Chemical Processes to Concentrate/Bind Radionuclides

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Outline of Presentation

• Focus is on removal of Alkaline earth metals
• Review Background: 2012 GE study
• Our Approach and Preliminary results
Marcellus Shale Flowback and Produced Water Profiles

- TDS plateaus at 150,000 mg/L around 20-22 days
- 27% of water (1-1.5 MM gallons/well) returned within 22 days

Silva, GE, RPSEA 08122-36 Report
Marcellus Frac Water Compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>Low-TDS</th>
<th>Medium-TDS</th>
<th>High-TDS</th>
<th>“Typical”</th>
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<tbody>
<tr>
<td>TDS</td>
<td>69,640</td>
<td>175,300</td>
<td>248,000</td>
<td>195,000</td>
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<tr>
<td>Mg</td>
<td>438</td>
<td>938</td>
<td>1,630</td>
<td>1,300</td>
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<tr>
<td>Ca</td>
<td>5,140</td>
<td>14,100</td>
<td>31,300</td>
<td>18,000</td>
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<tr>
<td>Sr</td>
<td>1,390</td>
<td>6,830</td>
<td>2,000</td>
<td>4,000</td>
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<tr>
<td>Ba</td>
<td>2,300</td>
<td>3,310</td>
<td>4,300</td>
<td>6,500</td>
</tr>
<tr>
<td>Fe</td>
<td>11.2</td>
<td>52.5</td>
<td>134</td>
<td>60</td>
</tr>
<tr>
<td>Mn</td>
<td>1.9</td>
<td>5.17</td>
<td>7</td>
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</tbody>
</table>

- Typical water composition
- Includes early flow back (less TDS) and later days (more TDS)
Current Produced Water Recovery Process

- Pretreatment includes oxidation and lime treatment
  - Water recovery poor (50%)
  - Disposal costs high
  - Disposal liquid high in TDS/NORM

Silva, GE, RPSEA 08122-36 Report
Produced Water Compositions from Pennsylvania Marcellus Shale Gas Wells

<table>
<thead>
<tr>
<th>County</th>
<th>Well-1</th>
<th>Well-2</th>
<th>Well-3</th>
<th>Well-4</th>
<th>Well-5</th>
<th>Well-6</th>
<th>Well-7</th>
<th>Design Case</th>
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<tbody>
<tr>
<td>pHb</td>
<td>7.3</td>
<td>6.3</td>
<td>5.4</td>
<td>5.8</td>
<td>5.9</td>
<td>6.2</td>
<td>6.6</td>
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<tr>
<td>TDS</td>
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<td>155,705</td>
<td>199,242</td>
<td>68,439</td>
<td>149,188</td>
<td>122,562</td>
<td>124,421</td>
<td>132,460</td>
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<tr>
<td>Na⁺</td>
<td>26,500</td>
<td>38,200</td>
<td>51,800</td>
<td>19,200</td>
<td>39,000</td>
<td>32,300</td>
<td>33,900</td>
<td>35,000</td>
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<tr>
<td>Mg²⁺</td>
<td>460</td>
<td>840</td>
<td>1290</td>
<td>570</td>
<td>1,000</td>
<td>800</td>
<td>1,170</td>
<td>800</td>
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<tr>
<td>Ca²⁺</td>
<td>5,560</td>
<td>10,280</td>
<td>13,120</td>
<td>5,360</td>
<td>13,000</td>
<td>8,700</td>
<td>10,880</td>
<td>9,500</td>
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<tr>
<td>Sr²⁺</td>
<td>2,030</td>
<td>3,670</td>
<td>4,580</td>
<td>1,290</td>
<td>2,600</td>
<td>2,340</td>
<td>1,750</td>
<td>2,500</td>
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<tr>
<td>Ba²⁺</td>
<td>6,580</td>
<td>13,200</td>
<td>11,600</td>
<td>32</td>
<td>3,500</td>
<td>5,800</td>
<td>147</td>
<td>6,200</td>
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<tr>
<td>Fe²⁺</td>
<td>26</td>
<td>74</td>
<td>123</td>
<td>55</td>
<td>32</td>
<td>75</td>
<td>47</td>
<td>50</td>
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<td>Mn²⁺</td>
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<td>2.5</td>
<td>3.4</td>
<td>1.7</td>
<td>2.7</td>
<td>4.3</td>
<td>1.2</td>
<td>3</td>
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<td>Cl⁻</td>
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<td>89,429</td>
<td>116,713</td>
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<td>90,014</td>
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<td>&lt;10</td>
<td>&lt;10</td>
<td>57</td>
<td>&lt;5</td>
<td>&lt;50</td>
<td>&lt;100</td>
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<td>SiO₂</td>
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<td>11</td>
<td>13</td>
<td>29</td>
<td>39</td>
<td>18</td>
<td>33</td>
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<tr>
<td>Hardness as Ca²⁺</td>
<td>9,167</td>
<td>17,196</td>
<td>20,727</td>
<td>6,899</td>
<td>16,860</td>
<td>12,782</td>
<td>13,653</td>
<td>13,772</td>
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<tr>
<td>°² Ra</td>
<td>5,400</td>
<td>7,600</td>
<td>4,200</td>
<td>4,600</td>
<td>5,600</td>
<td>820</td>
<td>2300</td>
<td>5,000</td>
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<tr>
<td>TSS</td>
<td>202</td>
<td>282</td>
<td>500</td>
<td>62</td>
<td>520</td>
<td>210</td>
<td>898</td>
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<td>Turbidity</td>
<td>78</td>
<td>399</td>
<td>1160</td>
<td>17.4</td>
<td>192</td>
<td>45</td>
<td>164</td>
<td>0</td>
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<tr>
<td>TOC</td>
<td>&lt;10</td>
<td>11.8</td>
<td>11.8</td>
<td>72</td>
<td>151</td>
<td>160</td>
<td>88</td>
<td>0</td>
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<tr>
<td>PW Type</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>III</td>
<td>I</td>
<td>III</td>
<td>III</td>
<td>I</td>
</tr>
</tbody>
</table>

