biological effect on the body due to the different types of radiation
  - 1 Rem = 1,000 mrem
  - The U.S. average annual dose from exposure to the natural background and man-made sources is approximately 620 millirem per year
Effects of exposure

- Effects that may appear in the exposed person:
  - Cells may become cancerous
  - Cell death
  - Cataract formation
  - Increased susceptibility to disease

- Note: In human populations, *genetic* (hereditary) effects have not been observed to appear in future generations
Radioactivity: Natural

- Oil and gas deposits exist in geologic formations that contain naturally-occurring radioactive materials (NORM)
  - Uranium (U-238)
    - Parent + 13 radioactive progeny
    - Alpha, beta, gamma radiation
  - Thorium (Th-232)
    - Parent + 10 radioactive progeny
    - Alpha, beta, gamma radiation
- Secular Equilibrium in the rock
Radioactivity: NORM
Radioactivity: TENORM

- Technologically-enhanced NORM (TENORM)
- Scale
  - Group IIA elements (barium, strontium, calcium, radium) form pipe / tank scales
  - Acidity, temperature, and pressure contribute to scale build-up
  - Gas transportation (radon)
- Sludge
  - Produced water
  - Water treatment- barium extraction inadvertently concentrates radium in filter cake sludge
  - Filter socks
Radioactivity: NORM and TENORM
The U.S. Nuclear Regulatory Commission (NRC) does not regulate or license NORM and TENORM

- Authority falls to the 50 individual states and miscellaneous federal agencies
- U.S. Department of Transportation regulates the packaging, labelling, and transportation of NORM- or TENORM- containing materials
- U.S. Environmental Protection Agency (EPA) regulates radioactivity in drinking water
- U.S. Occupational Safety and Health Administration (OSHA) regulates employee exposure to radioactive material
- States that have entered into an agreement with the NRC allow states to have their own radiation protection regulations
  - 37 Agreement States
Pennsylvania

- Agreement state
- Except for transportation, NORM is under regulatory control of the PA Dept. Of Environmental Protection
- Disposal options in PA do exist for some low-level NORM-containing wastes
  - Based on landfill specifics, require dose modeling and PA DEP approval
  - Volumetric annual limit and concentration limit
- NORM Study
Ohio

- Agreement state
- Regulated by ODH, ODNR, OEPA
- Chapter 3701 contains TENORM and radioactive materials handling standards
  - 20 pCi/g of Ra-226 requires license
  - 25 uR/hr for recyclable materials
- Exemption for possession, storage, use, transportation, and distribution of compressed gases containing NORM
- Waste Disposal- Injection Wells, Alternate Means Approved by Director
Develop NORM Management Program

• Managing Worker / Environmental Liabilities and Cost

• Industry Benchmarks
Implement NORM Management Program

- Detection of NORM
- Establish Action Limits
- Contamination Control Procedures
- Control of NORM-contaminated waste
  - Disposal Options
  - Minimize Waste Volumes and Costs
- Control of NORM-contaminated equipment
- Contingency SOPs
Worker Protection

- Worker Training and Awareness
- Hazard Identification Program
- Radiological controls
  - SOPs
  - Postings
  - Equipment
- Appropriate PPE
  - Dosimetry
Hydraulic fracturing for oil and gas is bringing radiological issues into the spotlight

NORM is brought to the surface in solids, liquids, and gases

- Vertical and horizontal drill cuttings contain U-238 and Th-232 decay series
- Flowback (produced) water contain radium and their decay progeny
  - May ultimately concentrate during waste water treatment
- Natural gas contains radon and its decay progeny
  - May ultimately deposit during decay in gas equipment and transportation

Implement NORM/TENORM Management Programs

- Basic radiation safety practices
- Reduce occupational and public exposures
- Reduce environmental liability
- Reduce costs
Questions?

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