- Produced water from Barnett Shale (TX)
- dimensionless
- pCi/Liter
- Turbidity units: NTU
- adjusted to force ion balance (prior analyses found other anions were <1% of the chloride on a molar basis)

• Classification of Produced Water (PW) Type based on Ba, Ra content

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Produced Water Type

- **PW I**
  - Ba < 1000 – 2000 mg/L
  - Ra - does not matter
- **PW II**
  - Ba > 2000 mg/L
  - Ra < 200 – 1000 pCi/L
- **PW III**
  - Ba > 2000 mg/L
  - Ra > 200 – 1000 pCi/L

Goals
- Recover Pure water (90%)
- Generate usable road salt (< 100mg Ba/liter in TCLP extract)
- Minimize Solid Waste (<25 pCi/g)
- Minimize NORM Waste

Radium itself is not an issue, very dilute
PW Type and Pretreatment Strategies

- Type I Pretreatment technology available (Ba removal unnecessary), NaCl usable product
  - Type II Pretreatment Sulfate Precipitation
  - Type III – Can use new technology

Silva, GE, RPSEA 08122-36 Report
Type III Pretreatment Strategies

Silva, GE, RPSEA 08122-36 Report
Radium Removal Performance for Adsorbents

- Ion-exchange, lime softening, reverse osmosis reported as “best available technologies” for removing Ra from groundwater
- Screening study shows BaSO₄, Dowex RSC, MnO₂ as good candidates
- RSC resin capacity for Ra decreases drastically in presence of Ba, raising cost ($143 K/million gallon).
- Chelating resins poor performance with high TDS
- Nanofiltration not economical

Silva, GE, RPSEA 08122-36 Report
Sulfate Precipitation

• Several commercial processes available
• Na$_2$SO$_4$ → BaSO$_4$; lime → Mg(OH)$_2$ + Others
• With Ra → Radiobarite Ba(Ra)SO$_4$
  (> 25 pCi/gm)
• Has to be disposed off as LLRW - cost prohibitive

• Recent study on mixing acid mine drainage (AMD) with flowback water led to recyclable water but large amounts of LLRW, primarily sulfates (Environ. Sci. Technol. 2014, 48, 1334–1342)
Modified Lime Soda Process

- Exploits difference in solubility of Group II carbonates
- Ca/Sr carbonates precipitates first (25 lb waste/bbl PW)
- Ba/Ra carbonates → HCl dissolution → Concentrate for UIC disposal (0.05 bbl/bbl PW)
- $3.5/bbl produced water ($84 K/million gallon)

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MnO₂ : Ba and Ra adsorption

- MnO₂ - adsorbs both Ba/Ra ($K_d = 2.8 \times 10^4$)
  - Salinity (~ 35000 ppm process slow, hours) (Applied Radiation and Isotopes 2003 255–262)
- MnO₂ – can be regenerated with 0.1 M HCl
- Ra (5000 pCi/Liter = 5 \times 10^{-6} mg/L), Ba ~ 6200 mg/L
- Equal percentages of Ba/Ra adsorbed/desorbed only at low salinity, retention lower at high salinity
- $1.70 - $2.30/ bbl produced water ($40-$55 K/million gallon)
Natural Zeolite - Clinoptilolite

(\text{Ca}_{0.5}\text{Na}_x\text{K}_y\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Mg}_{0.5})_6(\text{H}_2\text{O})_{20}\mid[\text{Al}_6\text{Si}_{30}\text{O}_{72}]$

- Ion exchange properties exploited in agronomy, horticulture and soil remediation
- Treatment of effluents containing radioactive contaminants or other heavy metals
- Trap gases for agricultural applications (e.g. ammonia).

$\text{Sr}^{2+} = \text{Ba}^{2+} > \text{Ca}^{2+} >> \text{Na}^+$
Our Goal

• Exploit the ion-exchange properties of zeolites
• Model System: remove $\text{Sr}^{2+}$ in the presence of $\text{Na}^+ / \text{K}^+$, equilibrium experiments
• 5 ppm $\text{Sr}^{2+}$/0, 2,000, 20,000 ppm MCI
• 10,000 ppm zeolite
Clinoptilolite

Effective at Sr$^{2+}$ removal at high TDS
Next step....

• Increase selectivity: Remove Sr$^{2+}$ at 35,000 ppm Na$^+$

• Combine adsorption/ion – exchange : 2$^{nd}$ Generation Material

• Move to Ba$^{2+}$
MnO$_2$/Zeolite: Second Generation Material

Zeolite + Mn$^{2+}$ → Mn$^{2+}$ - Zeolite
Mn$^{2+}$ - zeolite + KMnO$_4$ → MnO$_2$ - Zeolite
Strategy

• Combine adsorption (remove Ra$^{2+}$) / ion – exchange (remove Ba$^{2+}$)
• Use for PW III Pretreatment (after Ca$^{2+}$, Mg$^{2+}$ removal)
  • Regenerated with acid/M$^{+}$
  • Nanoscale MnO$_2$ will promote kinetics
• Synthesis complete : Ba$^{2+}$ removal studies planned
Zeolites can be made with different morphologies, including membranes. Provides flexibility in processing.
Hypothesis: Frac Sand is having an influence on TDS with time

Marcellus Shale Water Recovered (2012 RPSEA RPT)

Days Since Start of Flowback

Cumulative Water Recovery (relative to injected volume)

- % injected recovered
- Instantaneous TDS

Equations:
- \( y = 0.0665x - 0.0074 \)  
  \( R^2 = 0.9513 \)
- \( y = 0.0025x + 0.2151 \)  
  \( R^2 = 0.991 \)
- \( y = -199.63x^2 + 9550.3x + 38285 \)  
  \( R^2 = 0.9349 \)

TDS (mg/L)
Alternative Approach

• Can alkaline earth metals be trapped within well?
• Combine zeolite adsorbent with fracking sand
• 10,000 ppm zeolite, 100,000 ppm sand: Equilibration experiments
Clinoptilolite with Resin Coated Fracking Sand

- Fracking Sand alone will remove $\text{Sr}^{2+} \sim 55\%$ at 20,000 ppm NaCl
- Zeolite to fracking sand ratio 1:10 (wt)
- Combination more effective for $\text{Sr}^{2+}$ removal at high TDS
Summary

• Zeolites and Zeolite composites show promise for NORM mitigation
• Combination of ion-exchange/adsorption strategy not reported in literature